ZnO Particles Encapsulated in Porous Cu_2O Nanoparticle Layer Prepared by UV Light-Induced Photoreduction of $Cu(NO_3)_2{\cdot}3H_2O$ over ZnO in Methanol Suspension

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Nano Cu_2O particles with size of about 7 nm were directly coated on the surface of ZnO seeds by UV light-induced photoreduction of $Cu(NO_3)_2{\cdot}3H_2O$, forming Cu_2O/ZnO nanocomposites with a core-shell structure.

Cuprous oxide is a p-type semiconductor with a direct band gap of 2.0 eV, which makes it a promising material for the conversion of solar energy.[1,2] The interesting optoelectronic properties of Cu_2O-related materials also show potential applications in solid-state photovoltaic cells and in thin-film oxygen pressure sensors.[3–5] So far, Cu_2O has mainly been synthesized by electrodeposition,[6–8] spray pyrolysis,[9] and conventional hydrolysis processes. Cu_2O/TiO_2 was also synthesized by electrodeposition method.[7] To the best of our knowledge, however, little attention has been paid to Cu_2O/ZnO composite, which is not only an attractive semiconductor composite, but also an important catalyst or catalyst precursor for versatile chemical reactions such as methanol synthesis.

Recently we developed a novel photocatalytic approach to obtain the Cu/ZnO nanomaterial based on the tailored metal–organic precursor $[Cu(OCH(Me)CH_2NMe_2)_2]$ in a nonaqueous system under mild conditions.[10] We also suggested that the concept may be useful for synthesis of other catalytically active metal/semiconductor nanocomposites such as the widely studied Ag/TiO_2,[11] Ni/TiO_2,[12] Pt/TiO_2,[11] etc. Interestingly, in our oxygen-free and moisture-free reaction system, the metal–organic precursor clearly decomposes to pure metallic copper. We never observed the formation of any copper oxides as likely side products, even by using other metal–organic and oxygen-containing Cu precursor such as $Cu(acac)_2$. We thus got interests to investigate the difference between a metal–organic nonaqueous and an inorganic aqueous precursor route. Here we describe the photocatalytic deposition of nano Cu_2O particles on ZnO nanoseed and the growth of a Cu_2O/ZnO core-shell structure using $Cu(NO_3)_2{\cdot}3H_2O$ in methanol solution.

In order to eliminate the effect of oxygen in air, the photoreduction experiments were conducted under Ar atmosphere according to our standard operation procedure as reported before.[10] Briefly, a Pyrex Schlenk tube with an built-in water cooling finger was used as a reactor. Typically, 1 g of nano ZnO (NanoTeK, USA, average particle size of 56 nm) was transferred into the reaction vessel and then heated in oil bath at 493 K for 3 h under vacuum (about 10^{-3} Torr). After being cooled down to room temperature, 75-mL solution of $Cu(NO_3)_2{\cdot}3H_2O$ in methanol (0.1N) was added under Ar. After stirring for 1 h, the reaction suspension was irradiated by UV light (125 W, $\lambda \geqslant 320$ nm) for 3 h. IR beam and short wavelength UV light were filtered off by circulating water and by the Pyrex Schlenk tube, respectively. After photoreaction, the yellowish powders were collected by filtration and dried under vacuum. Then, the samples were kept under Ar.

A comparison by XRD of as-prepared samples kept under Ar and sealed in a capillary with a sample exposed to ambient conditions overnight showed no difference. Thus, we characterized the series of samples without further precautions.

