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Green Synthesis of Nanocrystals and Nanocomposites

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1. Introduction

Metal nanomaterials have attracted considerable attention because of their unique magnetic, optical, electrical, and catalytic properties and their potential applications in nanoelectronics (1–5) as well as in various wet chemical synthesis methods (6–14). There is also great interest in synthesizing metal and semiconductor nanoparticles due to their extraordinary properties—properties which are different than when they are in bulk. Green chemistry principles are also regaining popularity for this type of synthesis (8, 15–25). Green chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances that are hazardous to human health and to the environment (25). An example of a greener application of metal nanoparticles is the use of silver and gold nanoparticles, produced from vegetable oil, that are being used in antibacterial paints (26).

Polymer-inorganic nanocomposites have also attracted a lot of attention recently due to their unique, size-dependent chemical and physical properties (26–30). In response to this, different methods of preparing novel nanocomposites with desired properties and functions have been developed (31–35). Such methods should produce materials in which the unique properties of the nanoparticles are preserved (30). One of the main approaches is the dispersion of the previously prepared nanocrystals in polymers. Another is the generation of nanocrystals in polymers in situ. In the latter approach, various nanocables, nanowires and nanoparticulates, generated in situ, have been reported (36–45).

2. Production of nanomaterials using greener methods

Three areas of opportunity to engage in green chemistry when synthesizing metal nanoparticles by the reduction of the corresponding metal ion salt solutions are: (i) choice of solvent, (ii) the reducing agent employed, and (iii) the capping agent (or dispersing agent). There has also been growing attention in identifying environmentally friendly materials that are multifunctional in this area. For example, the vitamin B\(_2\) can function as both a reducing and a capping agent for Au and Pt metals (15). In addition to its high water solubility, biodegradability and low toxicity when compared to other reducing agents, such as sodium borohydride (NaBH\(_4\)), sodium citrate and hydroxylamine hydrochloride, and B\(_2\) is the most
widely used, behaviorally-active drug in the world. By using natural, available resources like B$_2$, it is possible to prepare nanospheres, nanowires, and nanorods by using solvents of varying densities. It is possible to make multiple shape nanostructures by altering the density of the solvents. This green approach can also be extended to silver and palladium noble nanostructures.

Similarly, vitamin B$_1$ has also been used as a reducing and a capping agent (46). The method is a one-pot method and is greener in nature. By this method, bulk quantities of nanoballs of aligned nanobelts as well as nanoplates of the noble metal palladium in water can be synthesized without the need of any external capping, surfactant agents, and/or large amounts of insoluble templates that have been commonly deployed.

Vitamin C has also been used to fabricate novel core-shell (Fe and Cu), metal (noble metals) nanocrystals. Transition metal salts such as Cu and Fe were reduced using ascorbic acid in solution, a benign, naturally-available antioxidant, and then the simultaneous addition of noble metal salts. This process resulted in the formation of a core-shell structure, depending on the core and shell material used for the preparation (21). Pt yielded a tennis ball-shaped structure, with a Cu core; whereas Pt and Au formed regular spherical nanoparticles. Au, Pt, and Pd formed cube-shaped structures with Fe as the core.

Another interesting route to the synthesis of dendritic Ag structures without the use of any reducing chemical is the transmetallic reaction between copper and silver. The copper–carbon substrate of a transmission electron microscopy (TEM) grid reacted with the aqueous silver nitrate solution within minutes to yield spectacular tree-like silver dendrites. This occurred without using any added capping or reducing reagents (47). These results demonstrate a facile, aqueous, room-temperature synthesis of a range of noble metal nano- and meso-structures (see Figures 1 and 2) that have widespread technological potential in the design and development of next-generation fuel cells, catalysts, and antimicrobial coatings.

Fig. 1. Scanning electron microscopy image of silver dendrite, formed with copper shavings and activated carbon.
Another material that was investigated in this study was green tea. Green tea has attracted significant attention recently, both in the scientific and consumer communities due to its health benefits for a variety of disorders, ranging from cancer to weight loss. This publicity has led to the increased consumption of green tea by both the general and the patient population, and the inclusion of green tea extract in several nutritional supplements, including multivitamin supplements. There are several polyphenolic catechins in green tea such as viz, (−) epicatechin (EC), (−) epicatechin-3-gallate (ECG), (−) epigallocatechin (EGC), (−) epigallocatechin-3-gallate (EGCG), (+) catechin, and (+) gallocatechin (GC). These compounds are strong antioxidants and hence, can reduce metals salts. One such example is the preparation of noble metals using tea/coffee extract (48). This one-pot method uses no surfactant, capping agent, and/or template. The size of the obtained nanoparticles ranges from 20-60 nm (see Figures 3 and 4) and are crystallized in face-centered cubic symmetry. This method is general and may be extended to other noble metals such as gold (Au) and platinum (Pt).

