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# The Role of Nanotechnology in Automotive Industries

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Additional information is available at the end of the chapter

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## 1. Introduction

Nanotechnology involves the production and application of physical, chemical, and biological systems at atomic or molecular scale to submicron dimensions and also the integration of the resulting nanostructures into larger systems. Therefore, nanotechnology deals with the large set of materials and products which rely on a change in their physical properties as their sizes are so small. Nanotechnology promises breakthroughs in areas such as materials and manufacturing. Nanoparticles, for example, take advantage of their huge surface area to volume ratio, so their optical properties become a function of the particle diameter. When incorporated into a bulk material, these can strongly influence the mechanical properties such as stiffness or elasticity. For example, traditional polymers can be reinforced by nanoparticles leading to novel materials to be used as lightweight replacements for metals. Such enhanced materials will enable a weight reduction together with an increase in durability and enhanced functionality.

There are different reasons why this length scale is so important. The wavelike behavior of materials predominates when the size lies in the atomic scale. This changes the fundamental properties of materials such as melting temperature, magnetization and charge capacity without changing the chemical composition. The increased surface area of nano materials make them ideal for use in composites, reacting systems and energy storage. By increasing the surface area the number of surface atoms increases dramatically, making surface phenomena play a vital role in materials performance. This is because a greater amount of a substance comes in contact with surrounding material. This results in better catalysts, since a greater proportion of the material is exposed for potential reaction. At nanoscale the gravitational forces become negligible and electromagnetic forces dominate. At nano scale surface and interface forces become dominant. From optical point of view, when the size of materials is comparatively smaller than the wavelength of visible light they do not scatter

light and can be used in applications where transparency is of great importance. The automotive sector is a major consumer of material technologies. It is expected that nanotechnologies improve the performance of existing technologies for car industries significantly. Applications range from already existing paint quality, fuel cells, batteries, wear-resistant tires, lighter but stronger materials, ultra-thin anti-glare layers for windows and mirrors to the futuristic energy-harvesting bodywork, fully self-repairing paint and switchable colors. The basic trends that nanotechnology enables for the automobile are : lighter but stronger materials (for better fuel consumption and increased safety); improved engine efficiency and fuel consumption for gasoline-powered cars (catalysts; fuel additives; lubricants); reduced environmental impact from hydrogen and fuel cell-powered cars; improved and miniaturized electronic systems; better economies (longer service life; lower component failure rate; smart materials for self-repair).

This chapter attempts to discuss the applications of nanotechnology in automotive sector and bring some examples of each set of products being used in car industries.

## **2. Exterior applications**

### **2.1. Nano-clearcoats with high scratch and wear resistance**

#### *2.1.1. An introduction on scratch/mar*

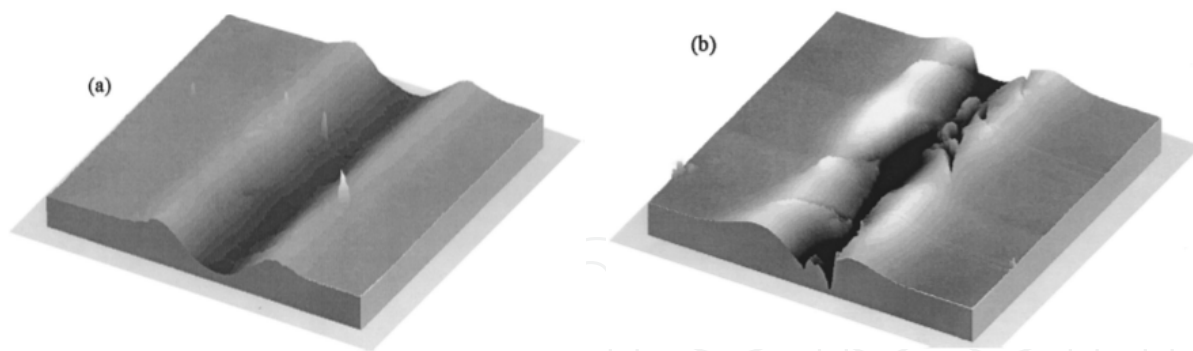
In a multilayer automotive coating system (basecoat/clearcoat), the main responsibility of the clearcoat layer is to protect the pleasing appearance of the metallic underneath layer from environmental factors. However, the clearcoat's appearance may be vulnerable to degradation in exposure to harsh environmental conditions, especially weathering and mechanical damages (Bautista et al., 2011, Barletta et al., 2010, Courter et al., 1997, Ramezanzadeh et al, 2011d, Ramezanzadeh et al, 2011e). Scratch and mar are the most important types of mechanical damages which impose serious challenges for the coatings formulators. Depending on the size and morphology of the scratch/mar, the appearance changes of the clearcoat may vary. Based on the viscoelastic properties of the clearcoat and scratching condition (the cause of scratch, scratches force, scratch velocity and environmental temperature) scratch can be produced by two primary mechanisms, i.e. plastic and fracture flow. The fracture type scratch has sharp edges and irregular shapes having high capability of light scattering (Ramezanzadeh et al, 2011f, Ramezanzadeh et al, 2011g, Yari et al., 2009a, Shen et al., 2004). On the other hand, plastic type scratch has smoother surface and less ability to light scattering (Fig. 1).

The plastic type scratches are deeper than fracture types and have greater tendency to self-healing at temperatures around clearcoat 's T<sub>g</sub>.

#### *2.1.2. Approaches to improve scratch resistance*

Two main strategies can be sought in order to produce highly scratch resistant clearcoats: the first is optimizing cross-linking behavior of the clearcoat utilizing appropriate components and the second is introducing reinforcing inorganic fillers into the clearcoat formulation. The

first approach deals with low enough  $T_g$ -clearcoats showing the reflow behavior or extraordinary high cross-linking density (Bautista et al., 2011, Barletta et al., 2010, Courter et al., 1997, Ramezanzadeh et al., 2011, Ramezanzadeh et al., 2011d, Ramezanzadeh et al., 2011e, Yari et al., 2009a, Shen et al., 2004). The clearcoats scratch resistance can be highly improved by these two ways. However, there exist disadvantages for each of these strategies alone. Producing low- $T_g$  clearcoats needs changing clearcoat chemical composition. This may negatively influence other properties of the clearcoat such as reduced chemical resistance. A highly cross-linked clearcoat can be obtained by the reaction of melamine based resins and polyols to form etheric bonds. Although this system may appropriately resist against scratch, the coating will be susceptible to acid etching and performs weakly in weathering. One alternative way to improve scratch resistance of the coating while the lowest weathering performance is maintained is the use of so called hybrid materials including both organic and inorganic domains simultaneously. In this system, the inorganic domains improve clearcoat scratch resistance and organic domain guarantees the stability in weathering. The hybrid materials can be obtained by direct embedding inorganic fillers into them or by in-situ production of inorganic domain in a method called sol-gel processing. The micro-sized inorganic fillers cannot be used due to their effects on clearcoat transparency. By using inorganic fillers in nano sized form, the mechanical properties of the clearcoat will be improved even at low loadings mainly due to their small particle size and huge surface area. Unlike conventional micron-sized fillers, they do not affect the transparency of the clearcoat. The advantages and disadvantages of incorporating nano-fillers into the clearcoat matrix or in-situ creation of inorganic domains in the clearcoat matrix will be discussed below (Shen et al., 2004, Schulz et al., 2001, Hara et al., 2001, Jardret et al., 2000, Weidian et al., 2001, Thorstenson et al., 1994, Ramezanzadeh et al., 2010d).



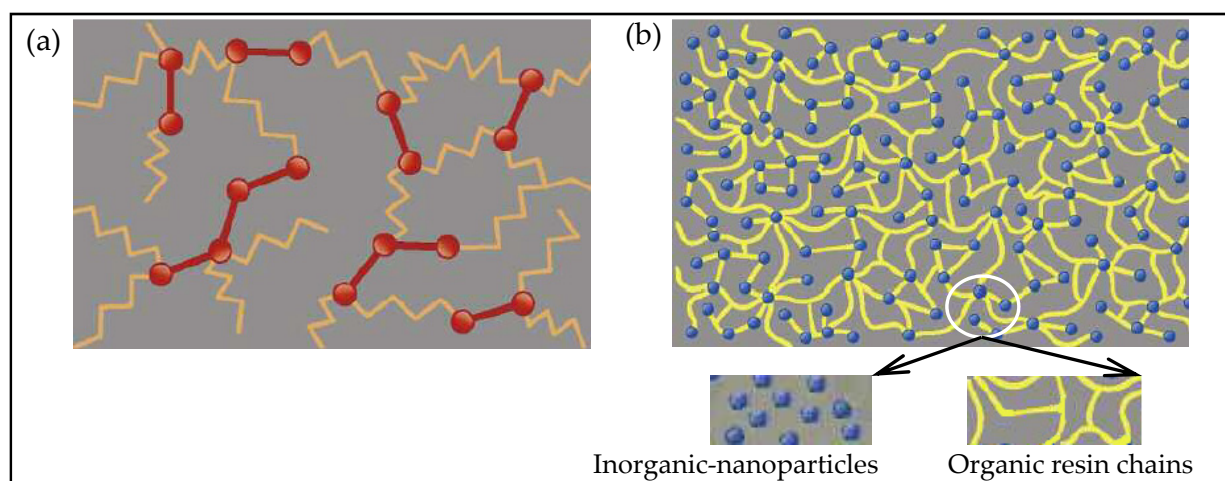
**Figure 1.** Visual illustrations of (a) plastic type and (b) fracture type scratches.

### 2.1.3. Highly scratch resistant clearcoat containing inorganic nano fillers

It has been found that incorporation of nanoparticles such as  $Al_2O_3$ ,  $SiO_2$ ,  $ZrO_2$  and  $TiO_2$  into a clearcoat matrix could significantly enhance the scratch resistance (Bautista et al., 2011, Amerio et al., 2008, Tahmassebi et al., 2010, Groenewolt et al., 2008, Sangermano et al., 2010). Ceramic nanoparticles have been found as appropriate hardening materials to significantly improve clearcoat hardness and therefore scratch resistance. However, the improvement cannot be easily obtainable when the particles are poorly dispersed. The inorganic fillers do

not have intrinsic affinity to organic phase. These lead to phase separation and aggregate formation. The aggregated particles (>100 nm) depreciate clearcoat properties especially the optical clarity. Attempts have been carried out to solve this problem by surface modification of fillers with organosilanes to render them hydrophobic and thereby improve their dispersibility into the polymeric matrix. The surface modification not only can influence dispersibility but also can result in stronger physical/chemical interfacial adhesion between particles and the matrix (Tahmassebi et al., 2010). Different factors may be influential for the effects of nano fillers on the scratch resistance of a clearcoat: the particles chemistry, size, shape and surface modification. It has been demonstrated that nanoparticles could improve clearcoat properties in different ways. The most important of which will be discussed here (Tahmassebi et al., 2010).

Inorganic nanoparticles have hardness and elastic modulus greater than organic polymers. Incorporation of these particles to the clearcoat matrix increases hardness and elasticity (Fig. 2). This depends on the content, the intrinsic hardness and the dispersion degree of the inorganic filler. Increased hardness and elasticity may result in better clearcoat resistance against sharp scratching objects penetrating into the surface.



**Figure 2.** Schematic illustrations of the chemical structures of the conventional coating consist of resin/cross-linker (a) and inorganic-nanoparticles loaded paint (b).

However, it has been shown that greater hardness does not necessarily guarantee clearcoat scratch resistance. There are problems with highly increased clearcoat hardness. For examples, when the applied forces are greater than the critical force, it leads to fracture type scratches. Increasing coating hardness can also result in an increase in clearcoat brittleness and therefore reduction of other properties like flexibility. To overcome this problem, attempts have been carried out to obtain tough clearcoat in presence of nanoparticles. Results obtained in recent researches show that nanoparticles could influence cross-linking density of the clearcoat by affecting curing reaction. Nanoparticles with organosilane modifications include functional groups with high capability of reacting with functional groups of resins. As a result, some chemical bonds between resin and hardener (curing agent) will be replaced by the bonds created between particle/hardener and/or particle/resin.

This results in a decrease in the cross-linking density of the clearcoat. On the other hand, nano fillers enhance the hardness and elasticity. These two phenomena result in clearcoat toughness improvement in presence of nanoparticles. A tough clearcoat can resist abrasive condition and show less fracture behavior (Amerio et al., 2008, Tahmassebi et al., 2010, Groenewolt et al., 2008, Sangermano et al., 2010).

#### *2.1.4. Highly scratch resistant clearcoat using sol-gel method*

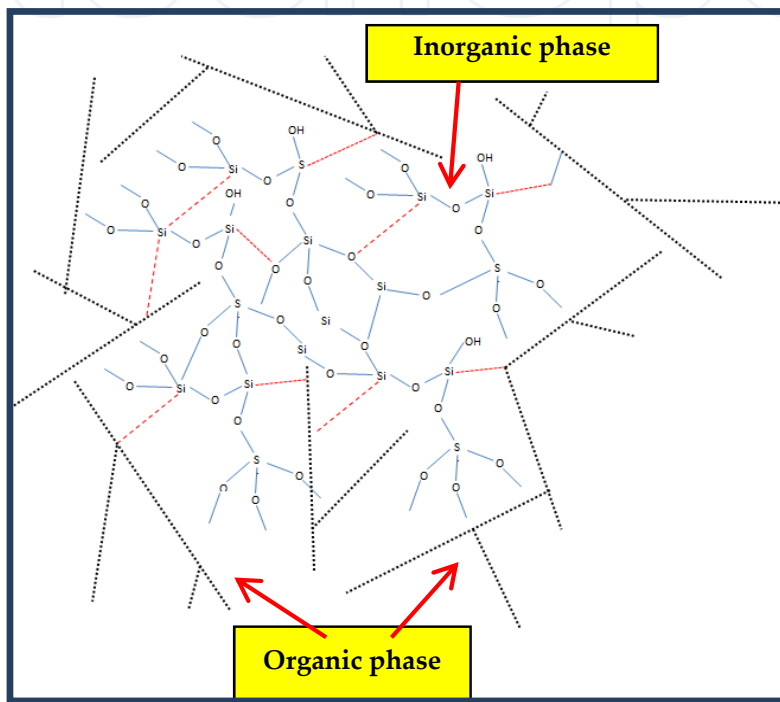
Nanofiller embedded clearcoats show enhanced scratch and wear resistance. However, the clearcoat transparency will be influenced as a result of nanoparticles aggregation. Obtaining appropriate dispersion needs surface modification as well as using different dispersing techniques. In-situ process of inorganic phase formation inside organic matrix using sol-gel technique has been considered (Ramezanzadeh et al., 2011d, Presting et al., 2003, Hernandez-Padron et al., Hernandez-Padron et al., 2003). Organic/inorganic precursors can be used to produce in-situ silica network in the matrix. These precursors, either as network former, such as tetraethyl orthosilicate (TEOS) or network modifier such as methacryloxy propyl trimethoxysilane (MEMO) and glycidoxy propyl trimethoxysilane (GPTS), can be introduced to the main polymeric film former to obtain a so-called hybrid nanocomposite films. This process includes precursor hydrolysis and self-condensation reactions. The hydrolyzed precursors could be cross-linked with the organic coating matrix by reacting with polyol and other curing cross-linkers such as amino or isocyanate compounds in the automotive coating formulation. In this way, a hybrid nanocomposite containing organic/inorganic phases can be obtained (Fig. 3). The organic phase presented in the hybrid nanocomposite can be responsible for the adhesion and flexibility and the inorganic phase can help coating resist mechanical damages (Ramezanzadeh et al. 2010).

## **2.2. Scratch resistant polymer glasses**

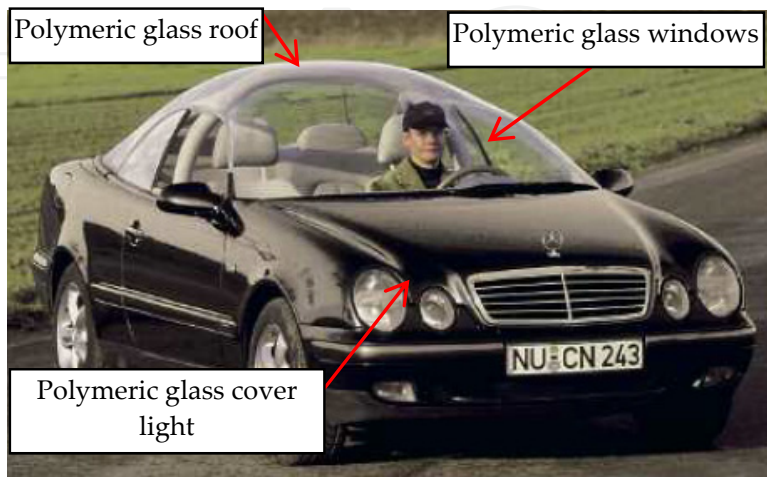
Nowadays, fuel consumption of a car is an important factor for both car manufacturers and consumers. Request for producing cars with lower fuel consumption has been enormously developed in recent years. Reducing the weight of the cars is one way reaching this target. The car weight can be significantly reduced by replacing heavy glass parts (i.e. head lights and windows) by light polymeric glass sheets (Fig. 4) (Yahyaei et al., 2011).

