

On-paper Synthesis of Silver Nanoparticles for Antibacterial Applications

Hiroataka Koga and Takuya Kitaoka
Kyushu University
Japan

1. Introduction

Recent years have seen remarkable progress in research and development of metal nanoparticles (NPs) that takes advantage of their unique optical, magnetic, electronic, catalytic and other physicochemical properties, in a wide range of practical and potential applications such as energy, environmental, biomedical and chemical engineering (Feldheim & Foss, 2002; Ma et al., 2006; Jena & Raj, 2008; Zotti et al., 2008). For example, gold (Au) is a chemically inert metallic element in bulk form; however, AuNPs possess colorful plasmon resonances useful for bio-sensing (Shukla et al., 2005; Yokota et al., 2008), and can catalyze chemical reactions (Bond et al., 2006; Ishida & Haruta, 2007), due to their quantum size effects. NPs of inexpensive base metals, such as copper (CuNPs) have recently attracted much attention as innovative nanomaterials for applications such as highly-active gas reforming catalysts for hydrogen production (Gadhe & Gupta, 2007) and effective marine antifouling coatings (Anyaoqu et al., 2008). In general, however, practical utilization of nanosized materials involves considerable difficulties since metal NPs are hard to handle directly, and easily aggregate to minimize their surface area. The inevitable aggregation of metal NPs often nullifies their unique functionalities, and eventually yields ordinary bulk metals. For that reason, an area of ongoing research has focused on effective immobilization of metal NPs on easily handled supports such as porous membranes (Dotzauer et al., 2006) and nanostructured inorganic sheets (Wang et al., 2008).

Of the various metal NPs, silver NPs (AgNPs) are of increasing interest because of their high conductivity (Li et al., 2005) and tunable optical responsiveness (McFarland & Van Duyne, 2003). Moreover, it is well known that Ag exhibits potent antibacterial properties with low toxicity for humans and animals by comparison with other heavy metals (Alt et al., 2004; Shah et al., 2008). Ag and Ag-compounded materials are effective for both Gram-negative and Gram-positive bacteria, whereas the efficacy of conventional antibiotics varies with the species of bacteria (Shah et al., 2008). Many researchers have recently reported that AgNPs demonstrate excellent antibacterial activity (Sondi & Salopek-Sondi, 2004; Gogoi et al., 2006; Pal et al., 2007; Navarro et al., 2008). However, effective methods for immobilization of AgNPs for practical use are insufficiently advanced, and incorporation of AgNPs into various matrices is being actively investigated. For instance, it was reported that AgNPs were synthesized on poly(ethylene glycol)-polyurethane-titanium dioxide (TiO₂) films *via*

TiO₂-mediated photocatalysis under UV light irradiation, which facilitated photoreduction of silver nitrate (AgNO₃) to form AgNPs on the polymer-inorganic hybrid matrix (Shah et al., 2008). Ag-nanocoated cotton fabrics were successfully developed by an ion-exchange method (Lee et al., 2007). Such types of Ag-organic polymer complexes are generally sensitive to external stimuli (e.g. heat, light and pH), resulting in poor stability and durability. Hence, Ag-doped antibacterial inorganics, such as Ag-hydrogen titanate nanobelt sheets (Wang et al., 2008) and thin silica films prepared from ionic Ag-incorporated tetraethyl orthosilicate (Jeon et al., 2003), have been developed using various approaches, including sol-gel processing, ion-exchange and surface modifications. Despite these efforts, however, there is still a need to find more facile ways of making and using AgNPs in practical antibacterial applications, without compromising their excellent bioactive functionality. Thus, one of the present challenges is to develop a novel method for immobilization of highly active AgNPs on multipurpose, convenient support materials.

In this chapter, we present a facile technique for *in situ* synthesis of bioactive AgNPs on an easily handled inorganic ‘paper’ matrix. Paper is one of the most familiar materials in our daily life, and has the potential for broad applications due to its flexibility and availability. The outline of our strategy is highlighted in Fig. 1. Novel ‘on-paper’ synthesis of AgNPs is accomplished using a paper matrix that consists of ceramic fibers as the main framework and zinc oxide (ZnO) whiskers as a selective support for AgNPs through a simple soaking treatment with an aqueous solution of AgNO₃. These as-prepared AgNPs@ZnO paper composites with paper-like utility demonstrate excellent antibacterial performance. Further promising developments for on-paper synthesis of other metal NPs are also introduced.

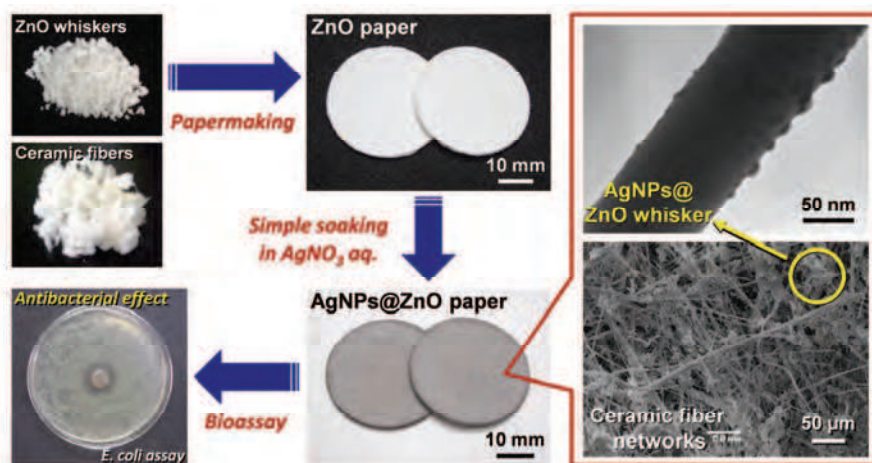


Fig. 1. Schematic illustration of on-paper synthesis of AgNPs and antibacterial application

2. Paper Composites

Paper is a versatile, ubiquitous material, commonly used for writing, printing, wrapping and packaging applications (Roberts, 1996). Paper materials have good practical utility (e.g. lightweight, flexible and easy handling), and many researchers and papermakers have developed new types of paper-like composites with various functions such as heat storage

capacity and bio-interface properties (Huang et al, 2006; Ichiura et al., 2008; Egusa et al., 2009). Paper has a porous, layered fiber network microstructure, and is consequently useful as a catalyst support. Basic technology of paper composite materials, an outline of the papermaking process, and our paper-like materials that have been developed for catalytic applications are described in the following sections.

2.1 Papermaking

The general papermaking procedure is carried out in an aqueous system, and can be summarized briefly as follows. A well-stirred fiber/water suspension is drained with a wire mesh so that a swollen mat of randomly entangled fibers is laid down on the wire. Water is then removed from the fiber mat by pressing and drying to produce a paper material. Most papers are made from organic fibers such as wood pulp and cotton: inorganic fibers such as ceramic and glass fibers are also used for further functional applications.

Papermakers often use powdery inorganic additives such as calcium carbonate, clay, talc, TiO_2 , zeolite and aluminum hydroxide for various purposes during the aqueous paper-forming process (Casey, 1981; Neimo, 1999). These inorganic particles, several micrometers in diameter, are much smaller than the mesh sizes of papermaking wires, and most of the particles are inevitably dropped off through the wire. Hence, various types of charged flocculants are used as aids for improving the retention of fine particles during paper formation. However, most inorganic materials including fibers and powders have weak negative charges in an aqueous papermaking system, and thus insufficient flocculation sometimes occurs. An effective solution to this problem is a dual polymer retention system (Scott, 1996; Ichiura et al.; 2001). The flocculation system can be summarised as follows. First, low-molecular-weight cationic polyelectrolytes with high charge density, such as poly(diallyldimethylammonium chloride) (PDADMAC), are overdosed to a water suspension containing negatively charged inorganics. The polymer molecules strongly adsorb onto the surface of these materials and form a patch of positive charges. Second, high-molecular-weight anionic polyelectrolytes with low charge density, such as anionic polyacrylamide (A-PAM), are added to the water suspension. The anionic polymers immediately connect the positively charged patches, and flocculating bridges are built up between the inorganic particles and fibers. Eventually, the resulting aggregates are effectively retained in the paper composites.

