Facile preparation of Ag/ZnO nanoparticles via photoreduction

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Abstract Ag/ZnO nanoparticles can be obtained via photocatalytic reduction of silver nitrate at ZnO nanorods when a solution of $AgNO_3$ and nanorods ZnO suspended in ethyleneglycol is exposed to daylight. The mean size of the deposited sphere like Ag particles is about 5 nm. However, some of the particles can be as large as 20 nm. The ZnO nanorods were pre-prepared by basic precipitation from zinc acetate di-hydrate in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide. They are about 50–300 nm in length and 10–50 nm in width. Transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDS), X-ray powder diffraction (XRD), UV–Vis spectroscopy, X-ray photoelectron spectroscopy (XPS), and photoluminescence (PL) were used to characterize the resulting Ag/ZnO nanocomposites.

Introduction

Metal/semiconductor oxide composite nanoparticles are interesting because of their optical, electrical, magnetic, and chemical properties that are not found in the single individual component. These properties that arise from their combination renders the materials interesting in different application areas including nanoelectronic devices, catalysis, nonlinear optical devices, etc. [1]. Materials that combine silver and zinc oxide have attracted attention not only because ZnO is one of the most important wide-band-

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gap semiconductors and has various applications including use in sensors, electronics and photoelectronics, but also because silver nanomaterials display some unique features in chemical and biological sensing, which are based on surface-enhanced Raman scattering, localized surface plasmon resonance, and metal-enhanced fluorescence [2]. The wide-band-gap semiconductors TiO_2 and ZnO have become important photocatalyst for the degradation of organic pollutants in air and water in recent years [3–7]. Ag–ZnO composite materials are currently experiencing growing attention as improved photocatalysts [8–14]. Many efforts have been made alone to synthesize ZnO with various morphologies, including rods [15], wires [16], rings [17], flowers [18], and many more. Preparation methods that were used include template-confined synthesis routes [19], high-temperature methods [20], hydrothermal synthesis [15], solution-phase methods using additives such as surfactants [21], and microwave heating [22]. Some core–shell structures of ZnO have been fabricated such as Zn–ZnO nanocrystals by combing liquid-solution colloids together with the vapor–gas growth process, [23] and the synthesis of Au–ZnO composites by a solution-phase method [24]. Classically, Ag/ZnO composite materials have been obtained from wet chemical precipitation–deposition methods [25], electrochemically [26–28], hydrothermally [14], via thermal decomposition of Ag_2O on ZnO [29], or by combined thermal evaporation and sputtering [30]. Sononchemistry is known to be an excellent method for the preparation of nanoparticles [31]. Room-temperature ionic liquids (RTILS) have aroused increasing interest for materials synthesis due to their advantages such as a comparatively high thermal and chemical stability, the ability to dissolve a variety of materials and, importantly, often no measurable vapor pressure [32–34]. In this report we describe the synthesis of Ag/ZnO particles. In a first step

ZnO-nanorods are synthesised in an ionic liquid by irradiation with ultrasound, then in a second step the as-prepared ZnO is redispersed in a solution of AgNO$_3$ in ethylene glycol. Upon exposing this reaction mixture to daylight photoreduction of silver at ZnO takes place. Interestingly, ordinary daylight is sufficient for the reactions as most times strong UV-radiation is used for the photodeposition of silver on zinc oxide [35, 36]. The presented method is a simple, fast, efficient, and low-cost way to Ag/ZnO nanoparticles.

Experimental

Synthesis

ZnO nanorods [37]

0.2 g Zn(CH$_3$COO)$_2$ · 2H$_2$O (Acros, 98%) was finely ground in an agate mortar. Then 1 mL (C$_4$mim)(Tf$_2$ N) (1-methyl-4-butylimidazolium bis(trifluoromethanesulfonyl) amide) and 0.1 g (2.5 mmol) fine sodium hydroxide powder (J.T. Baker, 98%) were added. The reaction mixture was irradiated with ultrasound (USC200T, VWR International) in a glass tube sealed with a screw cap for 12 h. The frequency and power applied were 45 KHz and 60 W, respectively, under ambient conditions. The product was separated by centrifugation, washed with ethanol and demineralized water twice, and finally dried at 90 °C for 2 h in vacuum.