One of the most used kinds of glass polymers is polycarbonate which has excellent impact strength, high toughness and light weight. Polycarbonates have been already used in light covers and lenses. However, polycarbonate has limited scratch/abrasion and chemical resistance together with the tendency to yellowing when it is exposed to UV light in long term. Glass is a hard material having excellent scratch resistance. However, it has higher weight and lower impact strength compared with polymeric glasses. Washing (both automatic carwash and hand washing) and sand/dust particles presented in air are main causes of scratching polycarbonates glass parts. This may result in a significant reduction in head lights transparency and therefore light scattering. Attempts have been carried out to solve the problem. Two methods have been sought for this purpose. Producing polycarbonate polymeric

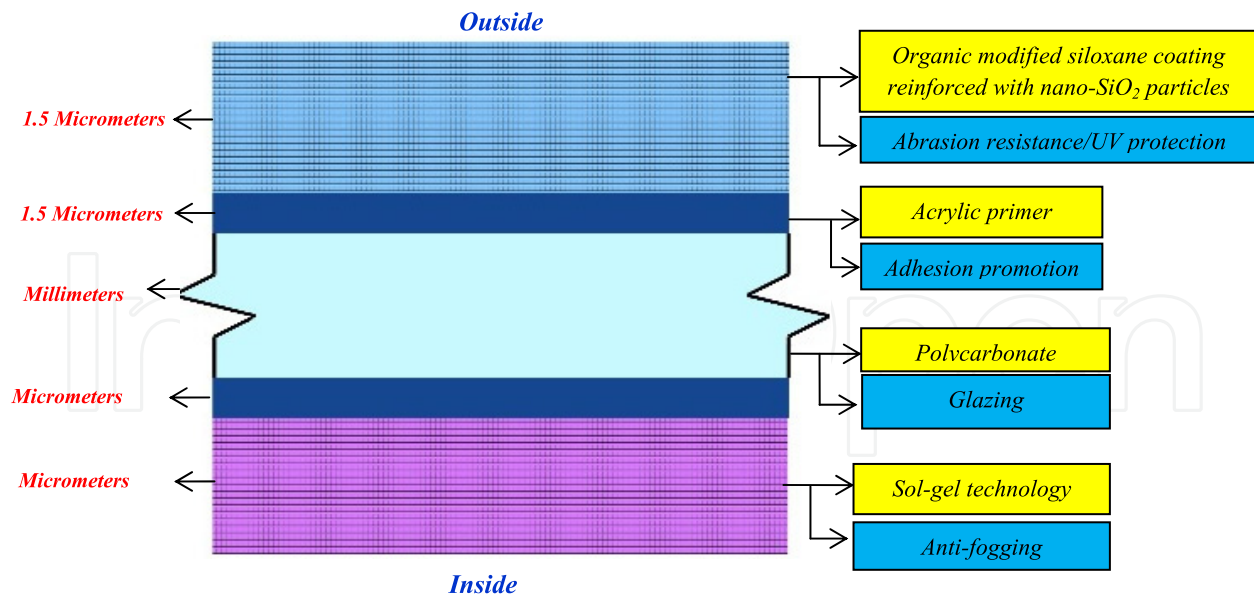
glass parts by embedding nanoparticles into it and/or using acrylate or polysiloxane paints over the head light. Aluminum oxide nanoparticles are also used in the coatings composition in order to make it hard enough to resist scratch and abrasion. This coating is highly transparent due to the small size of the filler particles and their fine distribution (Yahyaei et al., 2011, Pang et al., 2006, Brinker et al., 1990). Embedding nano-sized silica particles into an organic modified siloxane based coating results in nano-coating for automotive glazing application. This coating can produce various properties for the plastic glazing like hydrophobic/anti-smudge, infra-red (IR) and ultra-violet (UV) shielding and anti-fogging behavior. The schematic illustration of a nano-enhanced automotive plastic glazing is shown in Fig. 5.



**Figure 3.** Schematic illustration of a sol-gel based automotive clearcoat containing organic/inorganic precursors (Ramezanzadeh et al. 2010).



**Figure 4.** Modern automobiles equipped with nanostructure polymeric glasses for roof, windows and cover light.



**Figure 5.** Cross-section of a nano-enhanced layers in automotive glazing coatings (Pang et al., 2006).

The average thickness of the nano-embedded coating used for polycarbonate is approximately 1 mm. Different nanocoating layers (as shown in Fig. 5) are responsible for anti-scratch/easy-to-clean/anti-fogging and UV stabilization of polycarbonate plastic glazing. To this end, nanoparticles such as  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  for abrasion resistance improvement,  $\text{TiO}_2$  and  $\text{ZnO}$  for UV protection, sol-gel based  $\text{TiO}$  for anti-fogging behavior and  $\text{TiO}_2$  for easy-clean properties are used (Yahyaei et al., 2011, Pang et al., 2006, Brinker et al., 1990).

In premium optical glazing like glass panes, using coatings with extremely high scratch resistance is necessary. To this end, attempts have been carried out to apply hard materials over the polymer glass from gaseous phase. Using physical vapor deposition (PVD) and chemical vapor deposition (CVD) procedures as well as plasma polymerization, a highly cross-linked nanometric polymeric layer containing inorganic components can be obtained. Producing highly scratch-resistant polymer glass using these techniques opens new possibilities for designing transparent roof tops (Fig. 5) and car body shell parts.

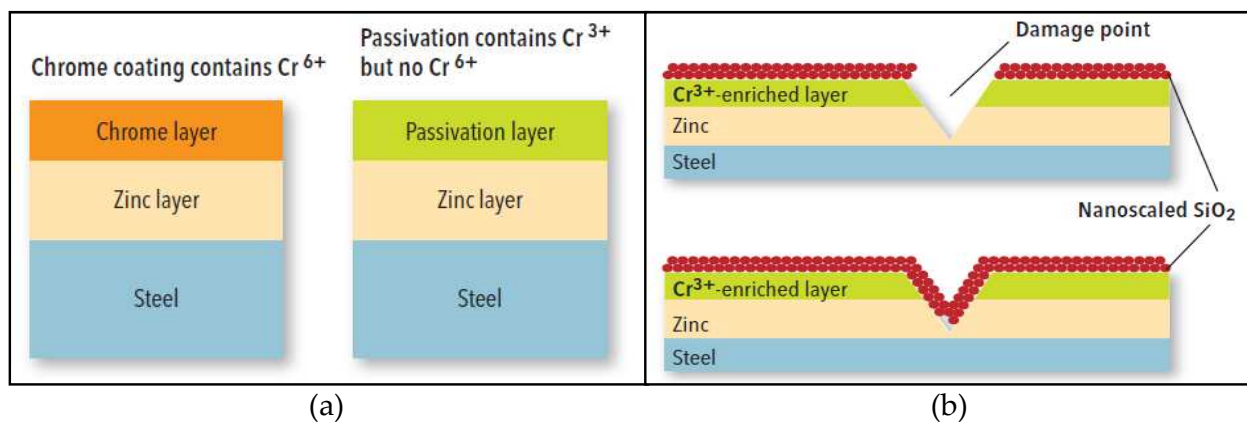
### 2.3. Nano-coatings with anti-corrosion performance for car bodies

Anti-corrosive coatings both in form of conversion and organic coatings are used to protect metal body against corrosive materials. The most important of these coatings are  $\text{Cr(VI)}$  and phosphate conversion coatings together with electrodeposition coating (ED).  $\text{Cr(VI)}$  due to its excellent anticorrosion performance has been widely used to protect car bodies from corrosion in the last decades. The high anticorrosion performance of this coating is related to its high self-healing behavior in corrosive environment. However, the toxic and hazardous nature of chromium compounds are well documented and their uses have been banned in recent years. Phosphate coating is another kind of conversion coating which has appropriate anticorrosion properties and is less toxic compared with  $\text{Cr(VI)}$ . However, the bath



containing these materials leave huge amounts of sludge (Nobel et al., 2007, Dhoke et al., 2009, Shchukin et al., 2007, Brooman, 2002, Kasten et al., 2001).

It has been shown that Cr(III) is less toxic compared with Cr(VI). However, compared to Cr(VI), Cr(III) does not have long-term protection. Nanotechnology has been employed to eliminate this disadvantage. A three layer system including zinc layer, Cr(III) enriched layer and nano-SiO<sub>2</sub> particles containing layer are used for this purpose (Fig. 6). Each layer has specific role for corrosion protection of steel. Zinc has higher negative potential than iron. And when it exposes to corrosive electrolyte, it can produce electron needed for cathodic reaction and prevents iron from oxidation. As a result, Zn<sup>2+</sup> cations produce positive charge at surface. On the other hand, SiO<sub>2</sub> nanoparticles have negative charges. Therefore, nanoparticles can migrate to corroded area and cover it. In fact, nanoparticles produce a layer with approximate thickness of 400 nm. This phenomenon is called self-healing by nano passivation.



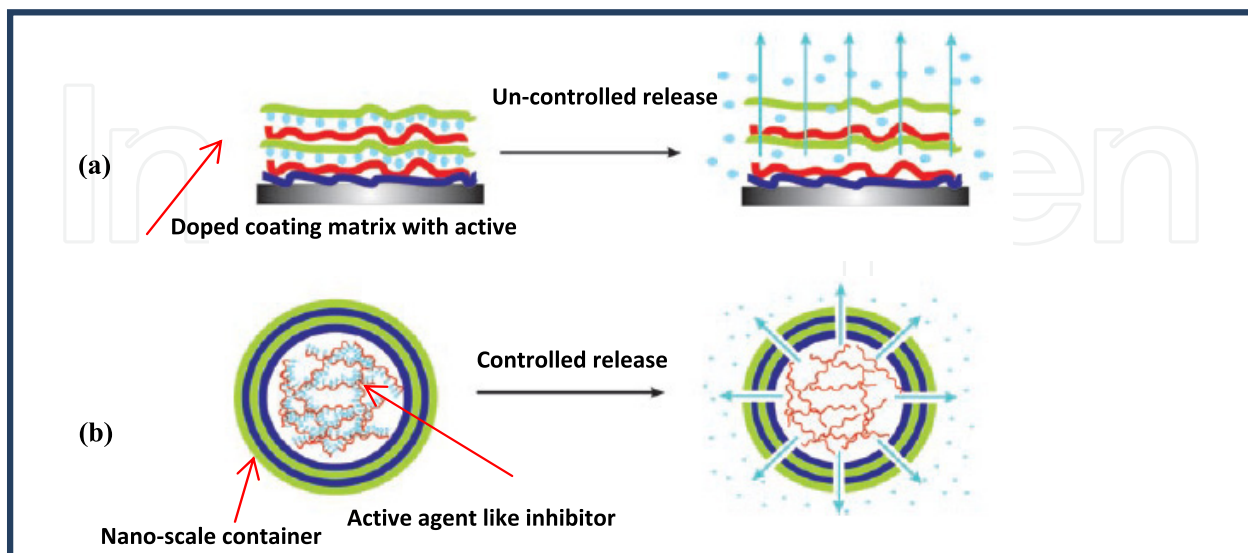
**Figure 6.** Conventional anti-corrosion coatings (a) and nanostructured anticorrosion system (b).

Incorporating nanoparticles into electrodeposition coating formulation is another approach to improve the anti-corrosion performance of car body. Nanoparticles such as Nano-SiO<sub>2</sub>, Nano-TiO<sub>2</sub>, Nano-Clay, Nano Carbon Tube etc. are used to improve electrocoating properties. What is important here is that electrocoatings are waterborne coatings. Therefore, the nanoparticles used for this system must be compatible with coating formulation. Hydrophilic surface modifications are used to produce nanoparticles compatible with this kind of coating. Nanoparticles due to their very small size and high surface area could improve barrier properties of the organic electrocoating against corrosive electrolyte penetration. These particles increase electrolyte pathways through the coating (Nobel et al., 2007, Dhoke et al., 2009).

#### 2.4. Smart nano-scale container anticorrosive coating

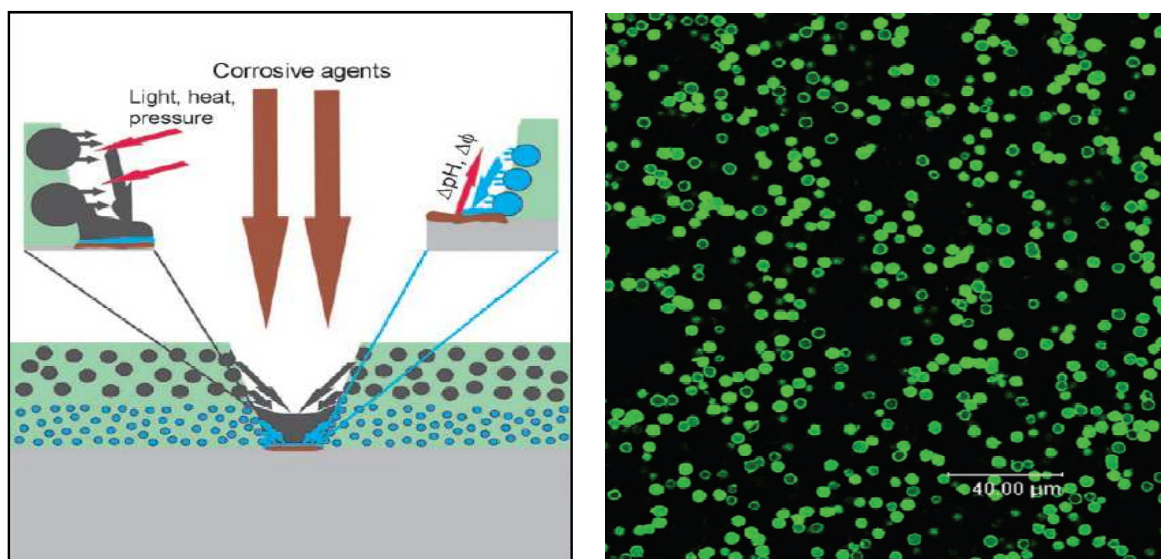
New generation of self-repairing coatings are developed to further enhance anticorrosive properties of metal substrates. In conventional systems, the barrier property of the coating is the main mechanism for metal protection against corrosion. However, the barrier

performance of a coating will be damaged soon and corrosive electrolyte comes into contact with the metal substrate. Use of corrosion inhibitors is another approach to produce active coatings in exposure to corrosive electrolytes. These active agents are soluble in corrosive electrolytes and protect metal surface by passivation mechanism. There are different kinds of corrosion inhibitors which can be divided to three main types based on the mechanism controlling corrosion process. Anodic inhibitor (only reduces anodic reaction rate), cathodic inhibitor (only reduces cathodic reaction rate) and mixed inhibitors (both cathodic and anodic reactions can be influenced) (Nobel et al., 2007, Dhoke et al., 2009, Shchukin et al., 2007, Brooman, 2002, Kasten et al., 2001, Sheffer et al., 2004, Garcia-Heras et al., 2004, Osborne et al., 2001, Vreugdenhil et al., 2005). The solubility of the inhibitors is found an important factor affecting its corrosion inhibiting efficiency. Very low solubility leads to low passivating behavior at metal substrate. There are disadvantages for very high solubility: first, the inhibitor will be rapidly leached out from the coating and second, the active surface blistering and delamination may occur due to osmotic pressure effect. As a result of osmotic pressure, water transportation into the coating matrix and passive layer destruction may occur. Because of this, adding active inhibitors at high concentration is not possible in conventional processes. This problem has been solved in modern coatings using nanoscale container (carrying active agents like inhibitors). In this approach, active inhibitor is loaded into nanocontainer. The nanocontainers have a permeable shell which could release active agents in coating matrix. In fact, the shell is designed in a way which release active agent in a controlled process. There is another approach which instead of nanocontainer in which the passive layer is doped with active agents. However, interaction of active materials with coating matrix leads to short-coming in the stability and self-repairing activity of the coating. The disadvantages cannot be seen for the system loaded with nanocontainers as the coating matrix does not directly contact with active agents. The system is schematically shown in Fig. 7 (Shchukin et al., 2007).



**Figure 7.** Active material is embedded in the “passive” matrix of the coating (a) and active material is encapsulated into nanocontainers (b) (Shchukin et al., 2007).

The nanocontainers will be uniformly distributed in coating matrix keeping active materials in a trapped state. The nanocontainers respond to any signal or when the environment undergoes changes they release encapsulated active materials. Controlling nanocapsuls permeability and nanocontainers compatibility with coating matrix are the most important parameters affecting their anticorrosion performance. The optimum nanocontainers size range is 300-400 nm. Using nanocontainers with larger sizes may lead to large hollow cavities formation inside coating matrix resulting in significant reduction of the passive protective properties of the coating. Depending on the sensitive components presented in nanocontainers (i.e. polyelectrolytes or metal nanoparticles) different parameters like ionic strength, pH changes, temperature, ultrasonic treatment, magnetic field alteration may influence shell permeability. The mechanism in which nanocontainers release active agents and protect attacked areas of metal surface by corrosive electrolyte forming a passive layer is schematically shown in Fig. 8 (Shchukin et al., 2007).



**Figure 8.** Schematic illustration of self-repairing mechanism of nanocontainers when metal is exposed to corrosive electrolyte (Shchukin et al., 2007).

## 2.5. Weathering resistant automotive coatings

Two main purposes of coating application in automotive industries are protecting the car body against environmental conditions and imparting desirable esthetic appearance. To fulfill these functions, the coatings themselves have to remain intact for a long time in a harsh environment. Photo and hydrolytic degradations respectively caused by sunlight and humidity are two common processes occurred, resulting in changes in all aspects and properties of automotive coatings (Yari, et al., 2009a; 2009b; Ramezanzadeh, et al., 2012a). These chemical alterations may greatly influence all aspects of the coating. Therefore, automotive coatings are required to be highly resistant against weathering condition. To enhance coating resistance against sunlight, HALS (hindered amine light stabilizer) and/or organic UV-absorbers has been added to clearcoat formulation. Although these ingredients considerably enhanced weathering performance, in addition to having high prices, they can

migrate to other layers and are also prone to undergo decomposition during service life. To fight weathering, nanotechnology has offered new solutions that have no drawbacks as mentioned above for organic UV stabilizers.