2.2 Catalytic Applications

Functional inorganic particles have been developed for a wide range of uses such as catalysts, adsorbents, electrodes, fillers and others. TiO_2 , a typical photocatalyst (Fujishima & Honda, 1972), is being commercialized for self-cleaning glasses, solar panels and air-purifying pigments. Cu/ZnO catalysts used in the methanol reforming process to produce hydrogen for fuel cell applications have been extensively upgraded by tailoring the elemental composition and nanometer-scale morphology of the catalyst surface, to improve their catalytic activity (Matter et al., 2004). However, such particulate materials are generally in the form of fine powders, and are difficult to handle in practical usage.

As described above, a dual polymer retention system enables effective retention of small inorganic particles in an easy to handle paper matrix. We have reported that various catalyst powders, *e.g.* zeolite (Ichiura et al., 2003), TiO_2 (Fukahori et al., 2003, 2007; Iguchi et al., 2003),

Cu/ZnO (Fukahori et al., 2006a, 2006b; Koga et al., 2006) and platinum/aluminum oxide (Pt/Al₂O₃) (Ishihara et al., 2010), can be incorporated into an inorganic paper matrix by a papermaking technique. The papermaking procedure is summarized as follows. A water suspension of ceramic fibers and catalyst powders is mixed with cationic polyelectrolyte PDADMAC (0.5 wt% of total solids), an alumina sol binder and anionic polyelectrolyte A-PAM (0.5 wt% of total solids), in that order. The mixture is added to pulp fiber suspension, and solidified by dewatering using a 200 mesh wire. The wet handsheets are pressed at 350 kPa for 3 min, then dried in an oven at 105°C for 1 h. The paper composites thus obtained are calcined to remove organic pulp fibers and to improve the physical strength by sintering with the alumina sol binder. As-prepared catalyst powder/inorganic fiber composites have the appearance of paperboard, and have good practical utility (Fig. 2).

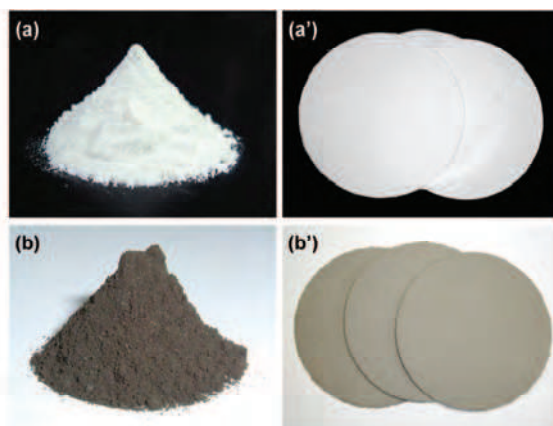


Fig. 2. Optical images of TiO₂ powders (a), Cu/ZnO powders (b), and respective paper composites containing each powder (a' and b'). The size of each paper composite is 2×10⁴ mm²

Compared to the original powders, these paper composites are far superior in terms of convenience of handling. As shown in Fig. 3, the retention of catalyst powders can be more than 95% with the dual polymer retention system (Fukahori et al., 2006a), and such polymer systems are applicable to large-scale production.

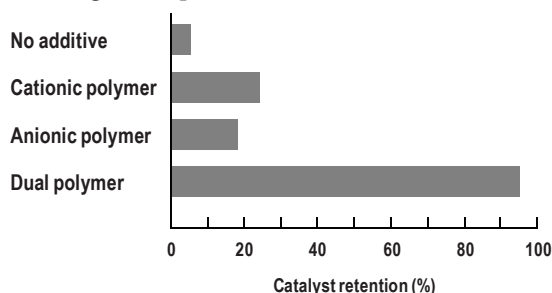


Fig. 3. Representative retention behavior of catalyst powders in paper composites by using polyelectrolyte-assisted retention systems

In addition, catalyst papers are highly effective for a wide range of catalytic processes such as the photodecomposition of bisphenol A in water (Fukahori et al., 2003), methanol reforming for hydrogen production (Fukahori et al., 2006a, 2008; Koga et al., 2006, 2008a) and removal of nitrogen oxides for exhaust gas purification (Ishihara et al., 2010). Moreover, our established papermaking technique allows the compounding of various functional fibers such as silicon carbide fibers (Fukahori et al., 2006b) and carbon fibers (Koga et al., 2009b) with high thermal conductivity, leading to further improvement of the catalytic performance. The results of these investigations suggest that paper-like fiber/catalyst composites prepared by a papermaking technique are promising catalytic materials for practical use. The combinational variation of fibers and functional particles is highly versatile. Further functional development of paper composites will be a significant challenge for exploring a wide range of applications.

2.3 Metal NPs Immobilization

Immobilization of metal NPs on a paper matrix has become of major interest. Immobilization of photoactive TiO₂ NPs on cellulose fibers has been investigated for preparation of self-cleaning paper (Pelton et al., 2006), which has a variety of potential applications such as food packaging. A simple method for immobilizing metal NPs on fibers by using charged polymers has been proposed (Dubas et al., 2006; Pelton et al., 2006). However, these approaches sometimes bring about fatal aggregation of metal NPs: excessive aggregation drastically decreases their specific surface area, resulting in insufficient functionality. There is, therefore, a need to establish more effective approaches for immobilization of metal NPs on paper materials. In the following sections, we describe a new concept whereby scaffold materials for metal NPs are prefabricated in paper composites, followed by *in situ* synthesis of highly-active metal NPs, especially AgNPs, on the paper matrices.

3. *In Situ* Synthesis of AgNPs on a Paper Matrix

This section provides a novel technique for immobilization of bioactive AgNPs on a paper matrix. Direct *in situ* synthesis of AgNPs is successfully achieved on a paper matrix that consists of ceramic fibers as the main framework and ZnO whiskers as a selective support for AgNPs.

3.1 AgNPs Synthesis on ZnO Whiskers

ZnO is an inexpensive, relatively-abundant and non-toxic material, and thus has been widely used as an inorganic additive for various products including rubbers, paints, pigments, foods and adhesives. Recently, a biomimetic membrane for immobilization of biomolecules has been prepared from ZnO due to its high biocompatibility (Kumar & Chen, 2008). Furthermore, ZnO-mediated photocatalysis has become the center of attention in relation to optical (Yang et al., 2002) and photoelectronic (An et al., 2007) applications as semiconductors, sensors, solar cells, etc. The band gap of crystalline ZnO is 3.37 eV (Yang et al., 2002), similar to that of the anatase form of TiO₂ which can reduce ionic Ag species to metallic AgNPs.

We propose a facile new method for using ZnO as a scaffold for the synthesis and immobilization of AgNPs, in which ionic Ag species are adsorbed on a ZnO support by ion exchange and are simultaneously reduced by the photocatalytic function of the ZnO (Koga et al., 2009a). Fig. 4 shows the ZnO whiskers with tetrapod-like nanostructure used in this method.