Ag–ZnO composite particles

0.2 g of the previously prepared ZnO was added to 6 mL of ethylene glycol (J.T. Baker, 99%) containing 0.1 g AgNO$_3$ (Aldrich, 99%). The reaction mixture was stirred for 15 min under daylight. The precipitate was separated from solution by centrifugation at 2,000 rpm for 5 min. The product was washed with ethanol and distilled water twice, respectively, followed by drying in air at 90 °C for 12 h.

Characterization

The powder X-ray diffraction (XRD) pattern of the reaction products was collected on a Huber G670 diffractometer with MoK$_\alpha$ radiation ($\lambda = 0.07107$ nm).

The product morphology, particle size, chemical composition, and crystalline phases were studied with transmission electron microscopy (TEM). The TEM and energy dispersive X-ray spectra (EDS) were obtained on a Hitachi H-8100 TEM at 200 KV. The Ag/ZnO samples for TEM measurements were prepared by suspending the dried sample in ethanol and treating it in an ultrasonic bath for

15 min. A drop of this slurry was deposited on a carbon film supported on a copper grid.

The X-ray photoelectron spectra (XPS) were collected on a Liobold RH 63. Mg X-rays were used to excite photoelectrons from Zn 2p, O 1s and the Ag 3d core level. UV–Vis reflection spectra were recorded on a Cary 5000 (Varian) in an ethanolic suspension. Photoluminescence (PL) measurements were carried out on a Fluorolog 3 (Horiba Jobin Yvon) with a photomultiplier as the detection system using a Xe lamp with the excitation wavelength of 365 nm at room temperature.

Results and discussions

Figure 1 shows XRD pattern of the Ag/ZnO core shell particles. The powder diffractogram consists of the typical pattern belonging to the hexagonal wurzite structure of ZnO (JCPDS card no. 36-1451) and face-centered-cubic (fcc) structure of metallic Ag (JCPDS card no. 04-0783). The diffraction peaks are labeled with the respective Miller indices. Judging from the peak profile the sample is well crystallized. No other crystalline impurities are observed.

TEM images in Fig. 2 show the morphology of a typical Ag/ZnO sample. It can be seen that the synthesized ZnO forms nanorods, which are about 50–300 nm in length and 10–50 nm in width. The silver particles exhibit sphere-like morphology. The mean Ag particles size is ca. 5 nm, however, some of the particles can be as large as 20 nm. While the majority of the Ag nanoparticles are found at the surface of the ZnO nanorods, the TEM images show that a few free-standing Ag aggregates can be found.

Energy dispersive X-ray spectroscopy (EDS) analysis (Fig. 2, right), confirms that Ag–ZnO composite materials only consists silver, zinc, and oxygen. The presence of Cu
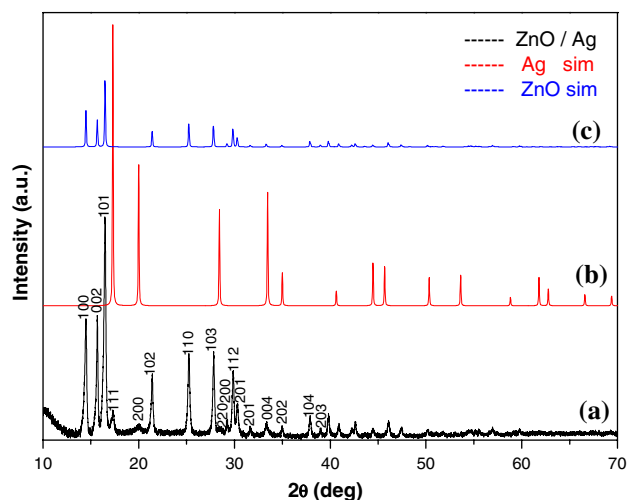