In recent researches, various nanoparticles such as zinc oxide, iron oxide, cerium oxide, titanium oxide and silica have been incorporated into conventional polymeric coatings to enhance their resistance against sunlight. Nanoparticles, possessing a high surface area for absorbing the harmful part of sunlight (ultraviolet part), prevent the coatings from weathering degradation. Since they are inorganic and particulate, they are more stable and non-migratory within an applied coating. So, they present better effectiveness and longer protection.

As mentioned before, TiO<sub>2</sub> nanoparticles are effective to fight against UV rays and can protect the coating against weathering. However, these nanoparticles especially can exert strong oxidizing power and produce highly reactive free radicals and degrade the coating in which has been incorporated. Thus, photocatalytic activity of TiO<sub>2</sub> nanoparticles has to be controlled. For this purpose, treatment of nanoparticles by different techniques such as silane agents not only suppresses photocatalytic activity of TiO<sub>2</sub> nanoparticles, also offers clear advantages like simplicity and low cost and processing temperatures. It has also been demonstrated that surface modification of TiO<sub>2</sub> nanoparticles with aminopropyl trimethoxy silane (APS), considerably has reduced photocatalytic activity of nanoparticles and enhanced the weathering resistance of a polyurethane coating (Mirabedini, et al., 2011).

In various researches, it has been shown that zinc oxide nanoparticle can be an effective option to nearly completely screen the UV rays and protect the coating (Lowry, et al., 2008; Ramezanzadeh & 2011a). In an attempt to improve the UV resistance of an aromatic polyurethane-based automotive electro-coating nano-ZnO particles were used. The results obviously illustrated that the presence of nano-zinc oxide particles could decrease the photodegradation tendency of the film and protect it against deterioration (Rashvand, et al., 2011).

### 2.5.1. Weathering due to biologicals

Although, humidity and sunlight are the two main factors which degrade automotive coatings, other environmental factors, i.e. those originated from the biological sources can have a spoiling impact on the appearance of a car body during its service life (Ramezanzadeh et al., 2009). In a systematic manner, the degradation mechanism and influence of various biological substances such as bird droppings, tree gums and insect gums on automotive coatings have been thoroughly studied (Yari et al., 2009c; Ramezanzadeh et al., 2010a; 2010b; 2011b). It was revealed that both natural gum and bird dropping seem to affect the coating physically (by imposing stress to coating while they are being dried) and chemically (by catalyzing the hydrolytic degradation) (Yari et al., 2011; Ramezanzadeh et al., 2010c; 2010b; 2011b). While natural gum has extensively created large cracks with scattered etched areas (Ramezanzadeh et al., 2010c; 2010b), the influence of bird droppings was formation of numerous etched regions with some small cracks (Yari et al., 2011). It was also found that the most important factors governing the degradation are the

coating chemical structure at surface and adhesion between coating surface and biological materials. Therefore, it was thought that any modification which could be able to alter both surface chemistry of the clearcoat and adhesion would be an ideal option to fight bio attacks. This idea was proved by a series of experiments. It was demonstrated that modification of clearcoat with a functional silicone additive significantly improved the coating performance against bird droppings and tree saps (Yari et al., 2012a, Ramezanzadeh et al., 2012b) (Fig. 9).

According to these new findings, creating a clearcoat with non-stick and superior water-repellency properties would significantly reduce the failure of coatings caused by biological materials. Ultra-hydrophobic self-cleaning coatings which are produced by nanotechnology is a powerful approach for this purpose. Contaminants on such surfaces are swept by water droplets or adhere to the water droplet and are removed from the surface when the water droplets roll off. Although these types of coatings for automotive glasses have been already commercialized, their development for automotive paints is in progress.

## 2.6. Smart windows based on electrochromism

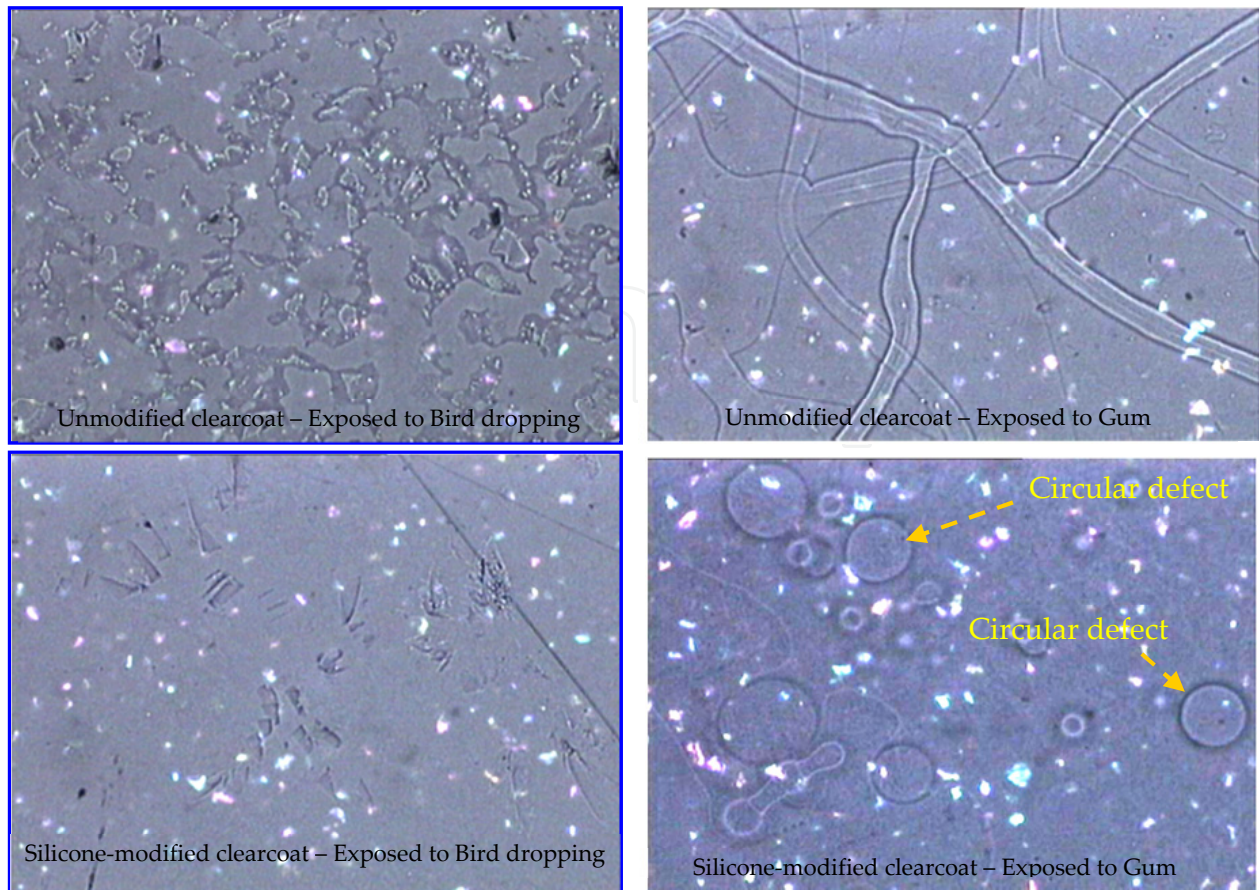
As stated before, providing a secure and comfortable condition for driver and passengers has become an important task in automotive industry. To this end, automotive experts strongly believe that all types of energy like sound, light and heat which enter the car body have to be controlled. Recent progresses in polymer and different types of dichromic technology have allowed the development of smart glasses which intelligently control solar radiation transmission and modulate glare, increase passenger comfort and safety. Among different kinds of smart glasses, electrochromic (EC) ones are very important.

EC materials alter their optical characteristics (darkness/lightness) when a small electric potential difference is applied. They are suitable for a wide range of applications. They can be employed in different parts of an automobile like for energy-efficient windows, antiglare rear-view mirrors, sunroofs and displays.

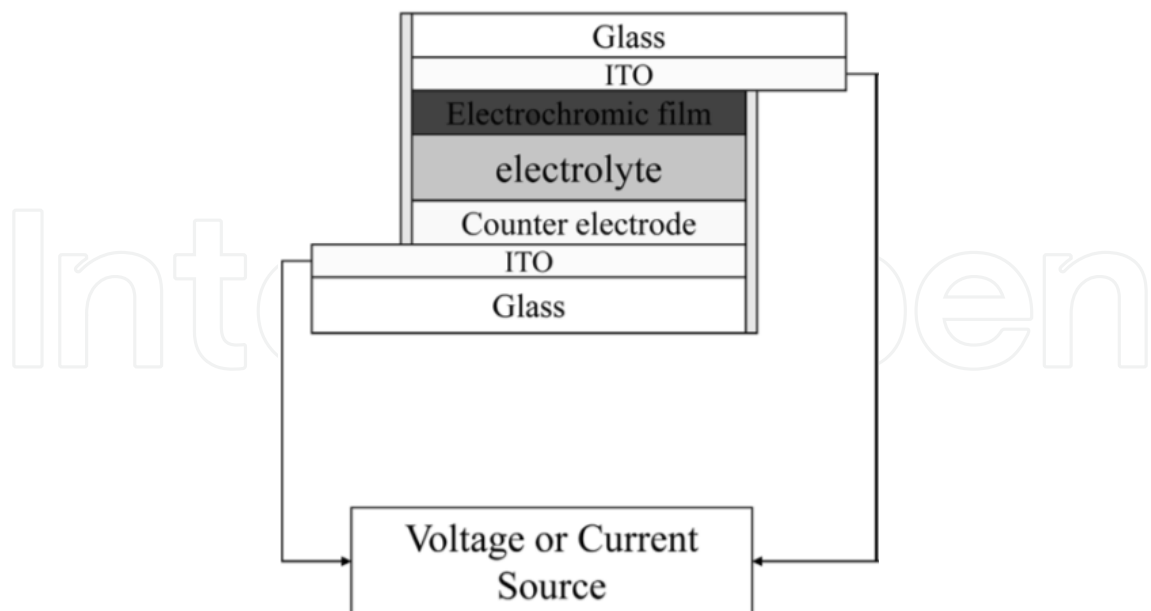
A typical ECD composition has a complicated structure. As shown in Fig.10, it usually consists of a five-layer sandwiched-structure which are applied between two glass substrates. This structure includes transparent conductor, an electrochromic coating, ion conductor and ions storage coating and another transparent Conductor (Pawlicka, 2009).

Since the layers in this structure are very thin, the technology used for this assembly can be considered in nanotechnology domain. The thicknesses of transparent conductor, EC, electrolyte and counter electrode (ion storage) layers in a typical EC structure are 1500Å, 4000Å, 100µm and 1250Å, respectively. These layers can be deposited by different techniques such as sputtering, CVD, spin- or dip-coating from sol-gel precursors, etc.

The EC devices operate based on the reversible electrochemical double injection of positive ions i.e.  $H^+$ ,  $Li^+$ ,  $Na^+$  and electrons into the host lattice of EC materials. Diffusion of mentioned ion and electrons into EC layer initiate some redox reactions, leading to a change in electrochemical state of EC material and therefore its resultant color. This variation in color of EC layer alters the color of the whole structure (for more details, see (Monk et al., 2007).



**Figure 9.** Microscopic images pure and silicone-modified clearcoats exposed to bird droppings and tree gums.



**Figure 10.** A typical EC system consists of different layers (Pawlicka , 2009).

EC technology becomes more and more important because it possesses low power consumption. However, due to slow diffusion of ions, response time (the time that a

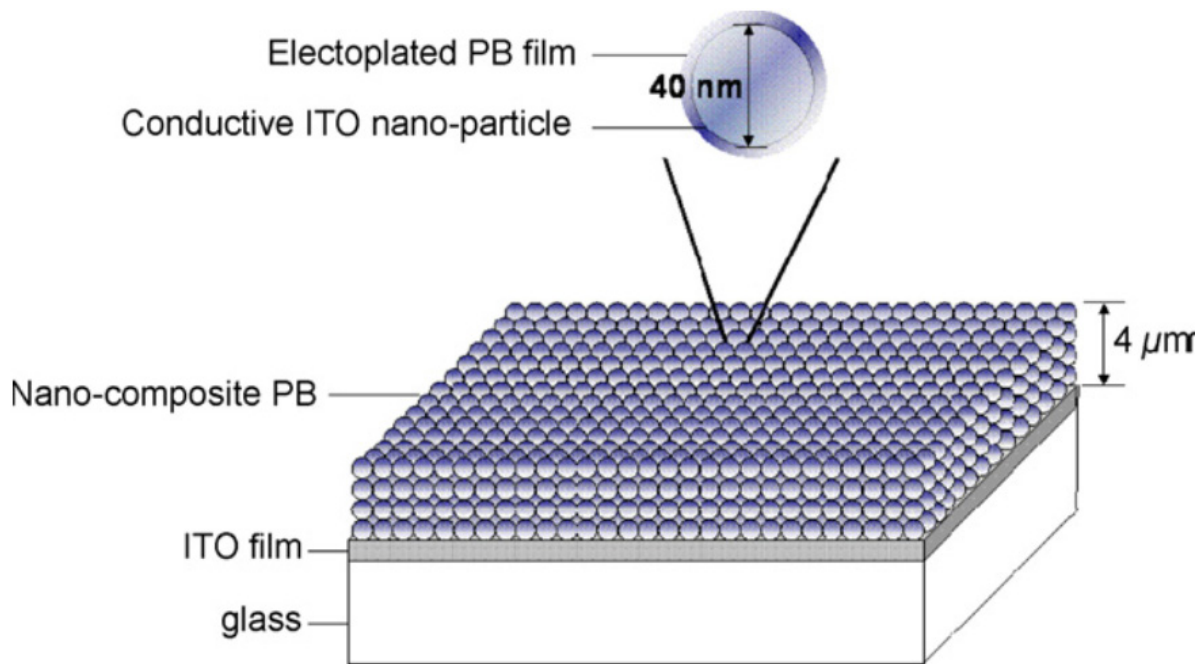
perceivable change in color occurs) in conventional EC systems is relatively slow and this drawback limits application of EC systems where a fast response is needed like in automotive rear-view mirrors. A significant portion of studies related to EC systems is devoted to new methods or materials to reduce the response time. In recent years, although scientists have achieved successes using new materials like hydrogen ions instead of lithium ions, nanotechnology has opened new rooms in this field and has triggered plenty of academic and industrial enthusiasms. In an EC process, if the surface area of the EC materials increases by producing nano-structured oxide films, migration of ions will be improved and consequently redox reactions will occur faster. Here, a few of nanotechnology-involved studies are briefly presented.

Among inorganic EC materials, tungsten oxide films have the highest coloration efficiency in the visible region and, therefore, have been most extensively studied so far. In a recent study, EC films from crystalline  $\text{WO}_3$  nanoparticles have been fabricated (Lee et al., 2006). Porous films of crystalline  $\text{WO}_3$  nanoparticles were grown by hot-wire chemical-vapor deposition and electrophoresis techniques. The nano-scale porosity of the films not only increases the surface area and ion-insertion kinetics, but also diminishes the overall material cost. It was also revealed that compared to conventional amorphous  $\text{WO}_3$  films, nanoparticle films demonstrated superior electrochemical-cycling stability in acidic electrolytes, a higher charge density, and comparable CE. It seems that these findings will eventually revolutionize current EC technology.

The first commercial EC product was based on a patented document from Gentex Corp. in 1992. It was a solution-phase EC rear-view mirror for automotive vehicles which had a reflectance greater than 70% to less than 10%. This technology has been installed in many cars. In addition, in 2007 Donnelly Corporation designed an EC system for use as automotive mirrors. In this invention, which was based on polymerization of an electrochromic monomer, the color of the mirror varies uniformly from a silver appearance to bluish purple, and its reflectance changes from 60% to 20%. In a similar study, Thin mesoporous films of nickel oxides and nanotube manganese oxides were electrochemically produced on indium tin oxide (ITO) coated glasses and compared with conventional structure ones (Yoshino, 2012). It was found that nano-structured films exhibited marked changes in optical transmittance and electric charge with respect to the electrochromic reactions.