The synthesized Cu_2O/ZnO materials were characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer), transmission electron microscopy (TEM, Hitachi H-8100, 200 kV, LaB_6 filament), and energy dispersive X-ray spectroscopy (EDX, attached to the TEM). Figure 1 shows XRD patterns of the samples. Three typical reflections of Cu_2O at 2θ of 29.55, 36.42, and 42.30 were detected which in turn represent the (110), (111), and (200) faces of Cu_2O crystal. Though crystalline Cu_2O particles were produced, the structure of the nano ZnO (wurtzite) particles remained unchanged. TOPAS P 1.0 software was used to analyse the X-ray line broadening by using Scherrer formula. The characteristic XRD reflection of Cu_2O (111) at 36.42θ overlaps with the ZnO peak, and the reflection of Cu_2O (110) at 29.55 is too weak, thus Cu_2O (200) was selected for the analysis. The average size of the crystallite domains of the Cu_2O material is roughly calculated to be about 7 nm.

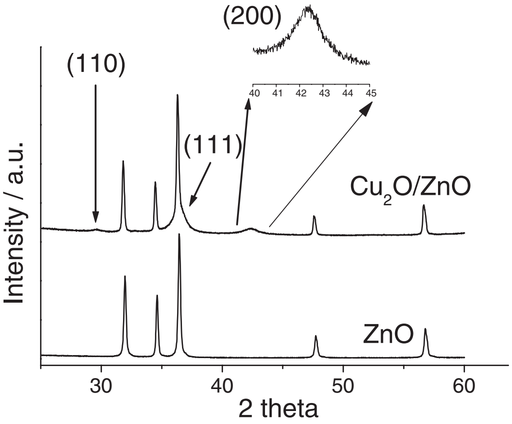

Figure 1. XRD spectra of pure nano ZnO and Cu_2O/ZnO prepared from photoreduction of $Cu(NO_3)_2{\cdot}3H_2O$ on nano ZnO in methanol suspension.

Figure 2 illustrates the TEM images of the pure nano ZnO starting sample and the Cu_2O/ZnO product sample. The TEM samples were prepared in air by suspending the powder in toluene in an ultrasonic bath, and dispersing a drop of the suspension on a carbon film supported by a gold grid. The TEM image of pure nano ZnO (Figure 2a) shows the anisotropic particle morphology. The hexagonal crystallites have different sizes and are generally smaller than 100 nm, which is in good agreement with the average value of 56 nm from XRD analysis. In contrast, as typically illustrated in image (Figure 2b), the Cu_2O/ZnO sample exhibits bigger spherical particles with sizes of about 100 to 180 nm, which is about twice or three times as big as the original size of nano ZnO particles. EDX analysis was then performed on this sample with an electron beam being focused on each of the two particles of the

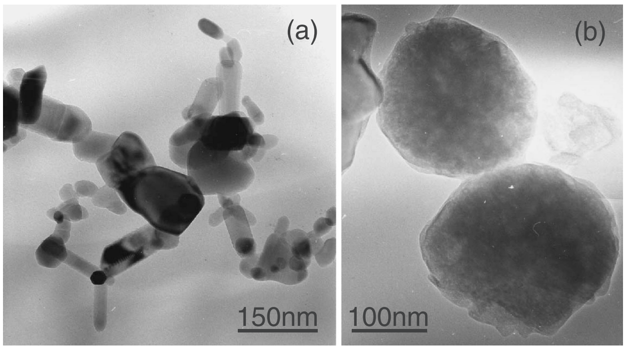

Figure 2. TEM images of (a) nano ZnO, (b) Cu_2O/ZnO sample prepared from photoreduction of $Cu(NO_3)_2 \cdot 3H_2O$ on ZnO in methanol suspension.

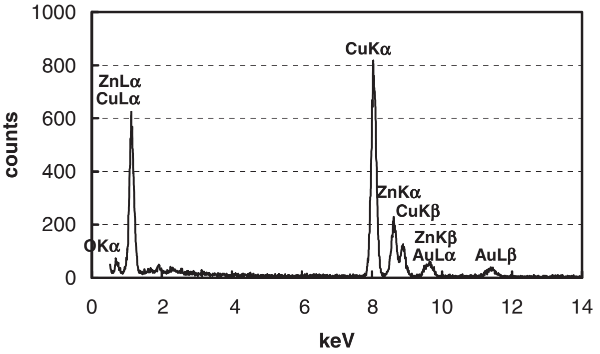

Figure 3. EDX spectrum of Cu_2O/ZnO sample prepared from photoreduction of $Cu(NO_3)_2 \cdot 3H_2O$ on ZnO in methanol suspension.

sample. Very similar EDX spectra were recorded and only the characteristic peaks of Cu, Zn, O, and Au (from the gold TEM grid) species were detected. A typical EDX spectrum is illustrated in Figure 3, which clearly shows the coexistence of Cu and Zn in the sample with a quite high amount of Cu.