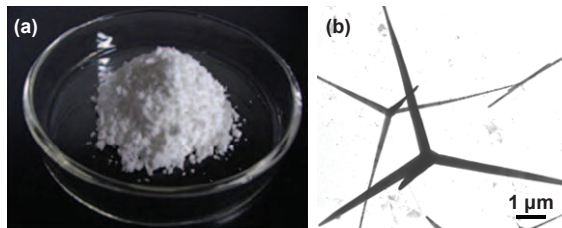


Fig. 4. Optical (a) and TEM (b) images of original ZnO whiskers

AgNPs synthesis on ZnO whiskers is achieved by the following simple procedure. ZnO whiskers are suspended in an aqueous solution of AgNO_3 with continuous stirring for 6 h, then filtered, washed with deionized water and air-dried. AgNPs with size 5–20 nm are formed on the ZnO whiskers through selective ion-exchange between Ag and Zn species, and simultaneous ZnO-mediated photoreduction under natural light irradiation (Fig. 5).

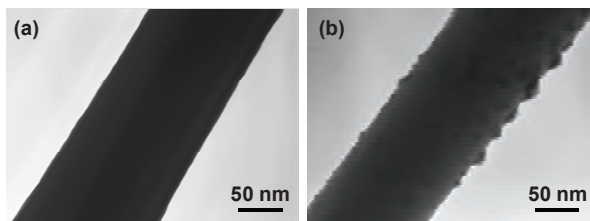


Fig. 5. TEM images of original ZnO whiskers (a) and AgNO_3 -treated ZnO whiskers (b)

X-Ray photoelectron spectroscopy (XPS) and X-ray diffractometry (XRD) reveal that AgNPs with crystallite size *ca.* 16 nm spontaneously form on ZnO whiskers *via* the simple soaking treatment with AgNO_3 solution (Fig. 6).

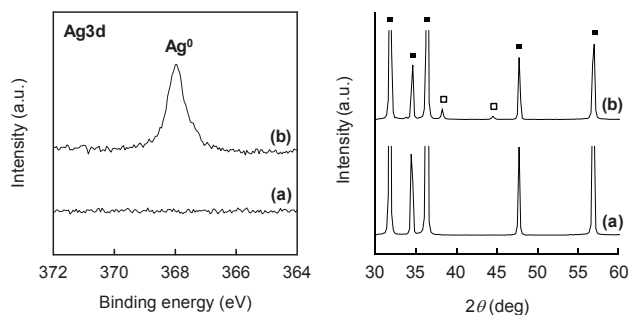


Fig. 6. XPS profiles (left) and XRD patterns (right) of original ZnO whiskers (a) and AgNPs@ZnO whiskers (b). □: Ag, ■: ZnO

In general, immobilization of metal NPs on support materials has required complicated, multi-step processes. For example, AgNPs-modified hydrogen titanate ($\text{H}_2\text{Ti}_3\text{O}_7$) nanobelts have been prepared according to the following procedure (Wang et al., 2008). AgNPs are prepared in advance and capped with 3-aminopropyl triethoxysilane through coordination between Ag and amino group. The modified AgNPs are then covalently fixed on the surfaces of the $\text{H}_2\text{Ti}_3\text{O}_7$ nanobelts, forming AgNPs-modified $\text{H}_2\text{Ti}_3\text{O}_7$ nanobelts. The synthesis and immobilization of PtNPs have been accomplished on a carbon fiber pretreated with nitric acid to activate the surface (Koga et al., 2009b). Surface-activated carbon fibers are immersed in an aqueous solution of hexachloroplatinic acid, followed by evaporation to complete dryness and reduction by reducing agents such as hydrogen and sodium borohydride. By contrast, our technique using ZnO whiskers allows one-pot, one-step immobilization of AgNPs in the absence of reducing agents, and this straightforward technique is expected to be a promising approach for practical AgNPs immobilization.

3.2 On-paper Synthesis of AgNPs

ZnO whiskers have the unique configuration of the tetrapod-like nanofibers shown in Fig. 4; however, as-prepared AgNPs supported on ZnO whiskers (AgNPs@ZnO whiskers) are still difficult to handle since the ZnO whiskers are fine fibers. Hence, a modified method of fabrication of AgNPs@ZnO whiskers is required for practical use, and paper fabrication is one of the promising methods. However, paper forming of AgNPs@ZnO whiskers inevitably causes functional deterioration of AgNPs, since AgNPs@ZnO whiskers are aggregated by flocculants, and the surfaces of AgNPs are partially covered with the binder components, which are necessarily added to enhance the physical strength of paper composites. To solve that problem, we have investigated direct, *in situ* synthesis of AgNPs on a ZnO whisker-containing paper composite (ZnO paper), that we refer to as on-paper synthesis (Koga et al., 2009a).

The on-paper synthesis of AgNPs is performed by first incorporating ZnO whiskers into a paper composite, then using the embedded whiskers as a scaffold for AgNPs. ZnO whiskers and ceramic fibers are fabricated into a paper composite by a papermaking technique. AgNPs-free ZnO paper composite can be easily prepared by substituting ZnO whiskers for catalyst powders in the aforementioned papermaking procedure (see section 2.2). ZnO whiskers are thus effectively retained inside the paper composite; virtually 100% retention of the inorganic materials is achieved. The paper composite obtained ($2 \times 10^4 \text{ mm}^2$) consists of ceramic fibers (5.0 g), ZnO whiskers (3.1 g) and alumina sol (0.50 g). Subsequently, on-paper synthesis of AgNPs is carried out. As-prepared ZnO paper is cut into disk-shaped pieces ($8 \times 10^2 \text{ mm}^2$) and immersed in an aqueous solution of AgNO_3 ($1.3 \times 10^2 \text{ mM}$, 100 mL) for 6 h. The disks are removed from the AgNO_3 solution using tweezers, thoroughly washed with deionized water, then dried at 105°C for 2 h. Optical images of the original ZnO paper and the ZnO paper treated with AgNO_3 solution are shown in Fig. 7a and b. These paper composites with the appearance of flexible cardboard are lightweight and easy to handle in practical use. The XPS and XRD profiles of AgNO_3 -treated ZnO paper (data not shown) were similar to those of AgNPs@ZnO whiskers shown in Fig. 6. AgNO_3 -treated paper without ZnO whiskers was prepared in a similar manner, in which case the amount of Ag adsorbed on the paper composite was less than 2.8% of the amount of Ag in AgNO_3 -treated ZnO paper, suggesting that AgNPs are synthesized selectively on the ZnO whiskers embedded in the paper composite.

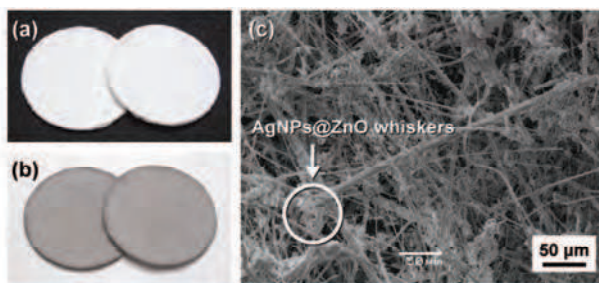


Fig. 7. Optical images of original ZnO paper (a), AgNO_3 -treated ZnO paper (b), and SEM image of the surface of AgNPs@ZnO paper (c). ZnO whiskers are well scattered throughout the ceramic fiber networks. The size of each paper composite is $8 \times 10^2 \text{ mm}^2$

Fig. 7c displays a scanning electron microscopic (SEM) image of the surface of ZnO paper after the synthesis of AgNPs. AgNP@ZnO paper has a characteristic porous fiber-network microstructure composed of ceramic fibers (average pore size *ca.* 16 μm , porosity *ca.* 50%), in which AgNPs@ZnO whiskers are well dispersed. Thus direct synthesis of AgNPs on an inorganic paper matrix is successfully achieved by using pre-compounded ZnO whiskers as a selective scaffold for AgNPs *via* a simple soaking treatment in AgNO_3 solution. To our knowledge, such on-paper synthesis of metal NPs is a hitherto unused approach for one-pot, one-step immobilization of metal NPs on easy to handle supports, *i.e.* paper.