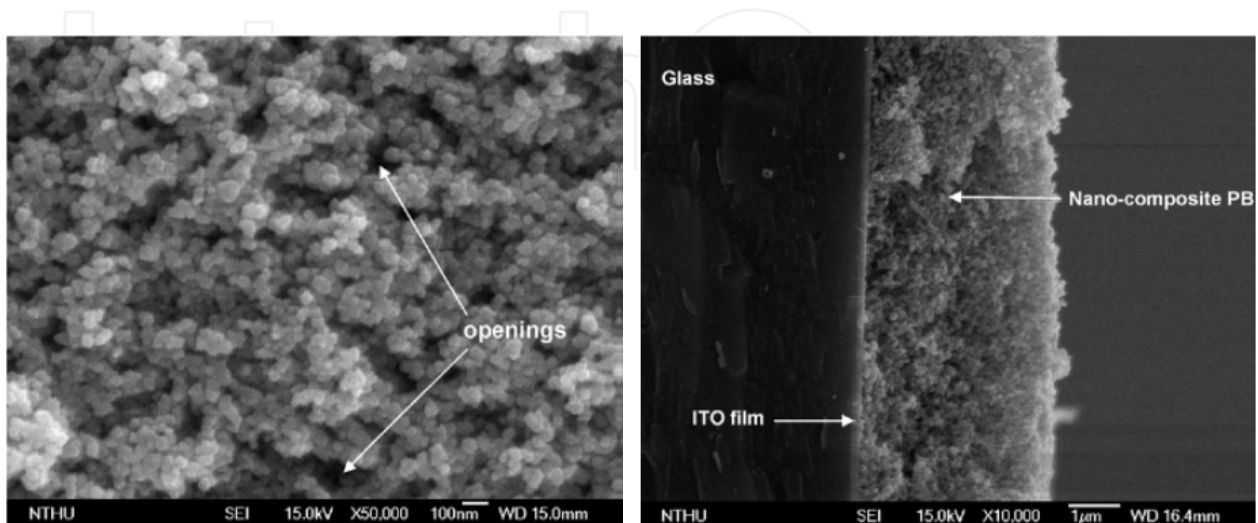
Coating EC material on different types of nano-particles are much more novel approaches to take advantage of large surface area granted by nano-materials to overcome the drawback of long switching time. Coating Viologen on  $\text{TiO}_2$  nanoparticles (Cummins, et al., 2000) or preparation of Poly(3,4- ethylenedioxythiophene) (PEDOT) nanotubes (Kim, & Lee, 2005) or arrangement of PEDOT films (Kimura, & Yamada, 2009) on Au nano-brush electrodes are of the most important published activities.

In a same research, in order to enhance the contrast and switching time of regular Prussian Blue (PB), which is widely used as a sole electrochrome in EC devices, the nano-technology concept has been applied (Cheng et al., 2007). Fig. 11 clearly describes this research.



**Figure 11.** Conceptual structure of nano-composite PB film.

In the nanocomposite shown in Fig. 11, indium tin oxide (ITO) nano-particles was applied as a medium layer for PB to gain larger operative reaction surface area. It was prepared by spraying a well-dispersed ITO nano-particle solution onto an ITO-coated glass and followed by electroplating PB on pre-sprayed ITO nano-particles. Due to proper covering of ITO nano-particles with PB, the final film produce a nano-porous electrochromic layer. Fig. 12 shows the SEM photograph of this nanocomposite from top and cross-sectional view. It was also revealed that switching speed and contrast of nano-structured film exhibit much better performances than traditional PB thin films. It was explained by this fact that Nanocomposite PB offers much larger operative reaction surface area than traditional PB film does.



**Figure 12.** SEM images of final PB nanocomposite film (a) top and (b) cross-sectional view.



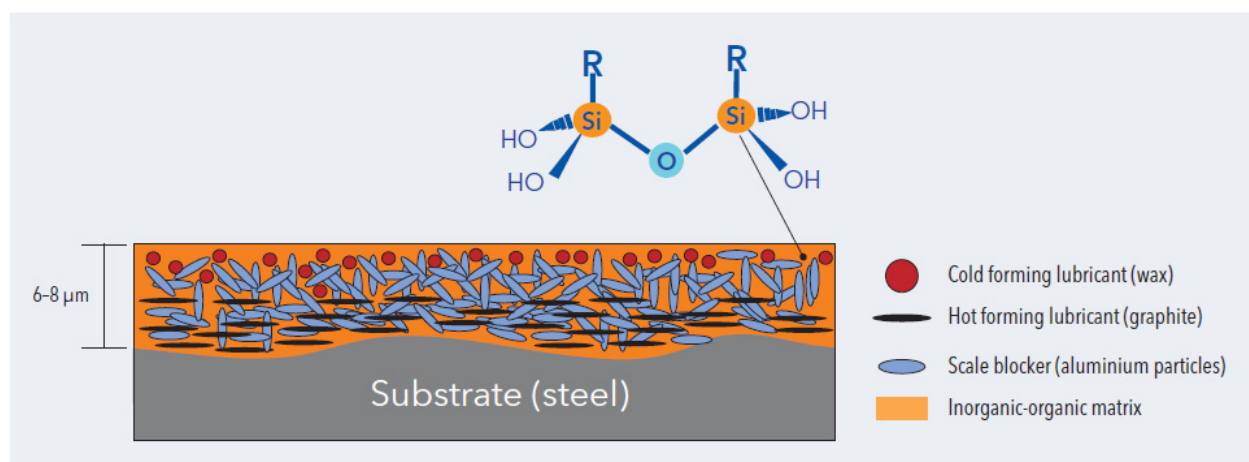
DuPont has developed an EC device based on an organic polymer technology to control light transmission in automotive applications. In comparison with current EC technologies, this not only is less complicated, but also it can be used in rigid and flexible forms, large sizes, and curved shapes. Target markets of this technology in automotive include sunroofs, mirrors, instrument clusters, windshield shade bands, sidelights, and backlights.

It is predicted that the market for smart windows will become a billion-dollar one by 2015 and will be doubling by 2018. The automotive market provides the next largest source of smart window opportunities for glass suppliers, after the architectural markets.

The Ferrari 575 M Superamerica had an electrochromic roof as standard, and the Maybach has a PDLC roof as option. Some Polyvision Privacy Glass has been applied in the Maybach 62 car for privacy protection purposes.

## 2.7. High-strength steels for car bodies

In order to enhance cars and passengers safety at crashes, the automotive producers have attempted to use high-strength steels in car bodies. However, it is difficult recasting of high-strength steel parts in cold state as the size accuracy changes and undesirable spring-back effects may occurs. Recasting in a hot state (at 1000 °C) helps us to avoid such disadvantages during recasting of high-strength steel parts. However, the scaling of this kind of steel is difficult at high temperatures. Nanotechnology is utilized to solve this problem. To this end, a multifunctional protective coating produced based on nanotechnological approach with the principles of conventional paint technologies. This multifunctional coating is produced using bonded and connected nano sized vitreous and plastic like materials together with aluminum particles. This system is schematically shown in Fig. 13 (21-22).



**Figure 13.** Nanostructured high-strength steel for car body.

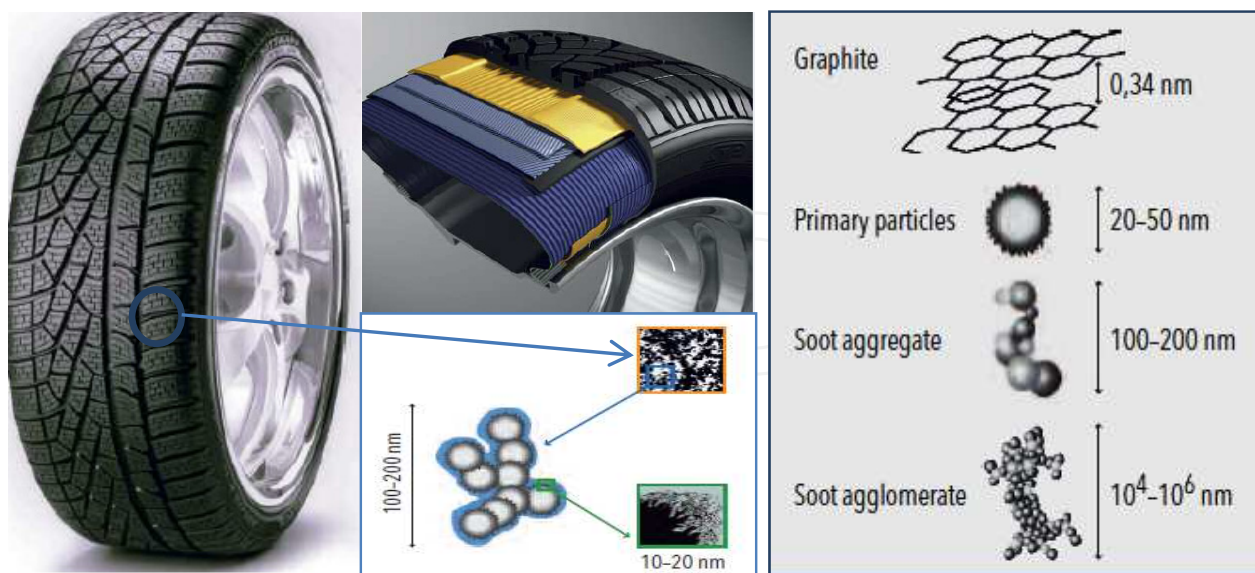
## 2.8. Nanostructured tyres

Tyres performance extremely depends on their cover composition which is continuously in contact with road. So the rubber composition of the cover plays an important role on its

properties. Different properties like abrasion resistance, grip and resistance against tear propagation are important. Incorporation 30% filler can improve such properties. Type and loading of filler as well as chemical and physical interactions between filler and rubber are influential parameters affecting its properties (Das et al., 2008, Zhou et al., 2010).

While the tyre resistance against grip should be high, its rolling resistance has to be low. Tyres need to resist abrasion but they should have slip-proof properties to reduce the car slide. In fact, there are three main factors which necessarily should be considered for a desired car tyre. These are reducing fuel efficiency by improving rolling resistance, increasing tyre life time by improving its abrasion resistance and reducing car fuel consumption by reducing friction. However, reducing friction can negatively influence car safety. The modern tyres consist of a mixture of synthetic and natural rubber, carbon black and silica, additives and steel/textile or nylon rod as reinforcement.

Soot (carbon black), silica and organosilane are the important examples of materials used to enhance rubber properties. Adding such materials to rubber composition at nanometric dimensions can significantly improve tyre properties. The size and surface modification of the particles can affect their chemical and/or physical interactions with rubber matrix. This varies the particles cross-linking with natural rubber molecules, affecting its properties. Nano sized soot particles can significantly enhance tyres durability as well as higher fuel efficiency. These particles have courser surface compared with traditional ones and due to their higher surface energy, they could produce stronger interactions with rubber matrix (Fig. 14). As a result, inner friction can be reduced which results in better rolling properties (Das et al., 2008, Zhou et al., 2010).



**Figure 14.** Schematic illustration of a modern nanostructured based tyre for cars (Das et al., 2008, Zhou et al., 2010).

It is well known that strain vibration will occur within tyre material at high car speed. Nanoparticles can reduce this strain vibration and results in superior traction, especially on

wet roads. The surface modification of the particles is important which will affect their interaction with rubber matrix and its final properties. It has been found that carbon nanotube (CNT) can improve mechanical properties such as tensile strength (600%), tear strength (250%) and hardness (70%) of styrene-butadiene rubbers. Tyres with higher stiffness and better thermoplastic stability can be produced using lamellar nano-sized organoclays like montmorillonite. The other nanoparticles used to enhance car tyre properties are nano-alumina, carbon nano fibers (CNF) and graphene. The rolling resistance of tyres can be significantly improved using silane-treated silica compared with traditional carbon black based tyres. Using nanoparticles, tyres with better traction on wet and icy roads can be produced. As a result, the stopping distance of car can be reduced by 15-20 % and 5% in fuel consumption (Das et al., 2008, Zhou et al., 2010).

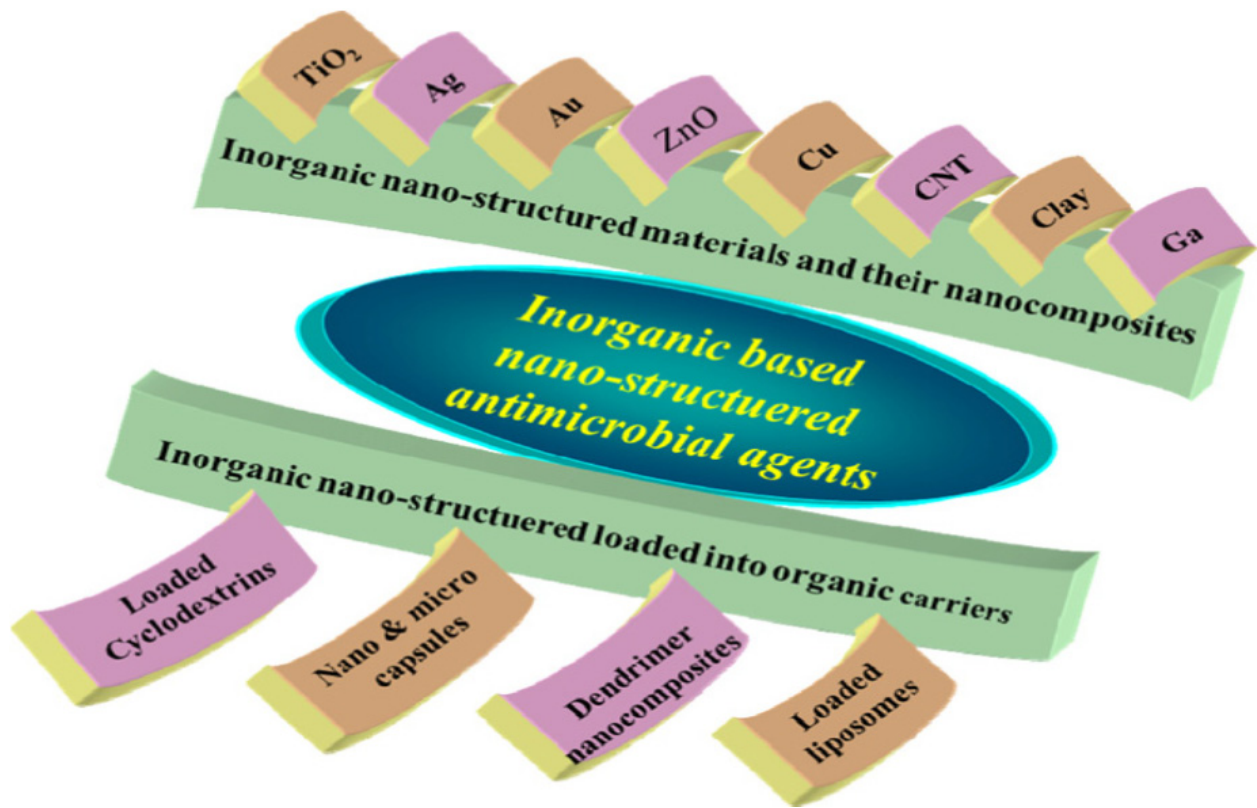
### 3. Interior applications

#### 3.1. Automotive fabrics

Car industry's commercial strategy today is to improve the safety and convenience aspects of automobiles. Textiles, especially fabrics, as the main substances in designing of interior parts of a vehicle, are very important. They are utilized in various parts such as interior panels for doors, pillars, seats coverings and paddings, parts of the dashboard, cabin roof and boot carpets, headliner, safety belts, airbags. Nanotechnology as a powerful tool has aided the auto-manufacturers to reach their goals in a short period of time. The most important properties of automotive fabrics which have been modified by the aid of nanotechnology include: a) anti-microbial b) self-cleaning c) fire-retardancy.

##### 3.1.1. Antimicrobial/antibacterial and Anti-odour properties

Textiles can grant an appropriate environment for micro-organisms growth especially at proper humidity and temperature in contact to human body. Rapid and uncontrolled fast thriving of microbes can lead to some serious problems. Because of public concern about hygiene, the number of studies about anti-microbial modification of textiles has been significantly increased in recent years. To this end, various anti-microbial agents such as Oxidising agents ( aldehydes, halogens), Radical formers (halogens, isothiazones and peroxo compounds), diphenyl ether (bis-phenyl) derivatives, Quaternary ammonium compounds and chitosan have been used. Nevertheless, application of many of these materials has been avoided because of their harmful or toxic effects. More recently, nanotechnology has been the basis of a great number of researches to produce novel anti-microbial textiles. As schematically presented in Fig. 15, the most important nano-structured anti-microbial agents are silver, titanium oxide, gold, copper and zinc oxide and chitosan nano-particles, silver-based nano-structured materials, titania nanotubes (TNTs), carbon nanotubes (CNTs), nano-clay, gallium, liposomes loaded nano-particles (Dastjerdi & Montazer, 2010). These nanoparticles can be coated directly on textiles or via a vehicle (incorporated nanoparticles in a matrix such as silica network). Various techniques can be utilized for coating of these antimicrobial agents on textiles like sol-gel processes and chemical vapor deposition.



**Figure 15.** Classification of inorganic based nano-structured anti-microbial agents(Dastjerdi & Montazer, 2010).

The anti-bacterial action in these agents is caused via either a photo-catalytic reactions or biocidal processes. An example of former type of anti-bacterials is titania-based agents that act through the absorption of light, photo-catalytic reactions. As a result of these reactions, excited charge carriers (an electron and a positively charged electron-hole) are produced. While the positively charged holes induce the oxidation of organic molecules, the electrons can react with oxygen, leading to formation of superoxide radicals. These radicals attack and oxidize the cell membranes of microorganisms. The described photo-catalytic process is the cleaning mechanism of superhydrophilic self-cleaning surfaces which leads to the degradation of stains (Banerjee, 2011; Fujishima et al., 2008). Silver and gold are examples of the latter type of anti-bacterial materials. In biocidal action, the antibacterial effect happens via interaction between the positively charged biocide and the negatively charged cell membranes of microorganisms which damages the microorganism. In the majority of researches a combination of both mechanisms (photo-catalytic and biocidal processes) are used to achieve an efficient anti-bacterial effect (Yuranova, et al., 2006; Yeo et al., 2003).

Among different anti-bacterial agents, silver has received the most attention because of potential advantages(Montazer et al., 2012a; Montazer, et al., 2012 b). Besides possessing a high degree of biocompatibility, silver is highly resistant to sterilization conditions and has a long-term antibacterial efficiency against different bacteria.