To prepare the coffee extract, 400 mg of coffee powder (Tata Bru coffee powder 99%) was dissolved in 50 mL of water. Then, 2 ml of 0.1NAgNO₃ (AgNO₃, Aldrich, 99%) was mixed with 10 ml of coffee extract and shaken to ensure thorough mixing. The 40 reaction mixture was allowed to settle at room temperature. For the tea extract, 1 g of tea powder (Red label from Tata, India Ltd. 99%) was boiled in 50 ml of water and filtered through a 25 µl Teflon filter. A similar procedure was repeated for Pd Q4 nanoparticles (using 0.1 N PdCl₂, Aldrich, 99%). To evaluate 45, the source (tea and coffee extract) effect on morphology of the Ag and Pd nanoparticles was prepared and several experiments were performed using the above described procedure using the sources as shown in Table 1.
Table 1. Various brands of tea/coffee used to generate nanoparticles.

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Item Brand Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sanka coffee</td>
</tr>
<tr>
<td>2</td>
<td>Bigelow tea</td>
</tr>
<tr>
<td>3</td>
<td>Luzianne tea</td>
</tr>
<tr>
<td>4</td>
<td>Starbucks coffee</td>
</tr>
<tr>
<td>5</td>
<td>Folgers coffee</td>
</tr>
<tr>
<td>6</td>
<td>Lipton tea</td>
</tr>
</tbody>
</table>

Fig. 3. TEM image of silver nanoparticles, synthesized using (a) Bigelow tea, (b) Folgers coffee, (c) Lipton tea, (d) Luzianne tea, (e) Sanka coffee, and (f) Starbucks coffee extract at room temperature. The process involved one step and did not use any hazardous reducing chemicals or non-degradable capping agents.
Fig. 4. TEM image of palladium nanoparticles, synthesized using (a) Sanka coffee, (b) Bigelow tea, (c) Luzianne tea, (d) Starbucks coffee, (e) Folgers coffee and (f) Lipton tea extract at room temperature. The process involved one step and did not use any hazardous reducing chemicals or non-degradable capping agents.

Apart from our work with noble nanometals, we have developed a greener, more straightforward, single-step approach for the synthesis of bulk quantities of nanofibers of the electronic polymer, fully-reduced polyaniline (leucoemeraldine) without using any reducing agents, surfactants, and/or large amounts of insoluble templates. The nanofibers undergo a spontaneous redox reaction with noble metal ions under mild aqueous conditions, resulting in deposition of various shapes such as leaves, particulates, nanowires, and cauliflower for Ag, Pd, Au, and Pt, respectively. Thus, this approach affords a facile entry into this technologically important class of metal-polymer nanocomposites (49).

3. Microwave assisted synthesis of noble nanostructures and composites

Microwaves play an important role in green chemistry. The use of microwaves can reduce energy consumption and the time used to obtain desired materials. Over the past couple of years, microwave (MW) chemistry has moved from a laboratory curiosity to a well-established, synthetic technique used in many academic and industrial laboratories around the world. Even though the overwhelming number of MW-assisted applications used today are still performed on a laboratory scale, it expected that this technology may be used on a larger, perhaps even production-size, scale in conjunction with radio frequency or conventional heating. Microwave chemistry is based on two main principles: the dipolar mechanism and the electrical conductor mechanism.
The dipolar mechanism occurs when, under a very high frequency electric field, a polar molecule attempts to follow the field in the same alignment. When this happens, the molecules release enough heat to drive the reaction forward. In the later mechanism, the irradiated sample is an electrical conductor and the charge carriers, ions and electrons, move through the material under the influence of the electric field and lead to polarization within the sample. These induced currents and any electrical resistance will heat the sample.

Microwave heating has received considerable attention as a promising new method for the one-pot synthesis of metallic nanostructures in solutions. Because of this, the microwave-assisted synthetic approach for producing silver nanostructures has recently been reviewed. In the review process, researchers have successfully demonstrated the application of this method in the preparation of silver (Ag), gold (Au), platinum (Pt), and palladium (Pd) nanostructures. MW heating conditions allow not only for the preparation of spherical nanoparticles within a few minutes, but also for the formation of single crystalline polygonal plates, sheets, rods, wires, tubes, and dendrites. The morphologies and sizes of the nanostructures can be controlled by changing different experimental parameters, such as the concentration of metallic salt precursors, the surfactant polymers, the chain length of the surfactant polymers, the solvents, and the operation reaction temperature. In general, nanostructures with smaller sizes, narrower size distributions, and a higher degree of crystallization have been obtained more consistently via MW heating than by heating with a conventional oil-bath.