Fig. 1 a XRD pattern of the synthesized Ag/ZnO core–shell particles, **b** Ag and **c** ZnO patterns simulated from single-crystal data
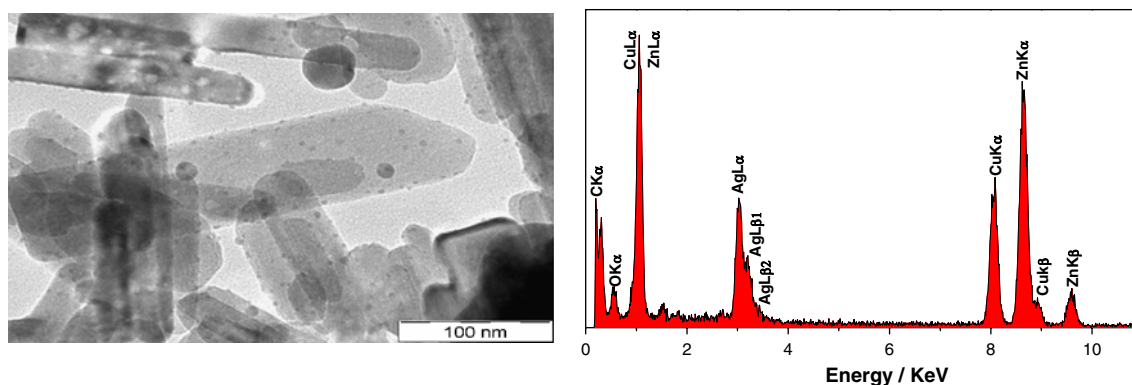
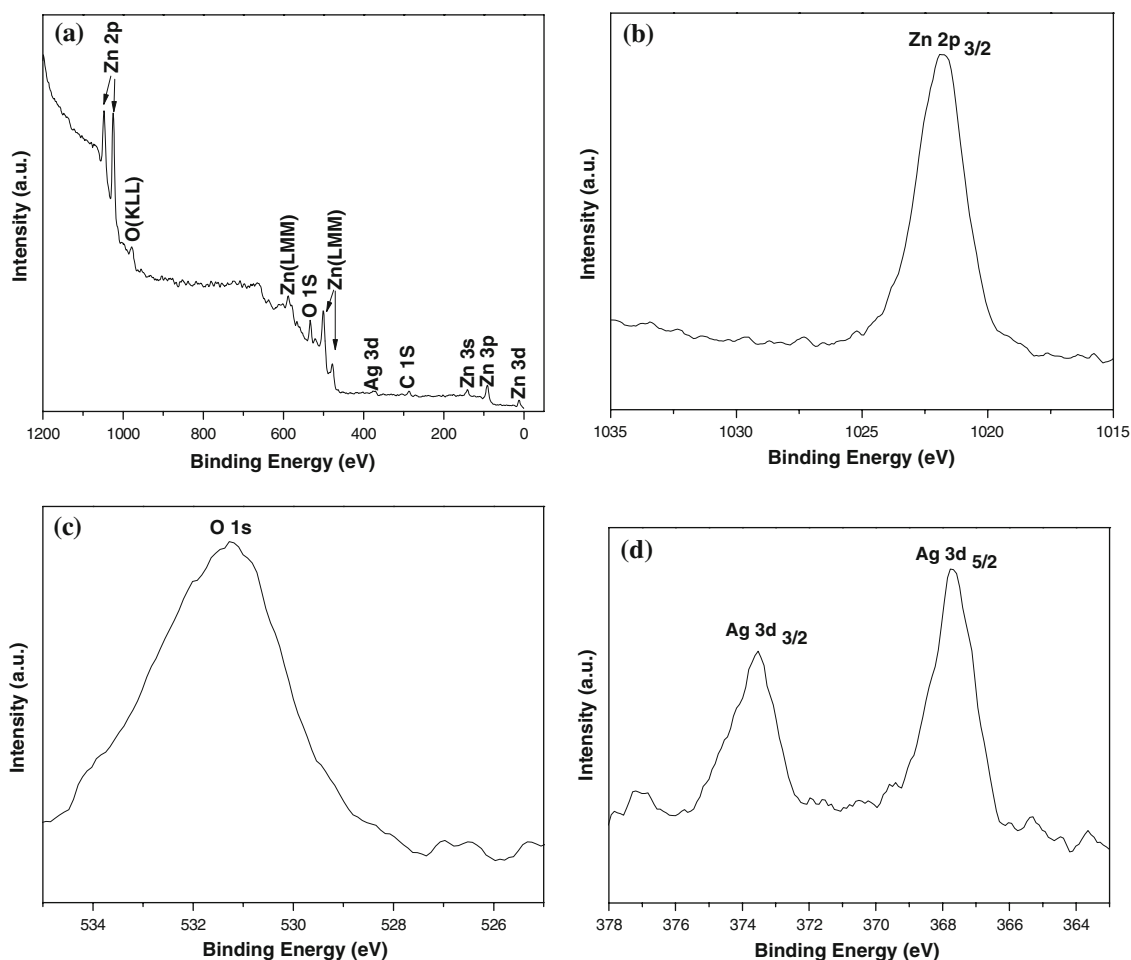**Fig. 2** TEM image (*left*) and EDS spectrum (*right*) of a typical sample of Ag/ZnO core–shell particles