According to our previous result, 0.5 wt % Cu on the same ZnO material will result in obvious pink color, and our sample contains about 30 wt % Cu in total analyzed by atomic absorption spectroscopy and shows the typical yellowish color of Cu_2O. It is reasonable to infer that the metallic Cu phase is negligible or in minority amount compared with Cu_2O in our sample, which agrees with the XRD results. Detailed XPS investigations are currently under going.

From these data, it can be concluded that some kinds of a core-shell type Cu_2O/ZnO nanocomposite are produced by this photoreduction technique. Most likely, the core of the particles contains ZnO, and Cu_2O has been deposited as an outside shell, giving rise to the large sphere morphology in the range of 100 to 180 nm in diameter. There may exist several small ZnO particles in one sphere particle, but we are unable to give any direct prove at present stage. The shell part is composed of a large amount of agglomerated nano Cu_2O particles with a size of about 7 nm, giving rise to a characteristic porous structure.

The photoreaction takes place in both aqueous and methanolic media, but with quite different reaction speed. Yellowish copper-containing material can also be slowly synthesized from aqueous solution under similar conditions. However, we could not find any XRD active particles, implying that Cu_xO species is amorphous. Methanol strongly speeds up the reaction and also improves the crystallinity of the Cu_2O particles as indicated by the XRD reflections. The coating amount of Cu_2O can be adjusted by changing the concentration of $Cu(NO_3)_2$ as well as the irradiation time. Since $Cu(NO_3)_2 \cdot 3H_2O$ is very soluble in methanol, the Cu content can be quite high.

Where does oxygen in Cu_2O species come from? Because dehydrated copper nitrate is almost insoluble in methanol, we can not make a strict comparison experiment under the same conditions. In the case of a very low concentration of anhydrous $Cu(NO_3)_2$ in 400-mL absolute methanol (copper amount not determined), we found the formation of Cu^0 rather than Cu_2O. We further use anhydrous $CuCl_2$ to replace $Cu(NO_3)_2 \cdot 3H_2O$ as the copper source, and the final product turned to be red and air sensitive material, which was proved by XRD to be metallic Cu particles on ZnO. This result suggests that the oxygen in Cu_2O is most likely from H_2O adsorbed on the surface of ZnO, which results in the formation of oxidative species during UV irradiation and then combines with copper produced in situ.

In summary, under strict nonaqueous, oxygen-free conditions, the photodeposition will lead selectively to Cu^0 deposition on ZnO while in the presence of water the photoreaction leads to the formation of Cu_2O. As the Cu_2O coating is becoming thicker, the whole process, initiated by the ZnO particle surface, seems to continue on the Cu_2O surface by a similar way as autocatalytic process. The photoexcited electrons and α-hydroxyl radicals from one-electron oxidation of methanol reduce the Cu^{2+}, and the positive holes are scavenged by methanol.

Cu_2O/ZnO is a multifunctional material as mentioned above, which can also be used to make Cu/ZnO. Conventional impregnation methods usually include three steps, impregnation of copper nitrate on ZnO, thermal decomposition, and chemical reduction. However, our discovery indicates an easy and short synthetic route without using any thermal decomposition steps. Moreover, our Cu_2O particles and the dimensions of the Cu_2O/ZnO core-shell composite are much smaller as compared with conventional techniques. We therefore suggest that our method may be suitable for further development of surface Cu_2O deposition processes in various fields of applications.

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