The use of microwaves to heat samples is a practical boulevard for the greener synthesis of nanomaterials (50) and provides many desirable features, such as shorter reaction times, reduced energy consumption, and better product yields. For example, Kundu et al. (51) have synthesized electrically conductive gold nanowires within 2-3 min using DNA as a reducing and nonspecific capping agent using a MW irradiation method. Similarly, uniform and stable polymer-stabilized colloidal clusters of Pt, Ir, Rh, Pd, Au, and Ru have been synthesized by MW irradiation with a modified domestic MW oven (52). The resulting colloidal clusters have small average diameters and narrow size distributions. Further, polychrome silver nanoparticles have been prepared using a soft solution approach under MW irradiation from a solution of silver nitrate (AgNO₃) in the presence of poly (N-vinyl-2-pyrrolidone) without any other reducing agent. Different morphologies of silver colloids with attractive colors could be obtained using different solvents as the reaction medium (53).

The MW method can find diversified applications; for example, bulk quantities of nanocarbons with pre-selected morphology can be synthesized in a simple and rapid MW heating approach directly from conducting polymers (54). On the same grounds, the successful preparation of highly active and dispersed metal nanoparticles on a mesoporous material has been accomplished in a conventional MW oven using an eco-friendly protocol in which ethanol and acetone–water were employed as both solvents and reducing agents. The materials exhibited different particle sizes, depending on the metal and the time of MW irradiation and the ensuing nanoparticles were found to be very active and selective in the oxidation of styrene (55).

Recently, Nadagouda et al. (23) have accomplished bulk syntheses of Ag and Fe nanorods using polyethylene glycol (PEG) under MW irradiation conditions. Due to tremendous increases in the biological applications of these nanostructures, there is a continued interest in using biodegradable polymers or surfactants to cap these nanoparticles in order
to prevent their aggregation. Most of these biodegradable polymers or surfactants have the tendency to be soluble in water and it is of great interest to know that good dispersion or capping can be obtained using these biodegradable polymers or surfactants. The PEG was chosen as a reducing agent and stabilizing agent for several reasons. First, PEG is biodegradable (as well as non-toxic) and has high water solubility at room temperature, unlike other polymers. It can also form complexes with metal ions and, thereafter, reduce to metals. Finally, it contains alcoholic groups that were exploited for the reduction and the stabilization of the nanoparticles. Favorable conditions to make Ag nanorods were established and the process was expanded to make Fe nanorods with uniform size and shape. The nanorods’ formation depended upon the concentration of PEG used in the reaction with Ag salt (see schematic diagram 1). Ag and Fe nanorods crystallized in face-centered cubic symmetry. In a typical procedure, aqueous silver nitrate (AgNO₃) solution (0.1 M) and different molar ratios of PEG (molecular weight 300) were mixed in a 10 mL test tube at room temperature to form a clear solution. The reaction mixture was irradiated in a CEM Discover focused MW synthesis system maintaining a temperature of 100 °C (monitored by a built-in infrared sensor) for 1 h with a maximum pressure of 280 psi. The resulting precipitated Ag nanorods (see Figures 5–7) were then washed several times with water to remove excess PEG.

Scheme 1. Schematic illustrations of experimental mechanisms that generated Ag (a) nanoparticles, (b) nanorods, and (c) nucleated nanorods and nanoparticles.
Fig. 5. Photographic image of (a) precipitated Ag nanorods after microwave irradiation for 2 min; and (b) control reaction of the same reaction composition carried out using an oil bath at 100 °C for 1 h.
Fig. 6. Reaction profile of 4 mL PEG(300) + 4 mL 0.1 N AgNO$_3$ irradiated at 100 °C for 1 h using MW.
Fig. 7. TEM images of Ag nanorods from (a) 4 mL PEG(300) + 4 mL 0.1 N AgNO₃ under MW conditions, and (b) its SAED pattern obtained, from a bundle of Ag nanorods randomly deposited on the TEM grid.