4. Antibacterial Performance of AgNPs@ZnO Paper

In recent years, there has been a major upsurge of interest in AgNPs with unique properties for use in a wide range of fields such as optical (Ohko et al., 2003), electronic (Zhang et al., 2008), catalytic (Mao et al., 2009) and biomedical applications (Alt et al., 2004; Sondi & Salopek-Sondi, 2004; Morones et al., 2005; Lok et al., 2006). In this section, we focus on the antibacterial properties of AgNPs, and describe the practical performance of AgNPs@ZnO paper. The antibacterial activity of AgNPs@ZnO paper is compared with that of Ag-free ZnO paper, AgNO_3 -impregnated paper and Ag powder-containing paper. AgNO_3 -impregnated paper, *i.e.* Ag^+ ion-containing ZnO-free paper, was prepared as follows. Disk-shaped ZnO whisker-free paper composite was immersed in aqueous AgNO_3 , followed by evaporation to dryness at 105°C for 30 min to force precipitation of Ag components on the paper composite. Ag powder-containing paper composites were prepared by the papermaking procedure mentioned previously (see section 2.2). Antibacterial tests of paper samples were carried out by the standard disk diffusion assay previously reported (Lee et al., 2007; Shah et al., 2008; Wang et al., 2008). In summary, Gram-negative *Escherichia coli* (*E. coli*) bacterial suspension (Luria-Bertani (LB) medium, 100 μL , 3.5×10^5 colony forming units per mL) was uniformly inoculated on the solidified LB agar gel (20 mL). Disk-shaped pieces (10 mm in diameter and 1 mm in thickness) of Ag-free ZnO paper, AgNPs@ZnO paper, AgNO_3 -impregnated paper or Ag powder-containing paper were placed on the LB agar plate, followed by incubation at 37°C for 24 h. The antibacterial activities were compared by the diameter of the zone of inhibition around each paper disk. Fig. 8 displays optical images of the zone of inhibition against Gram-negative *E. coli* for each paper composite.

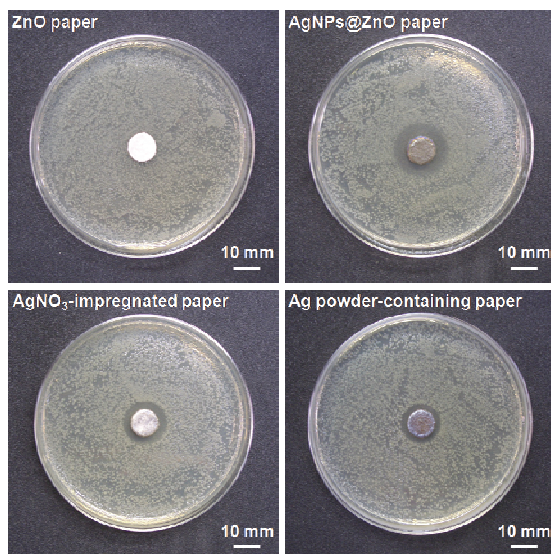


Fig. 8. Optical images of the zone of inhibition against *E. coli* for Ag-free ZnO paper, AgNPs@ZnO paper, AgNO₃-impregnated ZnO-free paper, and Ag powder-containing paper. Each paper composite is 10 mm in diameter. Ag content of the latter three samples is 2.0 mg. Incubation condition: 37°C, 24 h

ZnO paper exhibited no antibacterial activity, indicating that ZnO whiskers had no toxic influence on the growth of bacteria in these conditions. By contrast, the three paper composites containing Ag species showed clear zones of inhibition around each paper disk. AgNPs@ZnO paper demonstrated the largest zone of inhibition, *i.e.* highest antibacterial activity compared to paper composites containing either ionic Ag components (AgNO₃) or fine Ag powders (particle size: *ca.* 1 μm), although the same amounts of Ag components were used (2.0 mg per sample). In addition, AgNPs@ZnO paper exhibited the highest antibacterial activity even against Gram-positive *Bacillus subtilis* (*B. subtilis*) (Fig. 9), suggesting that AgNPs@ZnO paper is effective for a diverse array of bacteria.

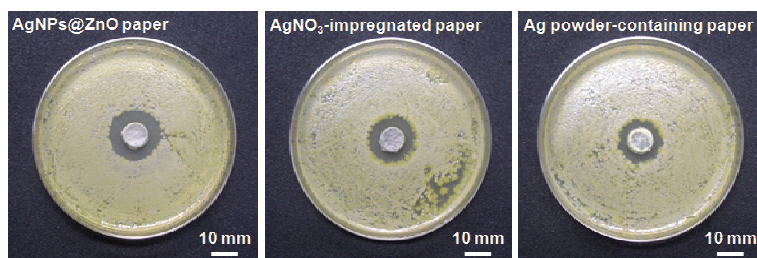


Fig. 9. Optical images of the zone of inhibition against *B. subtilis* for AgNPs@ZnO paper, AgNO₃-impregnated ZnO-free paper, and Ag powder-containing paper. Each paper composite is 10 mm in diameter. Ag content: 2.0 mg. Incubation condition: 37°C, 24 h

The antibacterial mechanism of Ag species has been a matter of debate for decades; credible rationales for the antibacterial activity are as follows. (1) Ag^+ ions interact with phosphorous moieties in DNA, resulting in deactivation of DNA replication, and/or (2) they react with sulfur-containing proteins, leading to inhibition of enzyme functions (Gupta et al., 1998; Matsumura et al., 2003). Albeit the mechanism of antibacterial action of AgNPs is still insufficiently understood, many researchers have reported that AgNPs can gradually release Ag^+ ions which play a key role in antibacterial effects (Jeong et al., 2005; Morones et al., 2005). On the other hand, Pal *et al.* have reported that spherical AgNPs had greater antibacterial activity against *E. coli* than Ag^+ ions in the form of AgNO_3 , and proposed that the nanometer size and the presence of Ag(111) crystal faces synergistically promoted the antibacterial effect of AgNPs (Pal et al., 2007). In that case the elution of Ag^+ ions from and the nanomorphology of AgNPs would synergistically contribute to the excellent antibacterial activity of AgNPs@ZnO paper.

Fig. 10 shows antibacterial behavior for repeated use. In all cases the diameter of the zone of inhibition gradually decreased in successive test cycles.

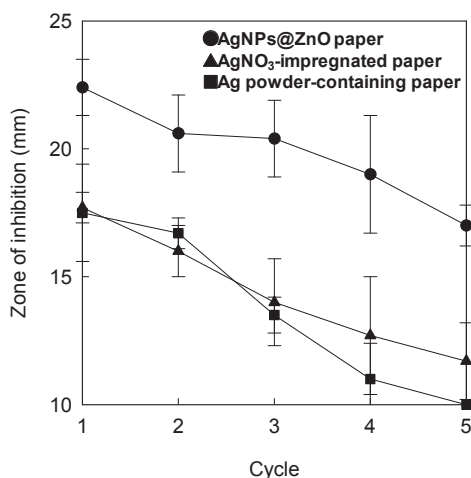


Fig. 10. Antibacterial durability against *E. coli* for repeated use: AgNPs@ZnO paper (circles), AgNO_3 -impregnated ZnO-free paper (triangles), and Ag powder-containing paper (squares)

The Ag content also decreased due to gradual release from each paper composite during the antibacterial tests, in accordance with the decrease in antibacterial effect. However, although the final Ag contents after the five-cycle test were similar, namely 0.2, 0.2 and 0.3 mg for AgNPs@ZnO paper, AgNO_3 -impregnated paper and Ag powder-containing paper, respectively, AgNPs@ZnO paper maintained much higher antibacterial activity than the other samples. The good durability of AgNPs@ZnO paper is possibly attributable both to the nanometer size and to the exposure of an active crystal face of AgNPs, leading to efficient antibacterial activity. Thus the AgNPs@ZnO paper with paper-like flexibility and convenience in handling is expected to be a promising bioactive material.