Fig. 3 XPS spectra of the Ag/ZnO core–shell particles: **a** Full XPS spectrum of a typical sample; **b** Zn $2P_{3/2}$, **c** O 1s and **d** Ag $3d_{3/2}$ and Ag $3d_{5/2}$ spectral regions in detail

and carbon signals arises from the TEM gird. Apart from that no other element peaks could be detected.

These findings are backed by XPS measurements. The XPS spectrum (Fig. 3) indicates that the sample is composed of Ag, Zn, and O. A weak C emission peak is observed in the spectrum which results from sample holder. No obvious peaks for other elements or impurities can be observed. The binding energies in the XPS analysis are obtained by referencing the C1 s signal to 284.8 eV. The peaks observed at 373.5 eV and 367.7 eV (Fig. 3d)

correspond to the Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ states of metallic silver. As observed for other Ag–ZnO composites the binding energy of the Ag 3d states is shifted to lower values when compared to bulk Ag (374.2 vs. 368.2 eV [38]). This effect is often ascribed to the fact that Ag and ZnO adjust their Fermi level upon contact resulting in a partial oxidation of Ag [11]. The peak at 1,021.8 eV can be attributed to Zn2p$_{3/2}$ (Fig. 3b). The peak at 530.2 eV (Fig. 3c) is due to the O 1s level of lattice oxygen in ZnO.

The PL spectra of the samples measured at room temperature are shown in Fig. 4. The ZnO nanorods and the composite material, Ag/ZnO, display similar green light emission peaks centered at 560 nm, when the samples are excited at 365 nm. This emission can be attributed to structural defects. The defect states in a ZnO can be of several types, including: neutral, singly or doubly charged Zn vacancies (V_{Zn}^{x}, $V_{Zn}^{'}$, $V_{Zn}^{''}$), neutral or singly charged oxygen vacancies (V_{0}^{x}, V_{0}), singly charged or neutral interstitial Zn (Zn$_i$, Zn$_i^x$), or interstitial O (O$_i^{''}$). The green emission results from the recombination of a singly ionized oxygen vacancy with a photo generated hole, which relate to structural defects [39]. That no change of the emission

wavelength is observed when comparing the emission of the ZnO nanorods and the Ag–ZnO particles indicates that Ag coverage of the ZnO nanorods has no effect on the green emission and hence, the defect concentration of the material.