Shape-controlled synthesis of gold (Au) nanostructures with various shapes such as prisms, cubes, and hexagons was accomplished via the MW-assisted spontaneous reduction of noble metal salts using an aqueous solution of varying concentrations of α-D-glucose, sucrose, and maltose (22). The expeditious reaction was completed under MW irradiation in 30-60s with the formation of different shapes and structures (see Figure 8) and potential application to the generation of nanospheres of Ag, Pd, and Pt. The noble nanocrystals underwent catalytic oxidation with monomers such as pyrrole to generate noble
nanocomposites, which have potential functions in catalysis, biosensors, energy storage systems, nano-devices, and other ever-expanding technological applications.

In a typical experiment, an aqueous solution of HAuCl₄ (5 mL, 0.01 N) was placed in a 20 mL glass vessel and then mixed with 300 mg of R-D-glucose. The reaction mixture was exposed to high-intensity microwave irradiation (1000 W, Panasonic MW oven equipped with inverter technology) for 30-45 s. Similarly, experiments were conducted using 0.01 N PtCl₄, 0.01 N PdCl₂, and 0.1 N AgNO₃. In the cases of PdCl₂ and AgNO₃, 300 mg of poly (vinyl pyrrolidinone) (PVP) was added to prevent aggregation and the formation of silver mirror (Tollén’s process) on the surface of the glass walls.

Fig. 8. TEM images of Au nanostructures, synthesized (low concentration of sugar) using MW irradiation with natural polymers such as (a) sucrose, (b) α-D-glucose, or (c, d) maltose. The insets show corresponding electron diffraction patterns.

A green approach was also developed that generated bulk quantities of nanocomposites containing transition metals such as Cu, Ag, In, and Fe at room temperature. A biodegradable polymer, carboxymethyl cellulose (CMC), was reacted with respective metal salts to obtain desired composites (20).

These nanocomposites exhibited broader decomposition temperatures when compared with control CMC and Ag-based CMC nanocomposites, exhibiting a luminescent property at longer wavelengths.

The other noble metals (such as Au, Pt, and Pd) did not react at room temperature with aqueous solutions of CMC, but did react rapidly under MW irradiation (MW) conditions at 100 °C.
This environmentally-benign approach provides facile entry to the production of multiple-shaped noble nanostructures without using any toxic reducing agents and/or capping/surfactant agents. The method also uses a benign biodegradable polymer, CMC, could find widespread technological and medicinal applications.

Recently, Yu et al. (56) prepared uniform water-soluble silver nanoparticles by reducing silver nitrate with basic amino acids in the presence of soluble starch via MW heating in aqueous medium. Although the fundamental of MW irradiation for this system has yet to be studied completely, the authors believed that MW irradiation plays a major role in the synthesis of the uniform silver nanoparticles. The choice of benign solvent and renewable reacting components and targeted heating approaches amply support the notion that the green chemical synthesis of metal nanoparticles with well-controlled shapes, sizes, and structures is possible.

Microwave irradiation that accomplishes the cross-linking reaction of poly (vinyl alcohol) (PVA) with metallic and bimetallic systems has also been achieved (19).

Nanocomposites of PVA cross-linked metallic systems such as Pt, Cu, and In, and bimetallic systems such as Pt-In, Ag-Pt, Pt-Fe, Cu-Pd, Pt-Pd, and Pd-Fe were prepared expeditiously by reacting the respective metal salts with 3 wt. % PVA under MW irradiation, maintaining the temperature at 100 °C. This is a radical improvement over the methods used for preparing the cross-linked PVA described in the literature (see Figure 9).

The general preparative procedure is versatile and provides a simple route to manufacturing useful metallic and bimetallic nanocomposites with various shapes, such as nanospheres, nanodendrites, and nanocubes.

Recently, there has been an increasing interest in synthesizing carbon nanotube (CNT)-metal nanoparticle/polymer composites. The larger surface areas and high electric conductivity render them as ideal supporting materials for metal nanoparticle catalysts such as Ag, Au, Pt, and Pd nanoparticles, which have shown great promise in catalysis, surface-enhanced Raman scattering (SERS), and electrochemical and fuel cells. CNTs are also ideal templates for attaching metal nanoparticles and nanoparticle-fused metal nanowires for hydrogen storage and for chemical and biological sensing applications.