In commercial viewpoint, anti-bacterial automotive textiles based on nanotechnology are beginning to enter the market. For example, Tencel™ material based on nanofibrils of

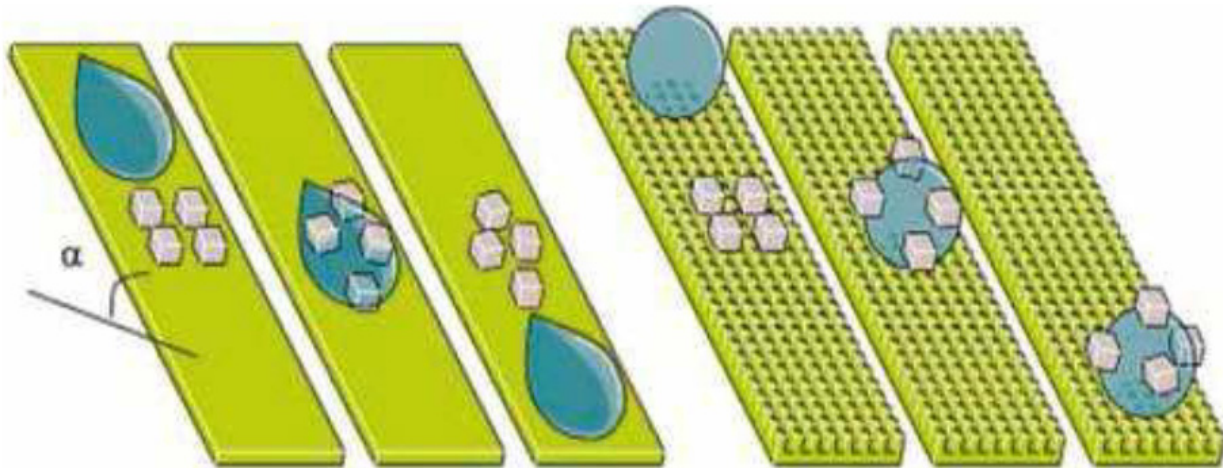
cellulose was produced by Lenzing. It has a combination of properties and in particular antibacterial properties which reduces growth of bacteria. This product has been introduced to the market as a good candidate for seat car covers.

### 3.1.2. Hydrophobic surfaces and anti-stain textiles

Lotus leaf is a natural model for super-hydrophobic surfaces. Very low surface energy materials (like fluoro- or silicone- containing polymers) and nano-scale roughness structures (created by nanoparticles or nanotechnology-based procedures) are required for creating a superhydrophobic self-cleaning surface. A schematic picture of such surfaces is shown in Fig. 16. On these surfaces the distance between summits of such nano-roughnesses is around few hundreds nanometer and they are so close together that a speckle of dirt would not fit between them (Wang et al., 2011). Therefore, a non-stick surface is produced. On the other hand, low surface energy substances make water roll off and easily wash off unattached dirt from surface.

Different methods based on nanotechnology like Layer-by-Layer Deposition, Electrodeposition/Electropolymerisation, Plasma and Laser Treatment, Electrospinning, Casting and Molding can be employed for creating nano-roughness.

Among researches to make super hydrophobic surfaces, carbon nanotube, silica and fluoro containing polymer nanoparticles were applied to the nylon, cotton and polyester fabrics in form of a coating (46-48). In these works, they could achieve artificial lotus leaf structures.



**Figure 16.** Self-clean action on a conventional and on a nano-structured textiles by removing dirt with water (lotus effect).

Opel Co. was the first manufacturer in the world to equip seating upholstery of Insignia (Car of the Year 2009) with the Nanogate coatings that repel dirt and liquid staining.

### 3.1.3. Flame retardant fabrics

For the last half a century, various compounds have been employed to improve the fire resistance performance of textiles. Inorganic chemicals such as antimony, aluminum and tin

as well as Bromine, Chlorine- and Phosphorus- based compounds are the main chemical families of flame retardants (Horrocks, 2011). These conventional chemicals are not usually harmless. It has been proved that halogen–antimony and phosphorus–bromine combinations, besides having limited performance have environmental concerns. Environmental regulations have restricted the use of these flame-retardant additives, initiating a search for replacing toxic flame retardants in polymer formulations with safer and more environmentally-friendly alternatives. This has sparked the interest of nanoscientists.

Recently, polymer nanocomposites offering significant advantages over conventional formulations have received many attentions in the field of flame retardancy. Nanoparticle fillers are highly attractive for this purpose, because they can simultaneously modify both the physical and flammability properties of the polymeric matrixes. Layered silicates (clay) and carbon nanotubes (CNTs) are two main nanostructured materials that have attracted the attention of scientists to promote fire performance of polymeric substrates like textiles (Bellayer et al., 2004; Kiliaris, & Papaspyrides, 2010). The nano-materials make fabrics less ignitable and self-extinguishable when the flame is removed.

Since flame retarding mechanisms of clay and CNTs are different, significant synergism happens when they are introduced to textile together, leading to a much more efficient approach to improve the flame retardancy.

In recent studies, polyhedral oligomeric silsesquioxane(POSS) compounds have been utilized as fire-retardant agents. In a series of experiments, Bourbigot and coworkers introduced POSS nanoparticles in polypropylene yarns, cotton and knitted polyester and showed that the time-to-ignition increased significantly as a result of presence of nanoparticles (Bourbigot, et al., 2005).

Since clays, CNTs and POSS nanoparticles are more expensive than traditional fire retardants, their uses are currently hampered even if they are more environmentally friendly. Therefore, cost reduction would likely change this situation.

### **3.2. Nano-coatings for engine application**

Coatings plays an important role in improving efficiency and life of the car engine. These are listed below (Dahotre et al., 2005, MacLean et al., 2003, Lin., et al 1993):

Lubrication (reduced frictional loss)

Thermal insulation (higher operating temperature)

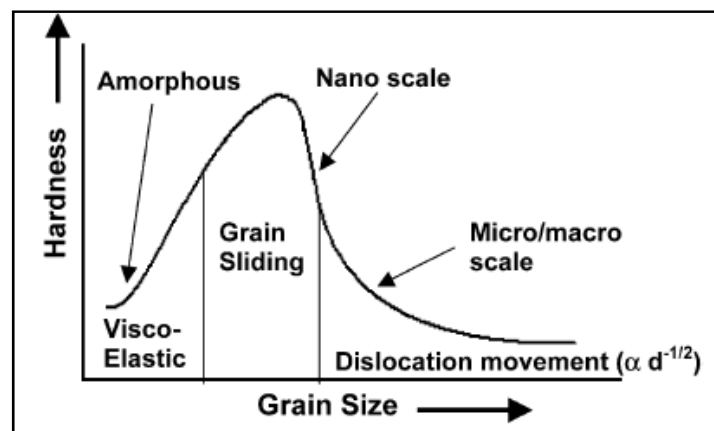
Reduced friction (surface finish and affinity or oil)

Reduce dimension weight (replaces cast iron block/liner)

It is well known that engine of a car can operate at higher temperatures by reducing external heat removal. Using lightweight materials in engine to reduce load, heat losses and frictional losses is another approach to improve fuel efficiency. One of the most important

factors to improve fuel efficiency is reducing weight of engine. Replacing cast iron (with density of  $7.8 \text{ g/cm}^3$ ) used in engine blocks with low-cast aluminum-silicone (with density of  $2.79 \text{ g/cm}^3$ ) is one possibility for engine weight reduction. However, aluminum alloys do not have adequate wear resistance and high seizure loads to be used in the cylinder bores. Because of these, cylinder bores are made of cast iron liners which have good wear resistance. Therefore, attempts have been carried out to improve aluminum bars properties using new composites and/or monolithic coatings (Dahotre et al., 2005, MacLean et al., 2003, Lin et al., 1993, Venkataraman et al., 1996, Rao et al., 1997).

Nanomaterials can be employed to achieve extraordinary properties for aluminum bars. Schematic illustration showing the variations of hardness versus grain size is depicted in Fig. 17.



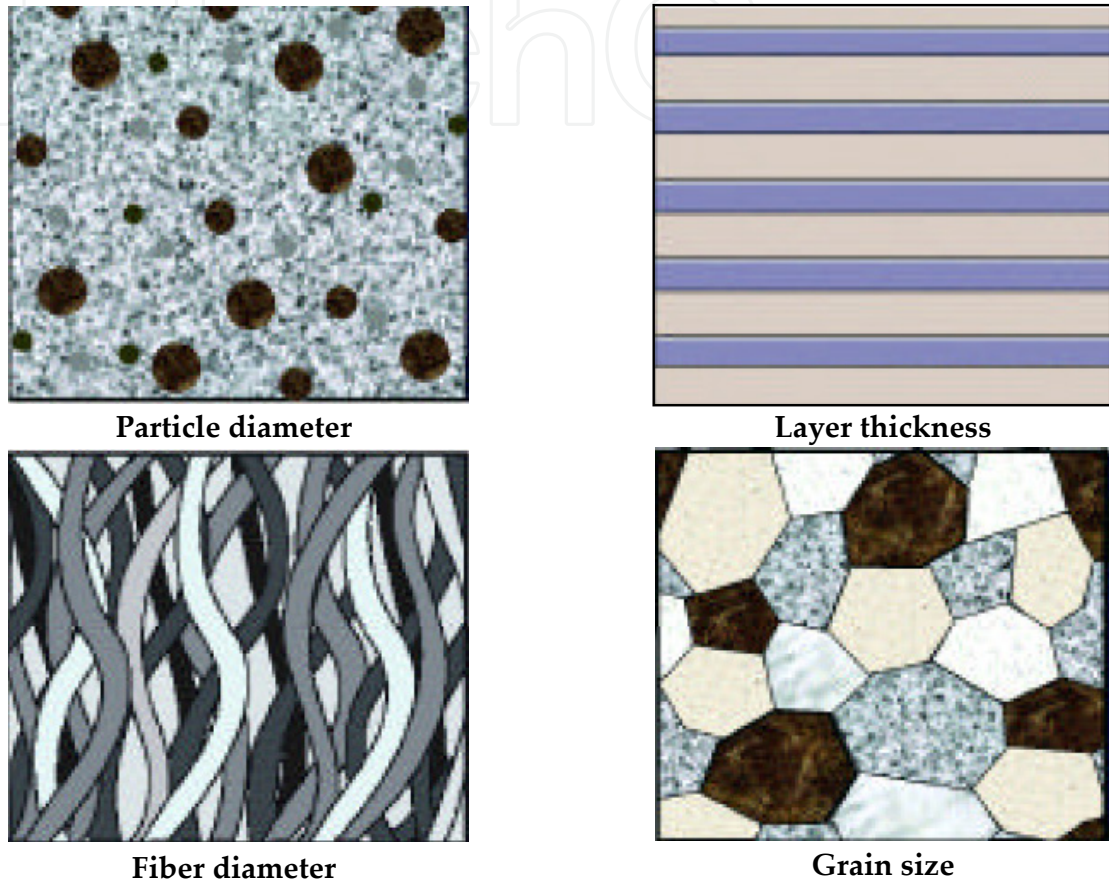
**Figure 17.** The effects of grain size of a metal on its hardness and other properties (Dahotre et al., 2005).

Fig. 17 clearly shows increase of hardness and flow stress as the grain size decreases ( $<100 \text{ nm}$ ). At grain sizes smaller than  $100 \text{ nm}$ , the deformation mechanism will be changed from dislocation-controlled slip to grain boundary sliding whilst the plasticity is increased simultaneously. Different parameters including toughness, flow stress, ductility and thermal insulation of the aluminum will be intensified when the grain size is in nano scale. Nanocoatings have been utilized in order to improve engine efficiency as described below:

### 3.3. Wear resistant nano-coatings for engines

Scratch and wear are criteria parameters which will be considered for the metal parts used in automobile engines. Electrodeposited hard chrome and microstructure ceramic coatings are the most used kinds of protective coatings for engine parts. The ceramic coatings are frequently applied on metal parts using thermal spray. In plasma spraying, the coating powder reinforced with ceramic particles is injected into a plasma stream following by heating and accelerating toward the metal substrate. The ceramic rapidly cools and produce a coating layer over the substrate. However, there are limitations for the use of microstructure ceramic and electrodeposited chrome coatings. Chrome coatings include hazardous materials influencing the environment and are also expensive. The conventional microstructure ceramic coatings are less expensive than chrome coating but are brittle and

show low adhesion to the substrate. Attempts have been carried out to find other replacements. Nanostructured containing ceramic coatings have been utilized to improve metal parts of engine against abrasion and wear. Reducing the scale of materials microstructure like grain size, particle size or layer thickness can significantly alter its properties (Fig. 18) (Rao et al., 1997, Wuest et al., 1997, Rastegar et al., 1997, Cole et al., 1997, Ebisawa et al., 1991, Kabacoff et al., 2002, Sanchez et al., 2007).



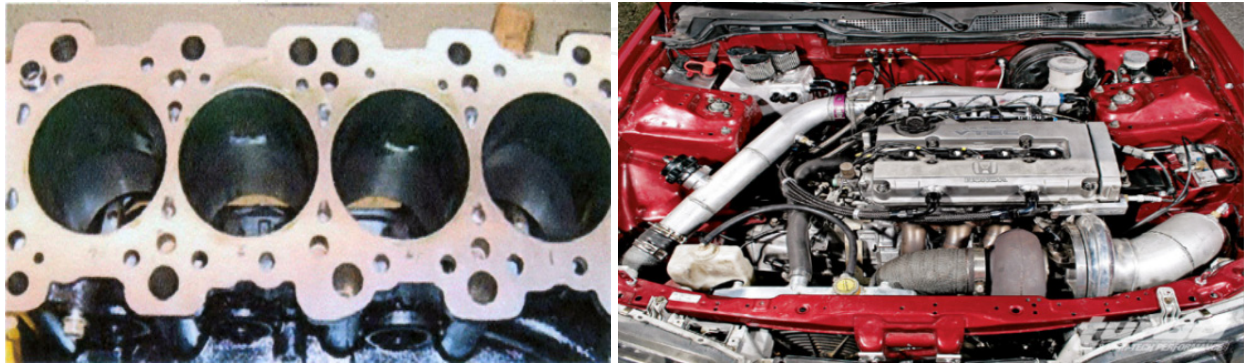
**Figure 18.** Different states of nanostructured materials used in order to improve car body properties (Kabacoff et al., 2002).

Recently, new nanoceramic composites (alumina-titania ceramic coatings) have exhibited excellent wear resistance. However, there are problems with spraying nanoparticles because of their low mass and poor fluidity. One way to solve this problem is agglomerating nanoparticles into micrometer-sized aggregates. However, in order to obtain initial nanostructure after spraying, the process must be carefully controlled. Alumina, alumina-titania, cemented tungsten carbides, or zirconia powders are examples for the nanostructured coatings obtained from agglomerated particles plasma spraying. Both wear and abrasion resistance of the metal substrate will be considerably improved after the nanostructured materials spraying. Recent findings have revealed that atmospheric plasma spraying of the nanostructured materials results in better nanostructure formation in final coating layer and better tribological properties of the coating (Dahotre et al., 2005, Kabacoff et al., 2002, Sanchez et al., 2007).



### 3.4. Nano-coatings with good lubrication for engine application

It is well known that mechanical friction could significantly influence the internal combustion (IC) engine fuel economy. Valve train, piston system crank and bearing system are the most important sources of frictions (Fig. 19) (Dahotre et al., 2005, Kabacoff et al., 2002, Sanchez et al., 2007).



**Figure 19.** New coatings used to improve (right) engine body structure and (left) cylinders.

These friction sources could reduce engine life and increase oil consumption. Coatings could reduce frictions and result in lower oil usage. Examples of these coatings are Ni-Mo-MoS<sub>2</sub>, Ni-BN, graphite-Ni, etc. Recently, nano-structured materials have been utilized to improve friction properties of piston rings. Zirconium ceramic coatings can modify surface properties. Nano-size zirconium powder can be dispersed in a mineral oil. The nanoparticles can reach working surface of the engine when the piston moves. The nano-size zirconium help ceramic particles better bond to the metal surface. Heat generated during engine operation would be enough to cure ceramic powder attached to the engine surface. After curing, ceramic coating produces hard and smooth surface at different parts of the engine including cylinder walls, piston rings, piston top, valve tops and bearing surfaces. The nano-size zirconium particles can also improve fuel economy, power output, oil burning and reduce noise, vibration of engine and pollution discharge (Rao et al., 1997, Wuest et al., 1997, Rastegar et al., 1997, Cole et al., 1997, Ebisawa et al., 1991, Kabacoff et al., 2002, Sanchez et al., 2007).