An absorption edge of 374 nm was found from the UV–Vis reflection spectrum of the as prepared ZnO nanorods. This corresponds to a band gap of 3.3 eV which compares well to the value found for bulk ZnO [40]. The resonance of silver nanoparticles has been found to strongly depend on the particle size as well as morphology [41, 42]. The maximum of the surface plasmon peak for Ag at ZnO in an ethanolic dispersion was found at 405 nm. To calculate the surface plasmon resonance peak for a given particle size the program "MiePlot v.4" was used [43]. Calculations are carried out according to the BHMIE algorithm anticipating a spherical particle shape [44]. The best fit between experimental and theoretical data was obtained for a mean particle size of 20 nm with standard deviation in size of 20%. Additional peaks may originate from interparticle dipole–dipole coupling (Fig. 5) [45–49].
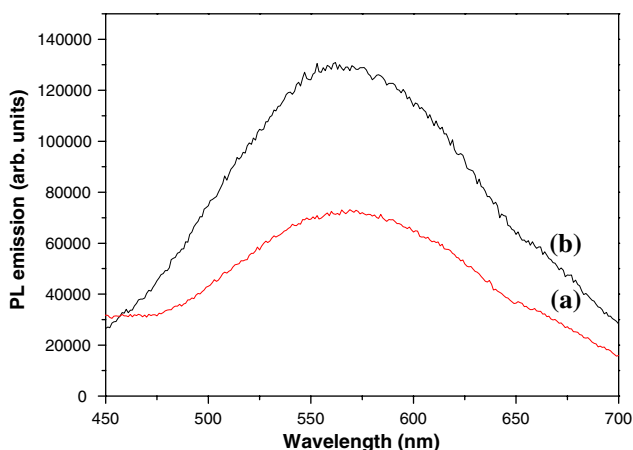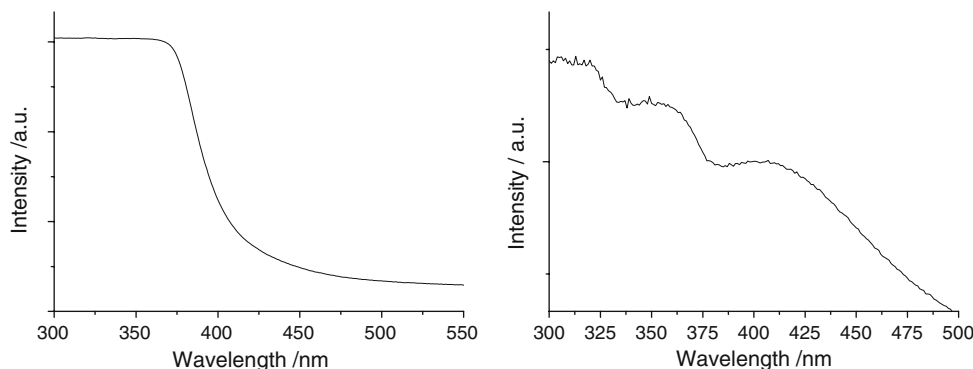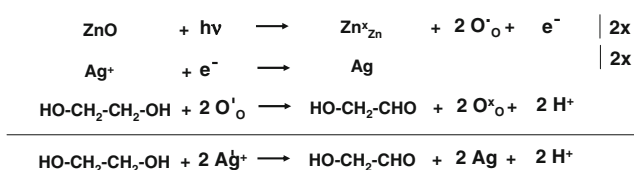

Fig. 4 Photoluminescence emission spectra of (a) Ag/ZnO; (b) ZnO. λ_{ex} = 365 nm

Mechanism of the Ag photoreduction

Silver is only deposited on the ZnO nanorods when the samples are exposed to direct daylight. Furthermore, when exposing a reaction mixture without ZnO nanorods to daylight no immediate formation of metallic silver was observed. Therefore, we think that ZnO serves as an electron source for the reduction of silver cations. Upon irradiation with sunlight electron holes are created in zinc oxide and the photoelectrons then reduce Ag$^+$. It is known that ZnO easily adsorbs Ag$^+$ cations at its surface. Once cationic silver clusters like Ag$_2^+$ are formed the reduction process is facilitated [36]. The photo-generated holes in ZnO are assumed to react with ethylene glycol and the corresponding aldehyde is formed. The reaction process can be summarized as follows: Scheme 1.

Fig. 5 Diffuse reflectance spectra of ZnO (*left*) and Ag/ZnO (*right*)

$$ZnO \quad + \; h\nu \quad \longrightarrow \quad Zn^x_{Zn} \quad + \; 2 \, O^{\cdot}_{O} + \; e^- \quad \Big| \; 2x$$

$$Ag^+ \quad + \; e^- \quad \longrightarrow \quad Ag \quad\qquad\qquad \Big| \; 2x$$

$$HO\text{-}CH_2\text{-}CH_2\text{-}OH + 2 \, O^{\cdot}_{O} \; \longrightarrow \; HO\text{-}CH_2\text{-}CHO \; + \; 2 \, O^x_{O} + \; 2 \, H^+$$

$$HO\text{-}CH_2\text{-}CH_2\text{-}OH + 2 \, Ag^+ \; \longrightarrow \; HO\text{-}CH_2\text{-}CHO \; + \; 2 \, Ag \; + \; 2 \, H^+$$

Scheme 1 Photochemical reduction of Ag^+ at ZnO

Conclusion

In summary we have successfully synthesized Ag/ZnO composite nanoparticles through a simple method at room temperature. It has been shown that daylight in combination with ZnO enables the reduction of Ag^+ with ethylene glycol. Without ethylene glycol added to the reaction mixture or when wrapping the container with aluminum foil a reduction of Ag^+ to the element could not be observed. The presented reaction protocol is a simple, fast, efficient, and low-cost way to a Ag/ZnO composite material.

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