In summary, we have established a novel technique for the efficient immobilization of AgNPs on an easy to handle paper-like support. AgNPs with excellent bioactivity can be

successfully synthesized *in situ* on ZnO whiskers as a selective support, which are pre-incorporated into a ceramic paper matrix, *via* ion-exchange between Ag and Zn species and simultaneous ZnO-mediated photoreduction. The easily fabricated AgNPs@ZnO paper demonstrates excellent antibacterial activity and durability. Furthermore, the use of AgNPs has been growing in various fields such as optical (Ohko et al., 2003), electronic (Zhang et al., 2008), and catalytic applications (Mao et al., 2009). Hence the inorganic AgNPs@ZnO paper composites with paper-like porous structure and practical utility are expected to be one of the advanced materials for a wide range of potential applications of AgNPs.

5. On-paper Synthesis of Metal NPs for Catalytic Applications

Recent years have seen considerable progress in the research and development of metal NPs for use as new catalytic materials with large surface area to volume ratio (Toshima, 2003). In most cases, the electronic properties of metal NPs are significantly different from those of corresponding bulk metals, leading to large enhancement of catalytic activity (Ishida & Haruta, 2007; Park et al., 2008).

Our proposed technique has great potential for wide applications of other metal NPs, and here we describe the on-paper synthesis of CuNPs and AuNPs, and their performance as catalysts.

5.1 CuNPs@ZnO Paper for Hydrogen Production

Catalytic reforming of methanol has widely been used to produce hydrogen for new power generation systems such as polymer electrolyte fuel cells (Palo et al., 2007). In particular, autothermal reforming (ATR), which is the combined process of endothermic steam reforming and exothermic partial oxidation, has recently been investigated as an efficient energy conversion process. The methanol ATR reaction is represented by Eq. (1) (Horny et al., 2004):



Methanol reforming has been performed mostly over Cu/ZnO catalysts (Agrell et al., 2002). However, the random packing of catalyst powders into the reactor inevitably causes a high-pressure drop and fluid bypassing, resulting in critical inefficiency of the catalytic reforming process. For that reason, one area of increasing attention has been the development of structured catalysts with micrometer-scale pores that have effective diffusion of heat and reactants, particularly in flow-type reactors (Kiwi-Minsker & Renken, 2005).

As previously described, an inorganic paper matrix prepared using our established papermaking technique has a unique porous microstructure derived from ceramic fiber networks (Fig. 7c). Such a paper matrix is an easy to handle support material, and is an effective microstructured support for catalytic applications. We have shown that a ceramic paper matrix containing Cu/ZnO catalyst powders, called paper-structured catalyst, demonstrates excellent catalytic performance in the methanol ATR process compared with the original catalyst powders and commercial catalyst pellets (Koga et al., 2006, 2008a). The fiber-network microstructure with connected pore spaces inside the paper-structured catalyst provides a suitable catalytic reaction environment by promoting a high degree of desirable gas accessibility to the catalyst surfaces (Koga et al., 2009d).

The on-paper synthesis of highly-active CuNPs using ZnO whiskers is a rational approach toward the further improvement of catalytic performance of paper-structured catalyst.

CuNPs with size 20–50 nm can be successfully synthesized from an aqueous solution of the metal salt precursor copper nitrate ($\text{Cu}(\text{NO}_3)_2$), due to ion exchange between Cu and Zn species (Fig. 11) (Koga et al., 2008b).

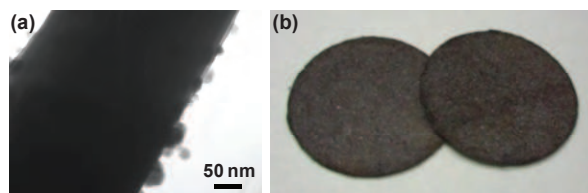


Fig. 11. TEM image of CuNPs@ZnO whiskers (a), and optical image of CuNPs@ZnO paper (b). The size of paper composite is $8 \times 10^2 \text{ mm}^2$

As shown in Fig. 12, CuNPs@ZnO paper offers exceptional catalytic performance in the methanol reforming process for hydrogen production.

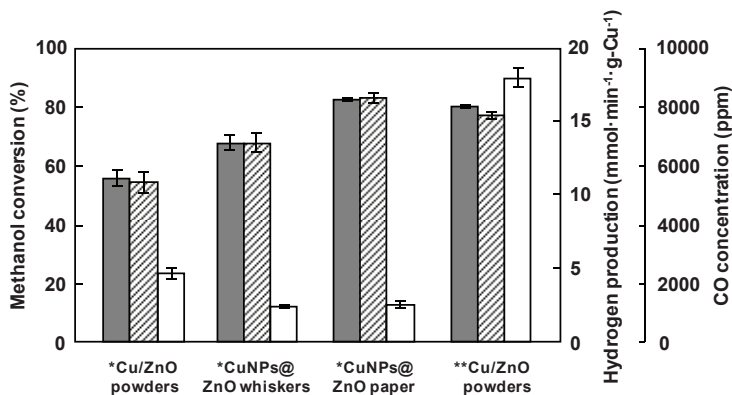


Fig. 12. ATR performance of Cu/ZnO powders, CuNPs@ZnO whiskers and CuNPs@ZnO paper; methanol conversion (filled bars), hydrogen production (striped bars) and CO concentration (open bars). Reaction temperature: 250°C^* or 310°C^{**} . Cu:ZnO=1.0:5.2 by weight. Cu content: $0.2 \text{ g}/8 \times 10^3 \text{ mm}^3$

For 80% conversion of methanol, suppression of by-product carbon monoxide (CO), which acts as a catalytic poison for Pt anode electrocatalysts in fuel cells, to ca. 14% is achieved at a 60 K lower reaction temperature than with conventional Cu/ZnO powders. Surprisingly, the catalytic performance of CuNPs@ZnO paper is superior to that of CuNPs@ZnO whiskers. These results suggest that the combination of CuNPs with high catalytic activity and a paper-structured support with a fiber-network microstructure is particularly effective for the ATR reaction, and CuNPs@ZnO paper is an innovative catalytic material for production of pure hydrogen for fuel cell applications.

5.2 AuNPs@ZnO Paper for Low-temperature CO Oxidation

Au has traditionally been considered chemically inert and regarded as catalytically inactive. However, nanosized Au has recently received increasing attention as an innovative

nanomaterial with unique properties in various fields such as electronics (Jena & Raj, 2008) and biomedical applications (Skrabalak et al., 2007). In particular, when Au in the form of NPs with diameter less than 10 nm is well dispersed on some metal oxides, it acts as a highly active catalyst for many chemical reactions (Ishida & Haruta, 2007). A great deal of effort has been directed toward low-temperature CO oxidation (represented by Eq. (2)) over Au supported metal oxide catalysts (Bond et al., 2006).



On-paper synthesis of AuNPs is accomplished by using the metal complex precursor tetrachloroauric acid (HAuCl_4). AuNPs with particle size <10 nm are spontaneously formed on ZnO whiskers *via* a simple soaking treatment with HAuCl_4 solution (Fig. 13), possibly due to electron transfer from Zn(II) in ZnO whiskers to Au(III) species through Zn-O-Au bonds (Koga et al., 2009c).