### 3.5. Nanofluids and nanolubricants

#### 3.5.1. Nanofluids: Properties and application in automotive industry

Adding nano sized materials like nanofibers, nanotubes, nanowires, nanorods and nanosheets to fluids results in producing new generation of fluids having superior properties in comparison with conventional fluids. In fact, nanoscale colloidal suspensions loaded with condensed nanomaterials are named nanofluids. This system consists of two phases: liquid phase (base fluid) and solid phase (nanoparticles). Using nanoparticles, the thermoplastic properties such as thermal diffusivity, thermal conductivity, viscosity and convective heat transfer coefficient of the fluid will be significantly enhanced. Achieving such properties need making stable nanofluids which has shown serious challenge in recent

years (Yu et al., 2011, Trisaksri et al., 2007, Wang et al., 2007, Wang et al., 2008). Using nanofluids, cooling systems with higher efficiency have been designed for cars. Decreasing cooling system weight and reducing its complexity are the most important advantages of using nanofluids. In this way, compact cooling system with smaller size and weight can be designed for cars' radiator. Improving thermal conductivity of ethylene glycol-based fluids using nanomaterials has attracted much attention as engine coolant. In conventional cooling systems, a ratio of 50:50 of water and ethylene glycol is used as coolant. However, there are advantages of using ethylene glycol based nanofluids such as low pressure operation compared with mixture of water and ethylene glycol. Nanofluids based coolants have boiling point higher than conventional ones helping it reject more heat through coolant system. It has been shown that using nanofluids in cars' radiator could reduce frontal area of radiator up to 10%. In this way, nanofluids could reduce aerodynamic drag and fuel saving up to 5%. Nanofluids could also reduce friction and wear in pumps and compressors, leading to fuel saving up to 6%. These all reveal that nanofluids are suitable materials which not only could improve cars cooling system performance but also can greatly influence the structure design of cars (Wang et al., 2008, Li et al., 2009, Kakac et al., 2009, Xie et al., 2009, Yu et al., 2009, Yu et al., 2007, Kole et al., 2007, Tzeng et al., 2005).

### *3.5.2. Heat transfer improvement using nanofluids*

Maxwell's model reveals that increase in volume fraction of spherical nanoparticles results in thermal conductivity improvement of a liquid. Moreover, increase in surface area-to-volume ratio of the particles leads to an increase of the conductivity of the liquid. In addition to particles size and particles loading, the particles sphericity (defined as the ratio of the surface area of a perfect spherical particle to that of non-spherical particle at the same volume) is another parameter influencing thermal conductivity of a suspension. Hamilton and Crosser's (Yu et al., 2009, Yu et al., 2007, Kole et al., 2007, Tzeng et al., 2005) revealed that decreasing particle sphericity from 1.0 to 3.0 results in significant increase in thermal conductivity more than two times. Particle with 10 nm diameters has surface-area to volume ratio of 1000 times greater than a particle with 10  $\mu\text{m}$  size. Consequently, it has been expected to enhance thermal conductivity using nanometer sized particles much greater than micrometer sized particles.

Attempts have been carried out to improve heat transfer ability of water/ethylene glycol liquids (used in a car radiator) using nanoparticles. Nano CuO and Al<sub>2</sub>O<sub>3</sub> particles are added to these liquids. Results showed significantly enhanced thermal conductivity of the liquids using these nanometric materials. It is shown that using 4 vol% nano-CuO (30 nm diameter) can increase thermal conductivity of the ethylene glycol by 20%. The same observation was seen in case of using nano-Al<sub>2</sub>O<sub>3</sub> particles in water. It has been found that reducing nano-CuO particles' size results in further increase in thermal conductivity of the liquid. In another research, the effects of addition of nano sized ZnO, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> particles (at 5 vol%) to an ethylene glycol on its thermal conductivity and viscosity was studied. The highest thermal conductivity and the lowest viscosity were observed for the liquid loaded with MgO nanoparticles. Carbon nanotube is found effective nanoparticle to enhance

thermal conductivity of water and ethylene glycol. Using 1 vol% carbon nanotube can improve water/ethylene glycol mixture conductivity up to 175% (Kakac et al., 2009, Xie et al., 2009, Yu et al., 2009, Yu et al., 2007, Kole et al., 2007, Tzeng et al., 2005).

### 3.6. Lubricating oils for cars using nanoparticle additives

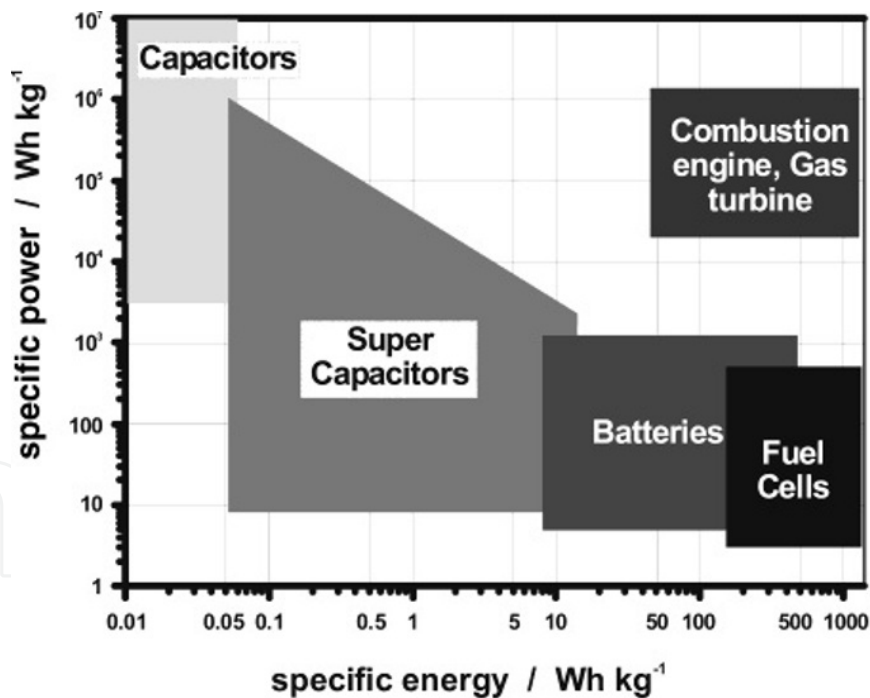
Lubricants like mineral oil are used to reduce friction and wear in automobile engine. The pistons movement in cylinder of an engine produces frictions as a result of metals wear. This may lead to reduced engine efficiency as well as lowered engine life. Oils are used as lubricant to reduce friction. The conventional oils need to be exchanged after a special engine working time. In fact, the oil lubricant properties will be gradually reduced. Researches to produce better oils with longer life are developed in recent years. Nanotechnology is one of the most effective ways of fulfilling this target (Wu et al., 2007, Chinas-Castillo et al., 2003). It has been shown that nanoparticles could improve lubricant behavior of conventional oils. Particles shape, size and concentration are influential parameters affecting wear and friction reduction. It has been shown that gold particles having particle size of 20 nm has the best lubricating effects. Dialkyldithiophosphate modified copper nanoparticles is shown as an effective nanoparticle with high ability of improving anti-wear ability of metal surface by producing an anti-friction film. Diamond and inorganic fullerene-like (IF) particles are other examples of anti-wear nanoparticles being used as additives for lubrication. The most important mechanisms which result in friction reduction are colloidal effects, rolling effects, protective film and third body. Diamond nanoparticles were added to oil to improve its anti-wear ability. This nanoparticle has found to improve oil lubricant behavior via various mechanisms including: (a) ball bearing effects of the spherical particles existed between rubbing surfaces, (b) the surface polishing and (c) increasing surface hardness. Adding CuO nanoparticles to oil could significantly reduce friction coefficient. Ball bearing at high temperature and viscous effect at low temperature are the reasons CuO nanoparticles can improve anti-wear behavior of oil. The nanoparticles depositions at worn surfaces would be responsible for shear stress reduction leading to tribological properties improvement of the surface (Wu et al., 2007, Chinas-Castillo et al., 2003, Zhou et al., 1999, Rapoport et al., 1999, Chen et al., 1998).

### 3.7. Energy criterion in cars

To replace combustion engines, different strategies and methods have been developed. Among them, electrochemical energy production/storage is the most important option owing to sustainability and being environmentally friendly (Schlapbach & Zuttel, 2001). The so-called electrochemical energy storage and conversion systems include fuel cells, batteries and supercapacitors. Although batteries have found their way in marketplace in different applications and fuel cells and supercapacitors are competing to establish promising applications, there are still many challenges to be solved to have energy conversion/storage systems which could surpass combustion engines in terms of power/energy performance and cost (Winter & Brodd, 2004). Nanomaterials are finding great contribution to overcome these challenges (Arico et al., 2005; Serrano et al., 2009).

### 3.7.1. Fuel cells

Automobiles powered by fuel cells are believed to have considerable market in near future and it is envisioned about 80 million fuel cell vehicles will be on the road by 2020 (Serrano et al., 2003). High efficient energy conversion, safety, high energy density, nonpolluting are the advantages of employing fuel cells as energy source for driving a car (Jacobson et al., 2005). However, high cost, low volumetric power density, low durability and cell life plus high sensitivity to purity gas stream and complex operation are disadvantage of using fuel cells. Thus, hybrid configuration of fuel cells with batteries or supercapacitors is being developed in order to supply power for peak-power demands such as acceleration and start-up and also recovering braking energy (Kötz et al., 2001). In fact, despite of comparable energy density of fuel cells ( $100\text{-}1000 \text{ Wh.kg}^{-1}$ ) relative to combustion engines, they have few order of magnitude lower power densities, rendering them as steady energy source. On the other hand, supercapacitors possess high power density comparable to combustion engines (Fig. 20). Therefore, hybrid systems of fuel cells and supercapacitors or batteries are an efficient configuration for replacing the combustion engines. In general there are six types of fuel cells systems including i) alkaline fuel cells ii) polymer electrolyte membrane fuel cells (PEFCs) iii) direct methanol fuel cells (DMFC) iv) phosphoric acid fuel cells v) molten carbonate fuel cells and vi) solid oxide fuel cells (Winter & Brodd, 2004).



**Figure 20.** Ragone plot of the energy storage domains for the various electrochemical energy conversion systems compared to an internal combustion engine and turbines and conventional capacitors (Winter & Brodd, 2004).

Although one can drive a car powered by some classes (PEFCs) of fuel cells, there are still some challenges associated with employing them which are mostly high cost, fuel supply/storage and life time. Generally the fuel choice is hydrogen and oxygen which finally

exhaust water. Hydrogen supplication, refuelling infrastructure and storage of hydrogen are still ongoing challenges (Chan, 2007). Although hydrogen has very high gravimetric energy density, its' application hindered due to low volumetric energy density. Storing hydrogen in liquid state require employing highly expensive cryogenic tanks (Fig. 21). Compressing hydrogen gas also urges using costly storage facilities. There has been considerable research to develop new materials enabling storage of hydrogen at high enough concentration at not too high pressure and too low temperature. Initial interest was focused on metal hydrides through chemisorptions of hydrogen (Fig. 22). However, efforts were quite unsuccessful to synthesis metal alloys reaching to theoretical limit (~8wt%) unless some promising results were reported for nanosized metal (oxide) composites (Arico et al., 2005). Metal alloys such as LaNi, TiFe, MgNi are generally expensive and in all cases are heavy which makes commercialization of products dealing with mobile applications problematical.



**Figure 21.** GM ElectroVAN, the first hydrogen fuel cell powered car introduced at 1966. The hydrogen and oxygen stored in super-cooled liquid in cryogenic tank.



**Figure 22.** Comparison of volumetric density of different systems to store hydrogen (Schlapbach & Zuttel, 2001)

In another set of research, the efforts are focused on physical entrapping of hydrogen in porous materials. Physisorption of  $H_2$  allows fast loading and unloading. Nanostructured

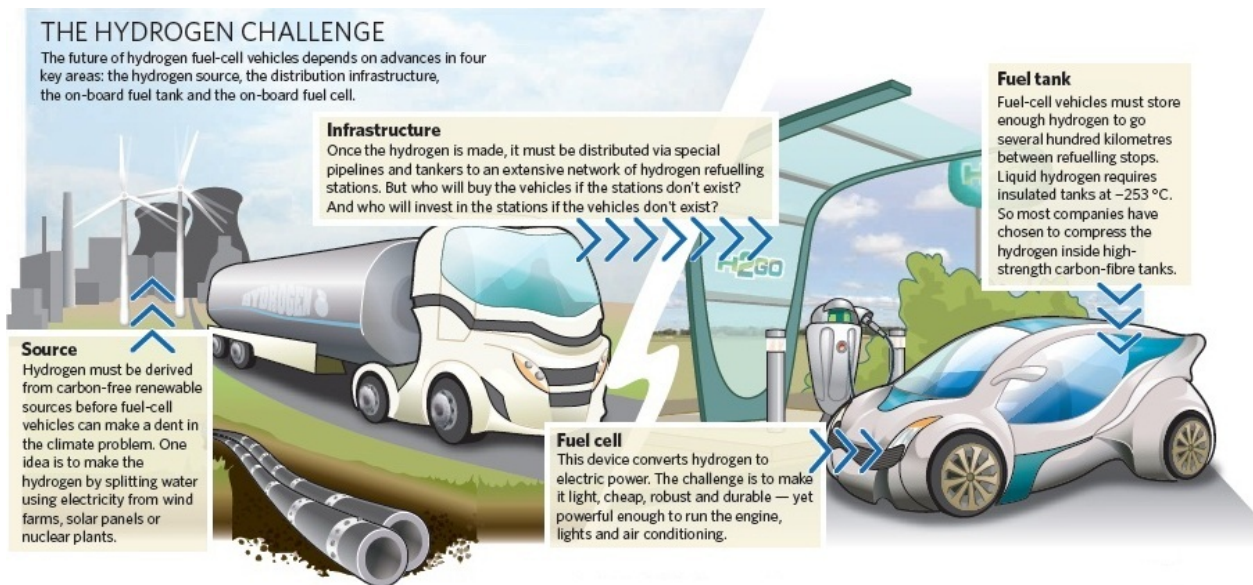
materials are the sole candidates for this purpose. Carbon nanomaterials (Dillon et al., 1997) and metal organic framework (MOFs) (Ce'te et al., 2005; Zhou et al., 2007) are two dominate studied classes of materials with the goal of solid-phase storage of H<sub>2</sub>. By the advent of carbon nanotubes at early 90s (Iijima, 1991; Iijima & Ichihashi, 1993), great deal of attention was attracted to this novel nanomaterial. Dillon *et. al.* (Dillon et al., 1997) for the first time reported high capability of single-walled carbon nanotubes (SWNTs) as porous media for H<sub>2</sub> uptake, reporting 5 to 10wt% of H<sub>2</sub> adsorbtion at ambient conditions. Chen *et. al.* (Chen et al., 1999) later reported significant enhancement of H<sub>2</sub> uptake (20wt%) of multi-walled carbon nanotubes (MWNTs) upon doping with alkali metals at 300K and 0.1MPa. These results were beyond the requirements that have been established by Department of Energy (DOE) of US where gravimetric density of H<sub>2</sub> must be at least 6wt%. However, subsequent studies revealed that CNTs are not promising candidates for H<sub>2</sub> uptake. The results indicate metal doping of CNTs can enhance the H<sub>2</sub> uptake of nanotubes, but hardly exceeds 4wt% (Liu et al., 1999; Béguin & Frackowiak, 2006).

Novel nano-porous materials, MOFs, have been centre of attention for gas adsorbtion. These materials are product of reaction of metals ions with rigid organic molecules (Ce'te et al., 2005). Due to exceptionally high surface area and tunable chemical structure of MOFs, high potential for high enough H<sub>2</sub> uptake is envisioned. In September 2011, Daimler introduced a concept vehicle, Mercedes-Benz F125!, which was pictured to be derived by 2025 (<http://media.daimler.com>). The most interesting technology of this conceptual car is its source of energy which is hybrid of Li-S battery (See below for more details) and hydrogen fuel cell. Despite current technology used in available fuel cell vehicles, liquid or compress hydrogen, storage facility of hydrogen is based on MOFs materials in this concept vehicle. The manufacturer claims one will be able to derive up to 1000km with maximum speed of 220km.h<sup>-1</sup> before it is needed to be refilled.

Although interest to fabricate solid-phase hydrogen reservoir using CNTs are now quenched, emergence of the carbon-based thinnest materials, *i.e.* graphene, again revived hopes to have carbon-based hydrogen storage tanks (Park et al., 2007; Dimitrakakis et al., 2008; Burress et al., 2010). In fact, as the H<sub>2</sub> storage mechanism in carbon nanostructures relies on physisorption on graphenic surface, the hydrogen uptake is proportional to specific surface area of nanostructure which reaches ultimate value for carbon nanostructures in graphene (2630 m<sup>2</sup>.g<sup>-1</sup>) (Dimitrakakis et al., 2008). Researches on developing high surface area graphene-based materials are ongoing and more time requires confirming whether graphene-based nanoporous materials are able to solve the mystery of the hydrogen storage or not (Subrahmanyam et al., 2011).

Another major issue which hinder widespread application of fuel cell vehicles, is high cost associated with manufacturing them (Fig. 23). The expensive constituents of fuel cells including the catalyst and electrolyte membrane are the origin of high cost of fuel cells (Steele & Heinzel, 2001). In addition, performance and life time of these classes of fuel cells (PEFC, DMFC) can be remarkably improved by nano-engineering of the catalyst and electrolyte membrane. In fact, the commercialization of fuel cells will very much rely on the ability to reduce the cost and improve the performance of catalyst, membrane and other

expensive parts to launch a fuel cell powered vehicle at a competitive cost and driving capabilities (Arico et al., 2005). To reach this goal, nanotechnology plays a dominant role.

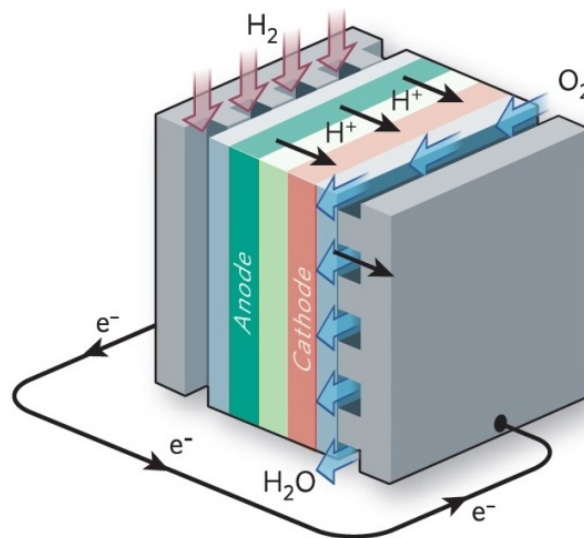


**Figure 23.** The challenges associated with implementing hydrogen as the next generation green fuel including hydrogen source and production, storage infrastructure, fuel tank and high efficient fuel cells (Tollefson, 2010).