Fig. 9. Photographic image of cross-linked PVA with various metallic and bimetallic systems: (a) Pt, (b) Pt-In, (c) Ag-Pt, (d) Cu, (e) Pt-Fe, (f) Pt with higher concentration ratio, (g) Cu-Pd, (h) In, (i) Pt-Pd, and (j) Pd-Fe.
The cross-linking reaction of PVA with single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs), and buckminsterfullerene (C-60) using MW irradiation was achieved with 3 wt. % PVA under MW irradiation, maintaining a temperature of 100 °C, representing a radical improvement over literature methods to prepare such cross-linked PVA composites (Figure 10) (57). This general preparative procedure is versatile and provides a simple route for manufacturing useful SWNT, MWNT, and C-60 cross linked PVA nanocomposites.

Fig. 10. SEM images of SWNT cross-linked PVA nanocomposites.

Alignment and decoration of noble metals on CNTs wrapped with CMC was also achieved under MW condition. CNTs, such as SWNT, MWNT, and C-60, were well dispersed using the sodium salt of CMC under sonication (58). The addition of respective noble metal salts then generated noble metal-decorated CNT composites at room temperature. However, aligned nanocomposites of CNTs could only be generated by exposing the above nanocomposites to MW irradiation. The general preparative procedure is flexible and provides a straightforward route to manufacturing functional metal coated CNT nanocomposites (Figure 11).

Varma et al. (59) have developed a simple method for the bulk synthesis of monodispersed spinel ferrite nanoparticles with size selectivity using readily available inorganic precursors via a water-organic interface. Hydrothermal as well as MW hydrothermal methods are applicable but the use of MW has the advantage of low temperature, expedient synthesis. The synthesized particles are highly dispersible and are stable in nonpolar organic solvents, which is important in their use as ferrofluids and other magnetic applications. Surface functionalization of the As-synthesized particles with lysine made them water dispersible for possible biological applications (Figure 12).

It has been stated that volumetric and selective heating using MW irradiation may reduce the thermal gradients in the reaction, thereby generating a more homogeneous product with faster consumption of the starting materials. (60)
Varma et al. (61) have synthesized, for the first time under MW irradiation conditions, dendritic ferrites with micro-pine morphology (see Figure 13) without using any reducing or capping reagents. With this adjustment, nano ferrites could then be functionalized (Scheme 2) and coated with Pd metal, which catalyzes various C-C coupling reactions. An assortment of magnetic, nanoparticle-supported metal catalysts have been readily prepared from inexpensive starting materials and shown to catalyze a variety of organic transformations such as oxidation (62), hydration (63), and reduction (hydrogenation) (64). Superior activity and the inherent stability of these catalyst systems coupled with their easy magnetic separation, which eliminates the prerequisite of catalyst filtration after completion of the reaction, are some of the supplementary sustainable attributes of these protocols.
Fig. 13. TEM image of dendritic $\alpha$-Fe$_2$O$_3$.

Scheme 2. Schematic diagram of $\alpha$-Fe$_2$O$_3$ functionalization with amino group and Pd.

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Microwave strategy can be also be expanded to a solid state reaction. Porous nanocrystalline TiO$_2$ and carbon coated TiO$_2$ using sugar dextrose as a template has been achieved through MW and the results were compared with conventional heating furnace (65). Out of three compositions, namely, 1:1, 1:3, and 1:5 (metal: dextrose), 1:3 favors formation of consistent porous structures (see Figure 14). This general and eco-friendly method uses a benign natural polymer, dextrose, to create spongy porous structures and can be extended to other transition metal oxides such as ZrO$_2$, Al$_2$O$_3$, and SiO$_2$.

Fig. 14. (a)–(c) SEM images of 1:1, 1:3, and 1:5 (titania: dextrose molar ratio) titania sponges synthesized by microwave combustion and subsequently heated at 850 °C for 1 h by a conventional furnace (the inset shows the x-ray mapping images of the same with the green region showing titania and the red region showing carbon). (d) Representative (1:3 titania: dextrose molar ratio) sample of energy dispersive x-ray analysis (EDX) showing the presence of titania. (e)–(g) SEM images of 1:1, 1:3, and 1:5 (titania: dextrose molar ratio) titania sponges synthesized by heating at 850 °C for 1 h by conventional furnace (the inset shows the x-ray mapping images of the same with the green region showing titania and the red region showing carbon). (h) Representative sample (1:3 titania: dextrose molar ratio) of energy dispersive x-ray analysis (EDX) showing the presence of titania.

4. References

In modern research and development, materials manufacturing crystal growth is known as a way to solve a wide range of technological tasks in the fabrication of materials with preset properties. This book allows a reader to gain insight into selected aspects of the field, including growth of bulk inorganic crystals, preparation of thin films, low-dimensional structures, crystallization of proteins, and other organic compounds.

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