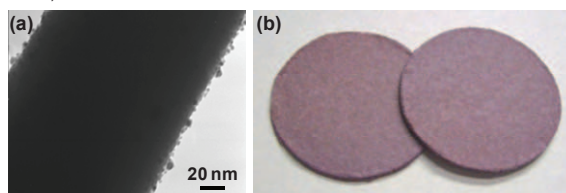


Fig. 13. TEM image of AuNPs@ZnO whiskers (a), and optical image of AuNPs@ZnO paper (b). The size of paper composite is $8 \times 10^2 \text{ mm}^2$

As-prepared AuNPs@ZnO paper has excellent catalytic performance in low-temperature CO oxidation. Complete conversion of CO to CO_2 is achieved at 20°C , which is 140 K lower than the reaction temperature for conventional Au/ZnO catalyst powders (Fig. 14).

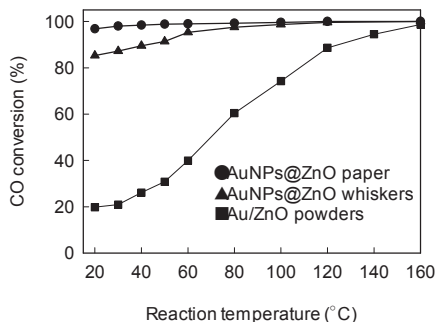


Fig. 14. CO conversion to CO_2 as a function of reaction temperature: AuNPs@ZnO paper (circles), AuNPs@ZnO whiskers (triangles), and Au/ZnO powders (squares). Au content: $10 \text{ mg}/8 \times 10^3 \text{ mm}^3$

The synthesis of AuNPs described here, which is achieved by use of a metal complex precursor, is clearly different from the formation of CuNPs and AgNPs through simple ion exchange. This strongly suggests that the on-paper synthesis of metal NPs can be performed using various metal precursors, and has great potential for future applications for a diverse array of metal species. Catalytic metal NPs@ZnO paper composites with paper-like

flexibility are able to fit various reactor configurations and are thus expected to perform as advanced catalytic materials for improving the practical utility and catalytic performance of these systems, for a wide range of industrial chemical processes.

6. Conclusion

This chapter provides a new concept and strategic approach to optimising use of AgNPs in practical applications without compromising their excellent functionalities. Direct, *in situ* synthesis of AgNPs, called on-paper synthesis, is successfully achieved by using a paper matrix composed of ceramic fibers as a main framework and ZnO whiskers as a selective support for AgNPs *via* a simple soaking treatment with AgNO₃ solution. As-prepared AgNPs@ZnO paper with the appearance of flexible cardboard is convenient for a wide range of practical uses, and demonstrates excellent antibacterial performance against both Gram-negative *E. coli* and Gram-positive *B. subtilis*, with much greater efficacy than paper composites containing either ionic Ag or commercial crystalline Ag microparticles. Thus, this method provides highly-functional AgNPs in a form that can be easily handled, and will open up a new avenue for promoting the effective use of AgNPs in practical applications.

On-paper synthesis has broad applications and can be extended to a diverse array of metal NPs. CuNPs are successfully synthesized from an aqueous solution of Cu(NO₃)₂, and CuNPs@ZnO paper offers exceptional catalytic performance in the methanol reforming process for hydrogen production. AuNPs@ZnO paper, which is prepared from HAuCl₄ complex as a precursor, can mediate the complete conversion of CO to CO₂ at room temperature. Thus the novel on-paper synthesis approach allows us to design a variety of nanomaterials containing metal NPs that maintain their original excellent functionality, and metal NPs@paper composites with convenience in handling are expected to be promising materials in a wide range of future applications. Such a new concept for practical immobilization of metal NPs will break new ground in metal NPs engineering fields.

7. References

- Agrell, J.; Birgersson, H. & Boutonnet, M. (2002). Steam reforming of methanol over a Cu/ZnO/Al₂O₃ catalyst: a kinetic analysis and strategies for suppression of CO formation. *Journal of Power Sources*, 106, 1-2, 249-257, ISSN 0378-7753
- Alt, V.; Bechert, T.; Steinrücke, P.; Wagener, M.; Seidel, P.; Dingeldein, E.; Domann, E. & Schnettler, R. (2004). An *in vitro* assessment of the antibacterial properties and cytotoxicity of nanoparticulate silver bone cement. *Biomaterials*, 25, 18, 4383-4391, ISSN 0142-9612
- An, X.Q.; Cao, C.B. & Zhu, H.S. (2007). Bio-inspired fabrication of ZnO nanorod arrays and their optical and photoresponse properties. *Journal of Crystal Growth*, 308, 2, 340-347, ISSN 0022-0248
- Anyagou, K.C.; Fedorov, A.V. & Neckers, D.C. (2008). Synthesis, characterization, and antifouling potential of functionalized copper nanoparticles. *Langmuir*, 24, 8, 4340-4346, ISSN 0743-7463
- Bond, G.C.; Louis C. & Thompson, D.T. (2006). *Catalysis by Gold*, Imperial College Press, ISBN 1-86094-658-5, London

- Casey, J.P. (1981). *Pulp and Paper: Chemistry and Chemical Technology Volume III*, John Wiley & Sons, Inc., ISBN 978-0-471-03177-2, New York
- Dotzauer, D.M.; Dai, J.; Sun, L. & Bruening, M.L. (2006). Catalytic membranes prepared using layer-by-layer adsorption of polyelectrolyte/metal nanoparticle films in porous supports. *Nano Letters*, 6, 10, 2268-2272, ISSN 1530-6984
- Dubas, S.T.; Kumlangdudsana, P. & Potiyaraj, P. (2006). Layer-by-layer deposition of antimicrobial silver nanoparticles on textile fibers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 289, 1-3, 105-109, ISSN 0927-7757
- Egusa, S.; Yokota, S.; Tanaka, K.; Esaki, K.; Okutani, Y.; Ogawa, Y.; Kitaoka, T.; Goto, M. & Wariishi, H. (2009). Surface modification of a solid-state cellulose matrix with lactose by a surfactant-enveloped enzyme in a nonaqueous medium. *Journal of Materials Chemistry*, 19, 13, 1836-1842, ISSN 0959-9428
- Feldheim, D.L. & Foss, C.A. (2002). *Metal nanoparticles: synthesis, characterization, and applications*. Marcel Dekker, Inc., ISBN 0-8247-0604-8, New York
- Fujishima, A. & Honda, K. (1972). Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238, 5358, 37-38, ISSN 0028-0836
- Fukahori, S.; Ichiura, H.; Kitaoka, T. & Tanaka, H. (2003). Photocatalytic decomposition of bisphenol A in water using composite TiO₂-zeolite sheets prepared by a papermaking technique. *Environmental Science and Technology*, 37, 5, 1048-1051, ISSN 0013-936X
- Fukahori, S.; Kitaoka, T.; Tomoda, A.; Suzuki, R. & Wariishi, H. (2006a). Methanol steam reforming over paper-like composites of Cu/ZnO catalyst and ceramic fiber. *Applied Catalysis A: General*, 300, 2, 155-161, ISSN 0926-860X
- Fukahori, S.; Koga, H.; Kitaoka, T.; Tomoda, A.; Suzuki, R. & Wariishi, H. (2006b). Hydrogen production from methanol using a SiC fiber-containing paper composite impregnated with Cu/ZnO catalyst. *Applied Catalysis A: General*, 310, 138-144, ISSN 0926-860X
- Fukahori, S.; Iguchi, Y.; Ichiura, H.; Kitaoka, T.; Tanaka, H. & Wariishi, H. (2007). Effect of void structure of photocatalyst paper on VOC decomposition. *Chemosphere*, 66, 11, 2136-2141, ISSN 0045-6535
- Fukahori, S.; Koga, H.; Kitaoka, T.; Nakamura, M. & Wariishi, H. (2008). Steam reforming behavior of methanol using paper-structured catalysts: Experimental and computational fluid dynamic analysis. *International Journal of Hydrogen Energy*, 33, 6, 1661-1670, ISSN 0360-3199
- Gadhe, J.B. & Gupta, R.B. (2007). Hydrogen production by methanol reforming in supercritical water: Catalysis by in-situ-generated copper nanoparticles. *International Journal of Hydrogen Energy*, 32, 13, 2374-2381, ISSN 0360-3199
- Gogoi, S.K.; Gopinath, P.; Paul, A.; Ramesh, A.; Ghosh S.S. & Chattopadhyay, A. (2006). Green fluorescent protein-expressing *Escherichia coli* as a model system for investigating the antimicrobial activities of silver nanoparticles. *Langmuir*, 22, 22, 9322-9328, ISSN 0743-7463
- Gupta, A.; Maynes, M. & Silver, S. (1998). Effects of halides on plasmid-mediated silver resistance in *Escherichia coli*. *Applied and Environmental Microbiology*, 64, 12, 5042-5045, ISSN 1098-5336