Principally, fuel cells (PEFCs and DMFCs) operate with a polymer electrolyte membrane which is sandwiched between cathode and anode that separate the fuel (hydrogen) from the oxidant (air or oxygen) (Fig. 24). The performance of these low-temperature fuel cells is mostly limited by oxygen reduction reaction (ORR) (Arico et al., 2005). The current generations of fuel cells are utilized platinum (Pt)-based catalyst for both the oxidization of fuel and reduction of the oxygen (Greeley et al., 2009). Several factors are motivating researchers to replace Pt which the high cost of this precious metal ( $40\text{--}70\text{ }\$.\text{g}^{-1}$ ) is one of them. In addition, this metal is so scarce (less than 0.005 p.p.m in the Earth's crust) and about 90% of the world's Pt supply comes from just two countries, South Africa and Russia (<http://en.wikipedia.org/wiki/Platinum>). A few approaches are being actively pursued with the goal of improving the electro-catalyst activity plus lowering the overall cost. However, these efforts have dominantly followed three major strategies including: i) improving the Pt-based catalyst ii) developing new class of non-precious catalyst using other transition metals and finally iii) metal-free catalyst materials.

Today Pt-carbon catalyst which are widely used in PEFCs and DMFCs, are nanoparticles of Pt decorated on carbon support (*e.g.* carbon black) (Greeley et al., 2009). Pt nanoparticles' activity increases as the particle size decreases reaching a minimum of  $\sim 3\text{nm}$  (Arico et al., 2005). Rational nano-engineering of Pt alone or with other metal atoms into specific arrangement of nanostructured alloys such as core-shell nanoparticles or nanowire (Koenigsmann et al., 2011; Koenigsmann et al., 2012; Hong et al., 2012; Lim et al., 2009) is a highly effective tool to synthesis new generation of catalyst if fundamentals of governing the performance of catalyst are understood. Core-shell nanoparticles of Pt-Cu, for example, are

more active than Pt which consists of cores made of a Cu-Pt alloy and Pt-rich outer shell (Mayrhofer et al., 2009). Such structure is obtained through a controlled dealloying the hybrid nanoparticles. However, many challenges associated with using precious Pt-based catalyst still remain untouched through these strategies. For instance, General Motor's fuel-cell set-up used around 80 grams of platinum as electrocatalyst to split hydrogen into electrons and protons which costs roughly 5000\$ (Tollefson, 2010). Although General Motors's officials hope to reduce the Pt loading to 30 grams in near future and less than 10 grams in the next decade, the price of catalyst would still be high considering the fact that the Pt is so scarce.



**Figure 24.** Basic structure of hydrogen fuel cell in which hydrogen split into electron and proton at anode and at cathode protons reduce oxygen exhausting water finally (Tollefson, 2010).

With the goal of achieving inexpensive catalyst for fuel cells' application, tremendous attempts have been done since 60s decade (Jasinski, 1964). Despite quite ineffective early catalysts, recent developments through nanoscale engineering of nanostructured catalysts revive the hopes to have non-precious replacement of Pt catalysts. Catalysts based on thermally annealed precursors comprising nitrogen, carbon and transition metals, especially Fe and Co (Fe (or Co)/N/C), have attracted more attention due to high activity and performance (Lefevre et al., 2009; Bashyam & Zelenay, 2006; Proietti et al., 2011). This class of catalysts consists of metal nanoparticles embedding in nanostructured nitrogen-doped graphenic carbon (Wu et al., 2011). Metal free catalysts have been also synthesized and evaluated as catalyst. Among them, carbon-based nanostructures are the most studied systems. At 2009, Dai's group (Gong et al., 2009) at Case Western University showed gas phase N-doping of CNTs would result in a metal free electrocatalyst. After that, many studies revealed promising performance of N-doped carbon nanomaterials such as SWNTs (Zhang & Dai, 2012), graphene (Qu et al., 2010), mesoporous graphitic array (Liu et al., 2010) and carbon quantum dots (Li et al., 2011), for replacing Pt-based catalysts (Gong et al., 2009; Chen et al., 2012; Wang et al., 2011). Findings in Fe (or Co)/N/C systems and N-doped carbon nanomaterials may be combined possibly through using CNTs or graphene as



support in Fe (or Co)/N/C catalysts instead of carbon black. However, it seems that carbon nanomaterials would have much more contribution in the next generation of catalyst in fuel cells than what they have in current Pt/C commercial catalysts. Rational design of nanostructure of the so-called upcoming catalyst would be the key issue.

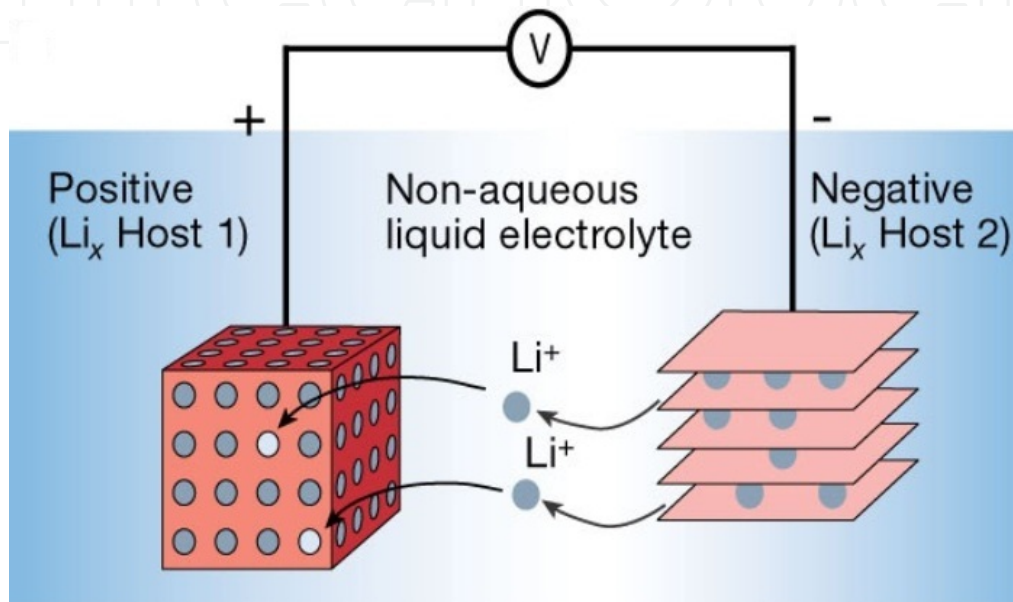
### 3.7.2. Batteries

Although fuel cell powered cars have been driven since more than 45 years ago (Fig. 21), the current efficiency as replacing the internal combustion engines hinders widespread use of FCV (additionally lack of hydrogen storage infrastructures and cost are real barriers) (Turner, 2004). In addition, from practical point of view, because of low power density of FCs, FC powered automobiles require an energy storage device to deliver required energy in power-peak demands. As a result, currently automakers have come to this decision to launch new versions of hybrid cars before FC cars, which has resulted to introduction of new generation of automobiles with considerably low gasoline combustion reaching to record less than one litre per 100 km (Demirdeven & Deutch, 2004). Therefore, at the heart of the upcoming automobiles, energy storage devices play a key role. Batteries are blooming in different markets and automobile industry is not an exemption. Among different classes of batteries, lithium ion batteries have higher potential for employing in the next generation of cars due to higher energy density, unless in the first generation of electric cars even lead-acid batteries (for example the EV1, GM introduced 1996) and Ni-MeH (Prius, Toyota) were used ([http://www.economist.com/sciencetechnology/tq/PrinterFriendly.cfm?story\\_id=10789409](http://www.economist.com/sciencetechnology/tq/PrinterFriendly.cfm?story_id=10789409)).

Similar to other batteries, Li-ion batteries also consist of cathode, electrolyte and anode (Fig. 25). Due to principles governing the electrochemistry of Li-ion batteries wide ranges of materials can be used in this class of devices which significantly affect the cell potential, energy density and safety of batteries ([http://www.economist.com/sciencetechnology/tq/PrinterFriendly.cfm?story\\_id=10789409](http://www.economist.com/sciencetechnology/tq/PrinterFriendly.cfm?story_id=10789409)). Therefore, huge amount of attention has been attracted towards developing high performance Li-ion batteries from both academic communities and industrial firms. The efforts are focused on improving the capacity, safety and the charging rate. Nanoscopic materials are presumed to have great contribution in the world's \$56 billion battery market in near future (Serrano et al., 2009).

The cathode and anode materials must be able to be intercalated with Li ions having high Li hosting capacity and also high electron conduction (Tarascon & Armand, 2001). Among the various materials employed as cathode for Li-ion batteries, iron (or other metal) phosphate is a promising and safe replacing candidate for conventional cathode material, cobalt oxide (Padhi et al., 1997). This case is interesting as nanoengineering helped a lot to see marketable version of this material. In fact, due to the low electrical conductivity of  $\text{FePO}_4$ , the energy charging rate is very low. Unless it is found that doping with other transition metals can enhance the material's conductivity,  $\text{FePO}_4$ -based materials found their way in marketplace when Chiang's group at MIT uncovered that nanosized  $\text{FePO}_4$  particles can store and deliver energy much faster than usual size ( $\sim 10 \mu\text{m}$ ) due to higher surface area which facilitate intercalation of Li ions (Chung et

al., 2002; Kang & Ceder, 2009). In fact, conventional Li-ion batteries equipped with cobalt oxide which are prone to catch fire due to thermal runaway, phosphates can be used to fabricate larger Li-ion batteries much more suitable for automobiles. For example, Volvo 3CC concept car, because of limitations associated with using cobalt oxide based batteries, is equipped with 3000 Li-ion cells with AA size. The safety issue can be overcome by employing phosphate-based cathode, the technology which is being commercialized by A123 Systems (co-founded by Dr. Chiang) which is collaborating with GM on a plug-in hybrid car, Chevy Volt (Fig. 26) ([http://www.economist.com/sciencetechnology/tq/PrinterFriendly.cfm?story\\_id=10789409](http://www.economist.com/sciencetechnology/tq/PrinterFriendly.cfm?story_id=10789409)).



**Figure 25.** Basic structure of a Li-ion battery in which lithium ion intercalation into anode and cathode during charge and discharge process, respectively, is employed to store electrochemical energy (Tarascon & Armand, 2001).

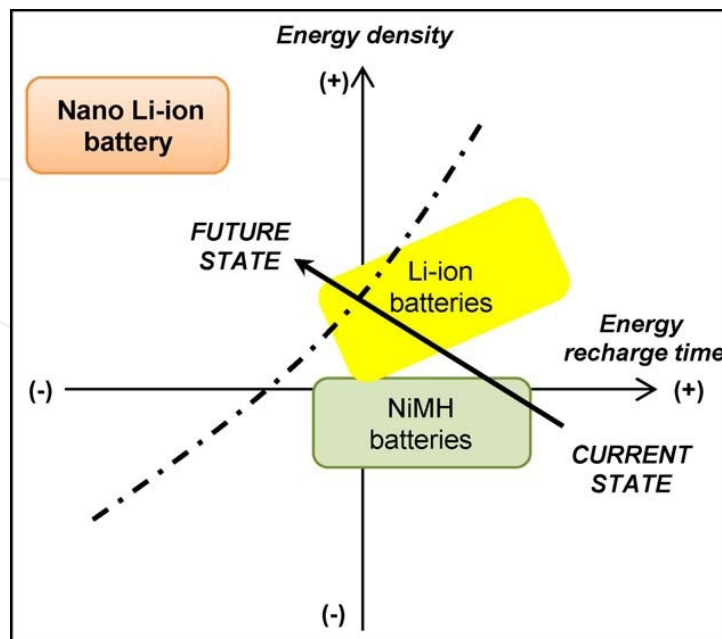
Nanosizing the cathode and anode materials are now tremendously followed in different battery materials (Fig. 27). Silicon, one of the most promising anode materials, may find somewhere in market if researchers could overcome instability of this materials during charge-discharge process through the nanostructuring of this element (Armand & Tarascon, 2008). Different nanostructures of Si such as nanoparticles (Lee et al., 2010), nanowire (Chan et al., 2008), nanotube (Wu et al., 2012), hierarchical nanoporous structures (Magasinski et al., 2010) and their composites with nanocarbons (Lee et al., 2010; Cui et al., 2009), have shown to have exceptionally high capacity and stability raising hopes to have commercial batteries with Si-based anode.

In the realm of cathode materials for Li-based batteries, sulfur boosts the capacity of Li-ion batteries with one order of magnitude higher theoretical capacitance (Peramunage & Licht, 1993). Therefore, the Li-S batteries may succeed Li-ion batteries as their energy density is extremely high plus low cost and density of sulfur (Kang et al., 2006). However, its capacity fades away during charge-discharge of the cell due to polysulfide ions (the reaction intermediates) dissolution in electrolyte causes irreversible loss of active materials diminishing the capacitance few times lower than theoretical value. At 2009, by employing

an innovative technique through the nanostructuring the sulfur inside the mesoporous carbon, capacitances near the theoretical limits were attained (Ji et al., 2009). After that, different carbon nanostructures such as hollow carbon nanofibers (Zheng et al., 2011), graphene oxide (Ji et al., 2011) and pyrolyzed PAN/graphene (Yin et al., 2012) were used to immobilize sulfur. This class of batteries (Li-S) would find market in automobile industries as also claimed by Daimler in its concept vehicles, Mercedes-Benz F125! having exceptional high range of 1000km (Fig. 28) (<http://media.daimler.com>).



**Figure 26.** Chery Volt, a plug-in hybrid car, was introduced by GM. The automaker is trying to use safer nanophosphate-based batteries ([http://www.economist.com/sciencetechnology/tq/PrinterFriendly.cfm?story\\_id=10789409](http://www.economist.com/sciencetechnology/tq/PrinterFriendly.cfm?story_id=10789409)).



**Figure 27.** Nanotechnology will make batteries with higher energy density which charge faster than current Li-ion batteries (Serrano et al., 2009).



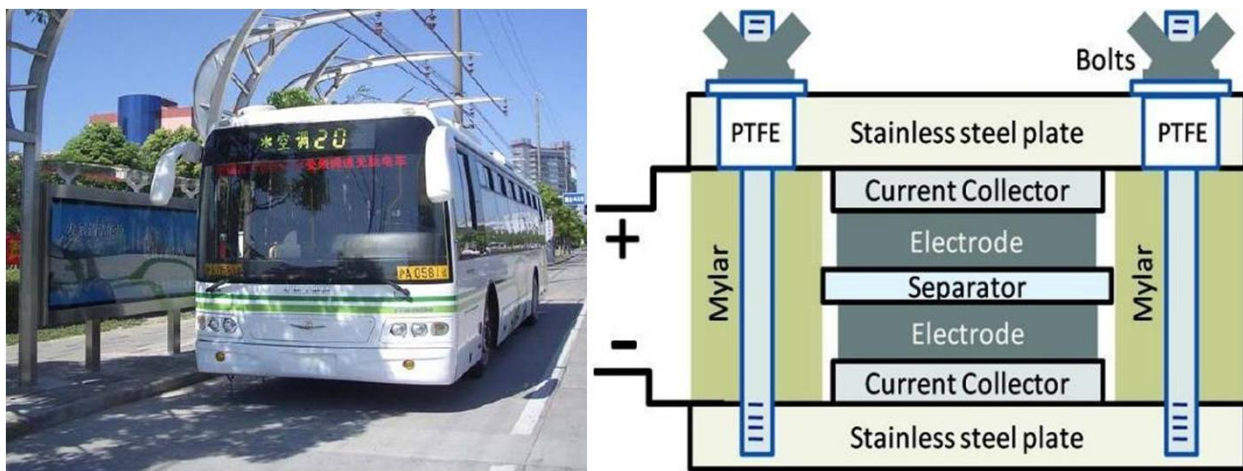
**Figure 28.** Mercedes-Benz F125! the concept vehicle introduced by Daimler at 2011 equipped with advanced technology in energy storage including high performance Li-S batteries having power density of  $350 \text{ Wh.kg}^{-1}$  (energy capacity 10 kWh) and revolutionary ultra-porous MOFs technology ( $104 \text{ m}^2.\text{g}^{-1}$ ) making it possible to store 7.5 kg of  $\text{H}_2$  in a flexible framework. All these technologies owe a lot to nanoscience and technology (<http://media.daimler.com>).

### 3.7.3. Supercapacitors

Despite of advantages of using batteries as energy storage device in hybrid cars including high energy density, challenges associated with employing batteries especially timely recharging, safety and lifetime bring the another electrochemical storage device as candidate for the same purpose, i.e. supercapacitors. Supercapacitors store energy by forming a double layer of electrolyte ions on the surface of conductive electrodes, called EDLCs (Miller & Simon, 2008). The widespread applications of supercapacitors are limited by their low energy density ( $1\text{-}5 \text{ Wh/kg}$ ) comparing to batteries ( $10\text{-}500 \text{ Wh.kg}^{-1}$ ) and as a result high cost of energy storage. But the fact that supercapacitors can be charged and discharged in less than a minute over a million cycles motivates scientific communities to enhance energy density of supercapacitors (Simon & Gogotsi, 2008; Chmiola et al., 2006). It is envisioned at energy density of  $40 \text{ Wh/kg}$ , the supercapacitors would be an improvement over the batteries used in some hybrid vehicles. In addition, the concept of supercapacitor powered urban bus which recharge at each bus stop in a minute is another intriguing idea (Fig. 29, left side).