- Horny, C.; Kiwi-Minsker, L. & Renken, A. (2004). Micro-structured string-reactor for autothermal production of hydrogen. *Chemical Engineering Journal*, 101, 1-3, 3-9, ISSN 1385-8947
- Huang, J.; Ichinose, I. & Kunitake, T. (2006). Biomolecular modification of hierarchical cellulose fibers through titania nanocoating. *Angewandte Chemie-International Edition*, 45, 18, 2883-2886, ISSN 1433-7851
- Ichiura, H.; Kubota, Y.; Wu, Z. & Tanaka, H. (2001). Preparation of zeolite sheets using a papermaking technique - Part I - Dual polymer system for high retention of stock components. *Journal of Materials Science*, 36, 4, 913-917, ISSN 0022-2461
- Ichiura, H.; Nozaki, M.; Kitaoka, T. & Tanaka, H. (2003). Influence of uniformity of zeolite sheets prepared using a papermaking technique on VOC adsorptivity. *Advances in Environmental Research*, 7, 4, 975-979, ISSN 1093-0191
- Ichiura, H.; Ohi, T.; Oyama, H.; Yokota, H.; Kunitake, T.; Ohashi, S. & Morikawa, M. (2008). Paper-paraffin composites prepared by interfacial polymerization reaction on paper surface and its function of thermal energy storage. *Journal of Materials Science*, 43, 4, 1486-1491, ISSN 0022-2461
- Iguchi, Y.; Ichiura, H.; Kitaoka, T. & Tanaka, H. (2003). Preparation and characteristics of high performance paper containing titanium dioxide photocatalyst supported on inorganic fiber matrix. *Chemosphere*, 53, 10, 1193-1199, ISSN 0045-6535
- Ishida, T. & Haruta, M. (2007). Gold catalysts: Towards sustainable chemistry. *Angewandte Chemie-International Edition*, 46, 38, 7154-7156, ISSN 1433-7851
- Ishihara, H.; Koga, H.; Kitaoka, T.; Wariishi, H.; Tomoda, A. & Suzuki, R. (2010). Paper-structured catalyst for catalytic NO_x removal from combustion exhaust gas. *Chemical Engineering Science*, 65, 1, 208-213, ISSN 0009-2509
- Jena, B.K. & Raj, C.R. (2008). Morphology dependent electrocatalytic activity of Au nanoparticles. *Electrochemistry Communications*, 10, 6, 951-954, ISSN 1388-2481
- Jeon, H.-J.; Yi, S.-C. & Oh, S.-G. (2003). Preparation and antibacterial effects of Ag-SiO₂ thin films by sol-gel method. *Biomaterials*, 24, 27, 4921-4928, ISSN 0142-9612
- Jeong, S.H.; Hwnag Y.H. & Yi, S.C. (2005). Antibacterial properties of padded PP/PE nonwovens incorporating nano-sized silver colloids. *Journal of Materials Science*, 40, 20, 5413-5418, ISSN 0022-2461
- Kiwi-Minsker, L. & Renken, A. (2005). Microstructured reactors for catalytic reactions. *Catalysis Today*, 110, 1-2, 2-14, ISSN 0920-5861
- Koga, H.; Fukahori, S.; Kitaoka, T.; Tomoda, A.; Suzuki, R. & Wariishi, H. (2006). Autothermal reforming of methanol using paper-like Cu/ZnO catalyst composites prepared by a papermaking technique. *Applied Catalysis A: General*, 309, 2, 263-269, ISSN 0926-860X
- Koga, H.; Fukahori, S.; Kitaoka, T.; Nakamura, M. & Wariishi, H. (2008a). Paper-structured catalyst with porous fiber-network microstructure for autothermal hydrogen production. *Chemical Engineering Journal*, 139, 2, 408-415, ISSN 1385-8947
- Koga, H.; Kitaoka, T. & Wariishi, H. (2008b). *In situ* synthesis of Cu nanocatalysts on ZnO whiskers embedded in a microstructured paper composite for autothermal hydrogen production. *Chemical Communications*, 43, 5616-5618, ISSN 1359-7345
- Koga, H.; Kitaoka, T. & Wariishi, H. (2009a). *In situ* synthesis of silver nanoparticles on zinc oxide whiskers incorporated in a paper matrix for antibacterial applications. *Journal of Materials Chemistry*, 19, 15, 2135-2140, ISSN 0959-9428

- Koga, H.; Umemura, Y.; Ishihara, H.; Kitaoka, T.; Tomoda, A.; Suzuki, R. & Wariishi, H. (2009b). Paper-structured fiber composites impregnated with platinum nanoparticles synthesized on a carbon fiber matrix for catalytic reduction of nitrogen oxides. *Applied Catalysis B: Environmental*, 90, 3-4, 699-704, ISSN 0926-3373
- Koga, H.; Kitaoka, T. & Wariishi, H. (2009c). On-paper synthesis of Au nanocatalysts from Au(III) complex ions for low-temperature CO oxidation. *Journal of Materials Chemistry*, 19, 29, 5244-5249, ISSN 0959-9428
- Koga, H.; Kitaoka, T.; Nakamura, M. & Wariishi, H. (2009d). Influence of a fiber-network microstructure of paper-structured catalyst on methanol reforming behavior. *Journal of Materials Science*, 44, 21, 5836-5841, ISSN 0022-2461
- Kumar, S.A.; Chen, S.-M. (2008). Nanostructured zinc oxide particles in chemically modified electrodes for biosensor applications. *Analytical Letters*, 41, 2, 141-158, ISSN 0003-2719
- Lee, H.Y.; Park, H.K.; Lee, Y.M.; Kim, K. & Park, S.B. (2007). A practical procedure for producing silver nanocoated fabric and its antibacterial evaluation for biomedical applications. *Chemical Communications*, 28, 2959-2961, ISSN 1359-7345
- Li, Y.; Wu, Y. & Ong, B.S. (2005). Facile synthesis of silver nanoparticles useful for fabrication of high-conductivity elements for printed electronics. *Journal of the American Chemical Society*, 127, 10, 3266-3267, ISSN 0002-7863
- Lok, C.-N.; Ho, C.-M.; Chen, R.; He, Q.-Y.; Yu, W.-Y.; Sun, H.; Tam, P.K.-H.; Chiu, J.-F. & Che, C.-M. (2006). Proteomic analysis of the mode of antibacterial action of silver nanoparticles. *Journal of Proteome Research*, 5, 4, 916-924, ISSN 1535-3893
- Ma, D.; Guan, J.; Normandin, F.; Dénonnée, S.; Enright, G.; Veres, T. & Simard, B. (2006). Multifunctional nano-architecture for biomedical applications. *Chemistry of Materials*, 18, 7, 1920-1927, ISSN 0897-4756
- Mao, J.P.; Deng, M.M.; Xue, Q.S.; Chen, L. & Lu, Y. (2009). Thin-sheet Ag/Ni-fiber catalyst for gas-phase selective oxidation of benzyl alcohol with molecular oxygen. *Catalysis Communications*, 10, 10, 1376-1379, ISSN 1566-7367
- Matsumura, Y.; Yoshikata, K.; Kunisaki, S. & Tsuchido, T. (2003). Mode of bactericidal action of silver zeolite and its comparison with that of silver nitrate. *Applied and Environmental Microbiology*, 69, 7, 4278-4281, ISSN 1098-5336
- Matter, P.H.; Braden, D.J. & Ozkan, U.S. (2004). Steam reforming of methanol to H₂ over nonreduced Zr-containing CuO/ZnO catalysts. *Journal of Catalysis*, 223, 2, 340-351, ISSN 0021-9517
- McFarland, A.D. & Van Duyne, R.P. (2003). Single silver nanoparticles as real-time optical sensors with zeptomole sensitivity. *Nano Letters*, 3, 8, 1057-1062, ISSN 1530-6984
- Morones, J.R.; Elechiguerra, J.L.; Camacho, A.; Holt, K.; Kouri, J.B.; Ramirez, J.T. & Yacaman M.J. (2005). The bactericidal effect of silver nanoparticles. *Nanotechnology*, 16, 10, 2346-2353, ISSN 0957-4484
- Navarro, E.; Piccapietra, F.; Wagner, B.; Marconi, F.; Kaegi, R.; Odzak, K.; Sigg, L. & Behra, R. (2008). Toxicity of silver nanoparticles to *Chlamydomonas reinhardtii*. *Environmental Science and Technology*, 42, 23, 8959-8964, ISSN 0013-936X
- Neimo, L. (1999). *Papermaking Chemistry*, Fapet Oy, ISBN 952-5216-04-7, Helsinki
- Ohko, Y.; Tatsuma, T.; Fujii, T.; Naoi, K.; Niwa, C.; Kubota, Y. & Fujishima, A. (2003). Multicolour photochromism of TiO₂ films loaded with silver nanoparticles. *Nature Materials*, 2, 1, 29-31, ISSN 1476-1122

- Pal, S.; Tak, Y.K. & Song, J.M. (2007). Does the antibacterial activity of silver nanoparticles depend on the shape of the nanoparticle? A study of the Gram-negative bacterium *Escherichia coli*. *Applied and Environmental Microbiology*, 73, 6, 1712-1720, ISSN 1098-5336
- Palo, D.R.; Dagle, R.A. & Holladay, J.D. (2007). Methanol Steam Reforming for Hydrogen Production. *Chemical Reviews*, 107, 10, 3992-4021, ISSN 1520-6890
- Park, J.Y.; Zhang, Y.; Grass, M.; Zhang, T. & G.A. (2008). Tuning of catalytic CO oxidation by changing composition of Rh-Pt bimetallic nanoparticles. *Nano Letters*, 8, 2, 673-677, ISSN 1530-6984
- Pelton, R.; Geng, X.L. & Brook, M. (2006). Photocatalytic paper from colloidal TiO₂ - fact or fantasy. *Advances in Colloid and Interface Science*, 127, 1, 43-53, ISSN 0001-8686
- Roberts, J.C. (1996). *Paper Chemistry*, Blackie Academic & Professional, ISBN 0-7514-0236-2, London
- Scott, W.E. (1996). *Principles of Wet End Chemistry*, TAPPI PRESS, ISBN 0-89852-286-2, Atlanta
- Shah, M.S.A.S.; Nag, M.; Kalagara, T.; Singh, S. & Manorama, S.V. (2008). Silver on PEG-PU-TiO₂ polymer nanocomposite films: An excellent system for antibacterial applications. *Chemistry of Materials*, 20, 7, 2455-2460, ISSN 0897-4756
- Shukla, R.; Bansal, V.; Chaudhary, M.; Basu, A.; Bhonde R.R. & Sastry, M. (2005). Biocompatibility of gold nanoparticles and their endocytotic fate inside the cellular compartment: a microscopic overview, *Langmuir*, 21, 23, 10644-10654, ISSN 0743-7463
- Skrabalak, S.E.; Chen, J.; Au, L.; Lu, X.; Li, X. & Xia, Y. (2007). Gold nanocages for biomedical applications. *Advanced Materials*, 19, 20, 3177-3184, ISSN 0935-9648
- Sondi, I. & Salopek-Sondi, B. (2004). Silver nanoparticles as antimicrobial agent: a case study on *E-coli* as a model for Gram-negative bacteria. *Journal of Colloid and Interface Science*, 275, 1, 177-182, ISSN 0021-9797
- Toshima, N. (2003). Metal nanoparticles for catalysis, In: *Nanoscale Materials*, Liz-Marzan, L.M. & Kamat, P.V. (Ed.), 79-96, Kluwer Academic Publishers, ISBN 978-1-4020-7366-3, Boston
- Wang, Y.; Du, G.; Liu, H.; Liu, D.; Qin, S.; Wang, N.; Hu, C.; Tao, X.; Jiao, J.; Wang, J. & Wang, Z.L. (2008). Nanostructured sheets of Ti-O nanobelts for gas sensing and antibacterial applications. *Advanced Functional Materials*, 18, 7, 1131-1137, ISSN 1616-301X
- Yang, P.D.; Yan, H.Q.; Mao, S.; Russo, R.; Johnson, J.; Saykally, R.; Morris, N.; Pham, J.; He, R.R. & Choi, H.J. (2002). Controlled growth of ZnO nanowires and their optical properties. *Advanced Functional Materials*, 12, 5, 323-331, ISSN 1616-301X
- Yokota, S.; Kitaoka, T.; Opietnik, M.; Rosenau, T. & Wariishi, H. (2008). Synthesis of gold nanoparticles for in situ conjugation with structural carbohydrates. *Angewandte Chemie-International Edition*, 47, 51, 9866-9869, ISSN 1433-7851
- Zhang, H.; Wang, G.; Chen, D.; Lv, X.J. & Li, J.H. (2008). Tuning photoelectrochemical performances of Ag-TiO₂ nanocomposites via reduction/oxidation of Ag. *Chemistry of Materials*, 20, 20, 6543-6549, ISSN 0897-4756
- Zotti, G.; Vercelli, B. & Berlin, A. (2008). Gold nanoparticles linked by pyrrole- and thiophene-based thiols. Electrochemical, optical, and conductive properties. *Chemistry of Materials*, 20, 2, 397-412, ISSN 0897-4756



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Nanotechnology will be soon required in most engineering and science curricula. It cannot be questioned that cutting-edge applications based on nanoscience are having a considerable impact in nearly all fields of research, from basic to more problem-solving scientific enterprises. In this sense, books like “Silver Nanoparticles” aim at filling the gaps for comprehensive information to help both newcomers and experts, in a particular fast-growing area of research. Besides, one of the key features of this book is that it could serve both academia and industry. “Silver nanoparticles” is a collection of eighteen chapters written by experts in their respective fields. These reviews are representative of the current research areas within silver nanoparticle nanoscience and nanotechnology.

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Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
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中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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