At the heart of the current EDLCs, nanoporous carbon acts as electrode. To improve the energy density of supercapacitors, different nanomaterials such as MWNTs (Frackowiak et al., 2000), SWNTs (Kaempgen et al., 2009), metal oxide nanoparticles (Hu et al., 2006) and conducting polymers (Zhang et al., 2010) (two later cases are classified as pseudo-capacitors), have been used but high cost of nanotubes and some metal oxide (e.g.  $\text{RuO}_2$ ) and poor stability of pseudo-capacitors render them not enough efficient storage device.

Emergence of graphene has revolutionized this field, as this material is the thinnest imaginable carbon allotrope (Fig. 29, right side) (Stoller et al., 2008). The graphene-based pseudo-capacitors are still in infancy stage, but initial results confirm high capacity of graphene-based EDLCs having improved energy density. At May 2011, Ruoff's group (Zhu et al., 2011) at university of Texas-Austin claimed they have developed graphene-based EDLCs through an industrial viable method having energy density of  $75 \text{ Wh.kg}^{-1}$  which is more than one order magnitude higher than conventional supercapacitors. It is foreseen by 2020, half of graphene's market (~ \$675 million) belongs to supercapacitors which clearly illustrate the impact of graphene-based materials on this field (<http://www.bccresearch.com/report/AVM075A.html>). It should be noted that hybrid systems of batteries and supercapacitors are indentified as the most effective and reliable solution for applications where lifecycle and reliability are vital including cars (<http://www.grapheneenergy.net/applications.html>).



**Figure 29.** Left side: Sinautec's Ultracapacitor Bus, an urban bus powered by on-board supercapacitors and batteries which charged at bus stop. Right side: a conventional set-up for supercapacitors in which forming a double layer of electrolyte ions on the surface of high surface area conductive electrodes store energy (Stoller et al., 2008).

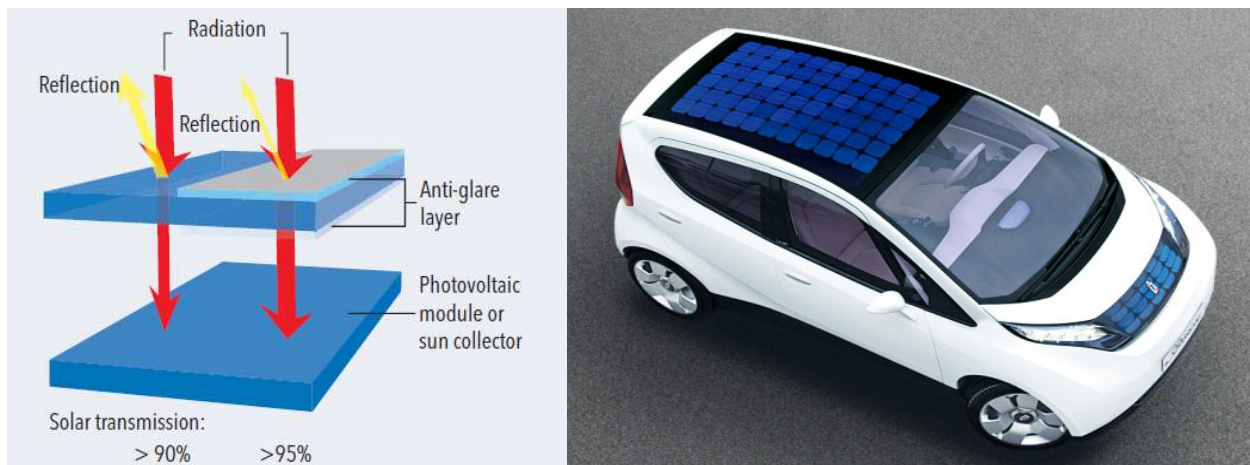
At June 2010, researchers at MIT introduced new concept of energy storage device, having both high density (comparable to Li-ion batteries) and power density (even higher than supercapacitors) (Lee et al., 2010). Again nanocarbons did excellent as electrode. The whole idea was to exchange Li ions between the surfaces of two nanostructured carbon electrode having functional groups (Jang et al., 2011). In fact, charging of Li-ion batteries is timely because Li ions must intercalate into cathode and anode which takes time. This strategy to store energy may be implemented in next generation of automobiles but further investigation are required to clarify the exact chemistry governing the device and also confirm feasibility and other issues.

### 3.8. Nanotechnology in solar cell in automobile

Solar cells are used to produce electricity from sunlight. This system has been gradually developed in different industries as it is an environmentally benign method of producing

electricity and helps industries to reduce fuel consumption. In recent years, research to find new sources of energy in automobiles are being carried out (Levitsky et al., 2010, Ong et al., 2010).

It has been found that solar cells can be used as an additional source of energy supporting some of electronic devices used in an automobile. Silica-based solar system is a conventional system for producing electricity from sunlight. However, production and large scale use of this system is complicated and costly. Therefore, attempts have been carried out to produce new solar system usable for automobile economically. In silicon based solar cells, the electron needed will be supplied by silicon after exposure to sunlight. The produced electron can be transferred to semiconductors from electrodes. In solar cells, an organic material like chlorophyll can be used as substrate. A large surface area layer based on nanoporous titanium oxide is used for the transmission to the electrodes. This system as shown in Fig. 30 consists of two glass plates each of them have a transparent electrode (Levitsky et al., 2010, Ong et al., 2010).

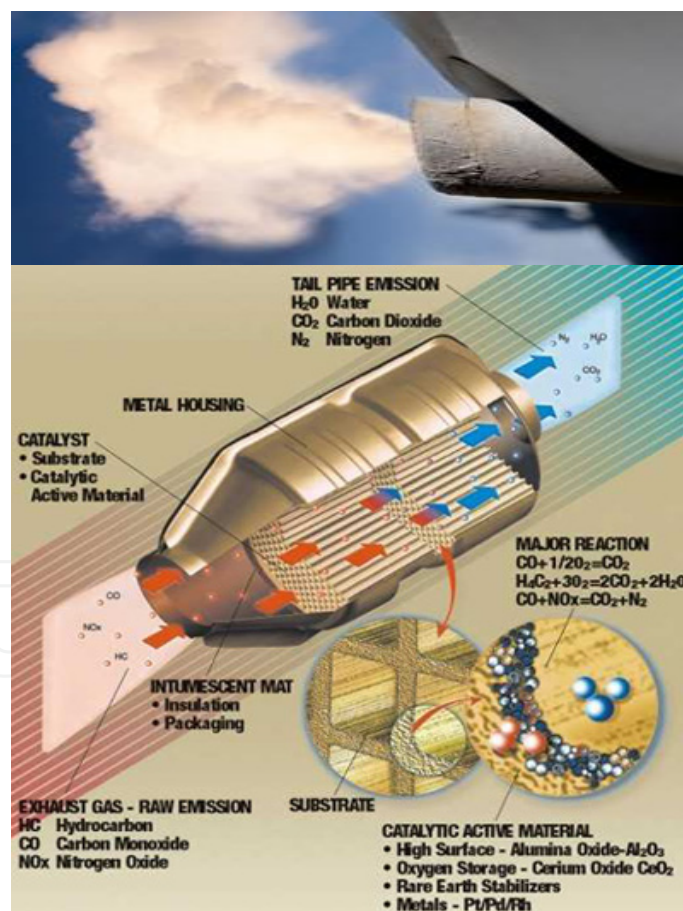


**Figure 30.** Solar cells based on nanotechnology for modern cars.

As it can be seen in Fig. 30, one of the plates covered with layer of dye-sensitive titanium oxide and another one is coated with platinum as catalyst. However, in conventional silicon-based solar cells, the efficiency is low due to light reflection at the solar glass pan. The reduction is approximately 10 percent for even high efficiency solar cells. This problem has been solved in new generation of solar cells using sol-gel method. Using this technique, a coating layer is applied over the glass pans. This coating could reduce light reflection from glass pans resulting in an increase in solar cell efficiency up to 6 percent. The sol used for this purpose includes a mixture of silica balls at two different sizes. To obtain best anti-reflective properties from coating, mixture of particles with diameter of 10 nm and 30 nm should be used. In order to apply coating layer over the cells, the glass pans should be immersed in the tank containing nano  $\text{SiO}_2$  sol. The optimum antireflective properties can be obtained at 120 nm thickness. The sol becomes dry using gel and nanoporous layer can be obtained after hardening glass coated pans at 600-700 °C. This novel coating layer has very low refractive index (of only 1.25) resulting in light reflection at 400-2500 nm. In this way, solar transmission will be increased from 90 percent for conventional one to 95 percent for this solar cell (Levitsky et al., 2010, Ong et al., 2010).

### 3.9. Nanotechnology based catalyst for reduction of exhaust emission

Today, environmental regulations forced car producers to reduce exhaust emission of automobiles. Using new generations of fuels can be one way achieving this target. However, at this time, technology needed for large scale production of fuel has not been developed maturely. Use of catalysts is a conventional approach reducing exhaust emission. These catalysts are made of high-grade steel housings containing catalytically active materials. These active materials are able to convert exhaust pollutants to nitrogen, steam, and carbon dioxide. Three most important polluting elements that exhaust included carbon monoxide, hydrocarbons and nitric oxides. To eliminate or reduce these pollutants emission from exhaust gas, three kinds of catalysts are needed. Nanotechnology can play an important role in converting toxic pollutants to non-toxic gases. It is well known that increasing surface area of catalyst enhance its catalytic activity. Designing catalytic materials to absorb nitric oxides from exhausted gas has become a big challenge for car manufacturers. To solve this problem, new generation of catalyst with high capability of NO<sub>x</sub>-absorbing are developed. The mechanism by which this system works is presented in Fig. 31 (Hvolbk et al., 2007, Kim et al., 2006, Nilsson et al., 2005, Zhou et al., 2010).



**Figure 31.** Three-way nano-structured catalyst for cleaning exhaust from pollutants (Hvolbk et al., 2005).

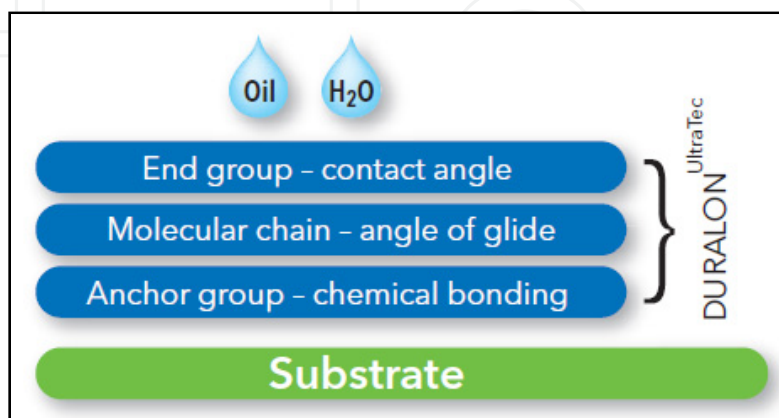
Recent researches revealed that Au nanoparticles having sizes lower than 5 nm are very effective catalysts. There are many different mechanisms indicating catalytic activity of nano

sized Au particles. The most important of them are the quantum size effects, charge transfer to or from the support or support induced strain, oxygen spill-over to or from the support, oxidation state of Au and the role of very low-coordinated Au atoms in nanoparticles. The metal nobility depends on the metal surface ability to oxidize or chemisorption of oxygen. From periodic table of elements, Au is the only metal with endothermic chemisorption energy. Because of this behavior, Au is a metal which could not bind with oxygen at all. Au is a very good catalyst for oxidation of carbon monoxide (CO) presented in exhausted gas in automobile. The activity of Au depends on particle size as the best activity can be seen at particle sizes  $< 5$  nm (Hvolbk et al., 2005).

### 3.10. Ultra-reflecting layer for automobile mirror

#### 3.10.1. Mirrors with high optical and self-cleaning properties

New generation of mirrors and headlights used in cars are based on glass and polymer components with high optical quality and efficiency. Nanotechnology is employed to achieve these unique properties. To this end, ultra-reflecting thin layer (with thickness lower than 100 nm) based on aluminum oxide can be applied over the surface of mirrors or headlights. Applying ultra-thin layers over the mirrors can also help us to equip surfaces with fat, dirt water and repellent features. Using chemical vapor deposition (CVD) technique, nanometric hydrophobic and oelophobic layers can be applied over the surface of mirrors. It has been found that fluoro-organic materials are able to improve hydrophobicity and oelophobicity of the surface at thicknesses of 5-10 nm. This nanometric layer could also produce smooth surface which impurities like water drop, dirt, oil and fingerprints can be easily cleaned. This ultra-thin layer has high resistance against friction and makes it applicable at longer times. As it can be seen in Fig. 32, the layer could chemically bonded to the surface of mirror from the side consisting anchor groups. The chemical groups at other side of the layer produce hydrophobic surface.



**Figure 32.** The composition of ultra-reflecting layers used on modern mirrors.



### 3.10.2. Anti-glare rear mirrors

Nowadays, safety regulations for car drivers lead to produce rear view mirrors to obtain an appropriate view at dawn and dusk. This can be done by equipping glasses with functional layer composite with electrochromic properties. For the glasses equipped with this technology, the optical properties will be changed by applying a certain voltage which moves the charges to intermediate layer. The incoming light will be absorbed by color centers produced by ions at the electrodes. As a result, small quantity of light will be reflected (Fig. 33).



**Figure 33.** The conventional mirrors (a) and modern anti-glare rear mirrors for cars (b).

Like charging and discharging of a car battery, the glass can get back to its original properties as the pole changes. This glass equipped by a rear sensor which could measure and control the glaring light of following vehicles. As soon as the glaring light disappears, the mirror gets back to original state.

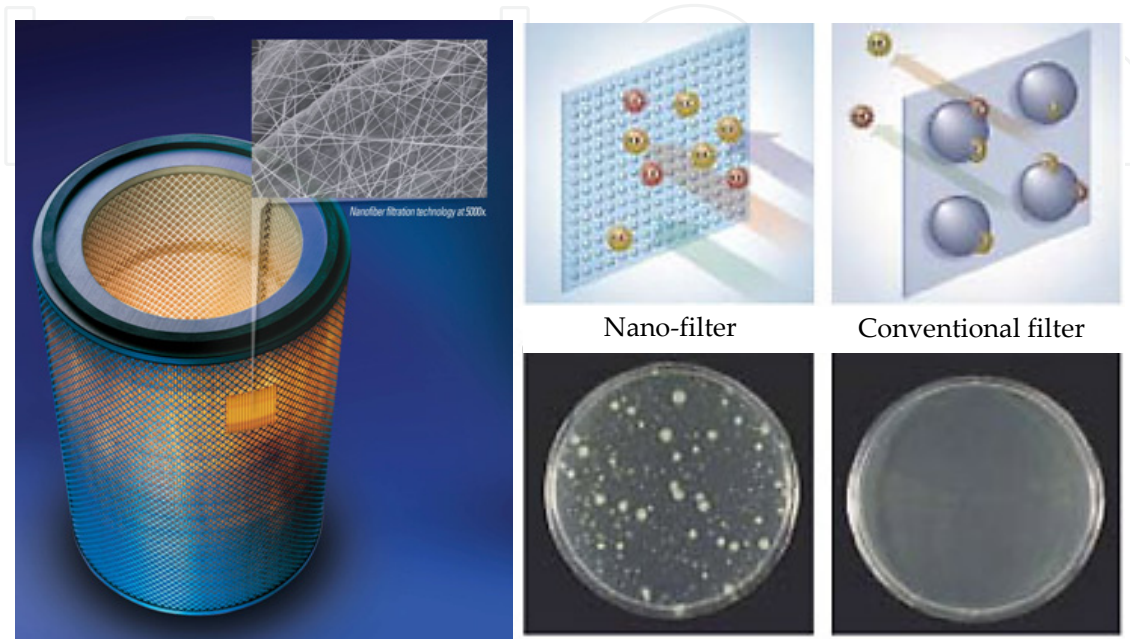
### 3.11. Nano-filters for air cleaning

In addition to safety improvement and fuel consumption reduction, the enhancing comfort for customers is of importance. The air quality inside the car is an important factor affecting customers comfort. The air inside cars contains particles and gaseous pollutions which need to be filtered. Achieving this target needs equipping cars with high quality interior air filters with high efficiency of pollens, spores and industrial dusts filtration. This filter could be used at variable temperature ( $-40\text{ }^{\circ}\text{C}$  to  $100\text{ }^{\circ}\text{C}$ ) and humid conditions. Nanofibers are utilized to produce novel filters with superior properties compared with conventional filters (Fig. 34).

For the fibers in nanometric range size the classical fluid dynamic laws is not true anymore. Because of the lower air resistance of nanofibers compared with micron-sized fibers, air can

be transported through filter easier with lower air pressure loss. This shows that the new filter work at lower level of energy.

This technology is also applied for soot filters. Using nanofibers in soot filters, the emission of pollutants in passengers and utility cars will be reduced. Using nanofilters, the dirt particles could not adhere to the foam materials used at roof of car and prevent polluting it.



**Figure 34.** Nano-filters for air cleaning in car interior.

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