

A novel preparation of nano-Cu/ZnO by photo-reduction of $\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2$ on ZnO at room temperature

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Room-temperature preparation of nano-Cu on ZnO by UV light induced photo-reduction of $\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2$ precursor was achieved, indicating a novel method of nano-Cu/ZnO synthesis from an organometallic copper precursor in non-aqueous media without further chemical reduction.

Cu/ZnO is an important material widely used in catalytic hydrogenation and dehydrogenation of organic functional groups, as well as in solid fuel cells. Investigation on Cu/ZnO has been attracting world wide interest during the past decades.^{1–4} In order to obtain information on supported nano-Cu particles, we started the exploration of direct synthesis of Cu/ZnO nanocomposites under very mild conditions.

Various techniques have been used for the synthesis of ligand-capped or supported nanoparticles of metals and metal oxides, including microemulsions,⁵ sol-gel method,⁶ pulsed electrodeposition⁷ and photoreduction,^{8–10} etc. Recently, we reported the unique properties of $[\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$ as a metal-organic precursor for the thermally induced synthesis of monodispersed Cu nanocolloids in non-aqueous media.¹¹ Similar results were obtained for TiO_2 ¹² and recently for ZnO.¹³ The photo-reduction method has been so far mainly applied in several inorganic aqueous systems to produce metal colloids of Pt, Rh, Ag, etc. However, there is less study relating to non-aqueous photo-reduction systems, especially relating to the preparation of Cu/ZnO. Here we describe a novel method to form Cu/ZnO nanocomposites by using $[\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$ as the Cu source and taking advantage of the photocatalytic properties of ZnO.

The precursor $[\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$ was prepared according to the literature.¹⁴ Briefly, copper methanolate reacts with the corresponding aminoalcohol ligand in toluene in an alcohol exchange procedure at room temperature. After removing the solvent, the product was purified by sublimation at 343 K under vacuum. The photo-reduction experiments were conducted under Ar atmosphere for all steps in a Pyrex Schlenk tube with a built-in water cooling finger to keep the reaction at constant room temperature. Typically, 1 g of nano-ZnO (Nanotech, USA, average particle size of 56 nm) was transferred to a Schlenk and then heated in oil-bath at 493 K for 3 h under vacuum (about 10^{-3} Torr) to remove surface adsorbents and moisture. After being cooled to room temperature, a 50 ml solution of 1 mmol Cu precursor in absolute methanol was added to the Schlenk under Ar protection. After being stirred for 30 min for a better homogeneous adsorption of the precursor on the ZnO surface, the reaction suspension was irradiated by UV light (125 W) for 3 h. The UV lamp and all reaction systems were shielded by aluminium foil. IR radiation in the UV light was mostly filtered by passing through a water circulation tube while short wavelength UV light was cut off by the Pyrex Schlenk tube itself. In this photocatalytic experiment, metallic Cu was directly deposited on ZnO without further chemical reduction. At the end of the reaction, the white ZnO powder turned red, while the purple colour of the Cu precursor in methanol solution disappeared showing the complete conversion of the precursor. The mixture was filtered, and the residue was further dried at 300 K under vacuum for a few hours and then kept under Ar.

The structural characteristics of the synthesized Cu/ZnO materials have been studied by X-ray diffraction (XRD) analysis using a Bruker-AXS D8 Advance diffractometer with a rotating capillary sample holder. The morphology of the samples were studied using a Hitachi H-8100 transmission electron microscope (TEM) operating at accelerating voltages up to 200 kV with a single crystal LaB_6 filament. The chemical compositions of the samples were analysed by energy dispersive X-ray spectroscopy (EDX) on an EDX system attached to the TEM.

During preparation for XRD measurement, the very air-sensitive Cu samples were filled in a capillary tube (0.5 mm ID) in a dry box (Ar , $\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 1$ ppm). The grease pre-sealed capillary tube was further fused by a flame after being removed from the dry box to avoid oxidation of Cu during measurement. As indicated in Fig. 1, typical reflections of Cu at (111) and (200) were clearly detected, indicating formation of well crystalline metallic Cu particles, while the wurtzite structure of the nano-ZnO remained unchanged. By using the Scherrer formula to analyse the X-ray line broadening, the average crystallite size of the Cu is calculated to be 30 nm from Cu(111) and 22 nm from Cu(200).

Fig. 2 illustrates the TEM image of the Cu/ZnO sample prepared from photo-reduction of $[\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$ on nano-ZnO in methanol solution. The TEM sample was prepared in an Ar dry glove-box with a special O-ring sealed Ar protection sample holder. Cu/ZnO was dispersed in toluene and a drop of the suspension was then dispersed on a gold grid. The Ar protected sample was directly transferred into the TEM chamber and then evacuated for measurement. The TEM image shows that the sample particles are not uniform with a size distribution mainly in the range of 20–100 nm, which corresponds to that of nano-ZnO used in this study. EDX analysis was then performed on this sample with an electron beam being focused on several sections of the sample as shown

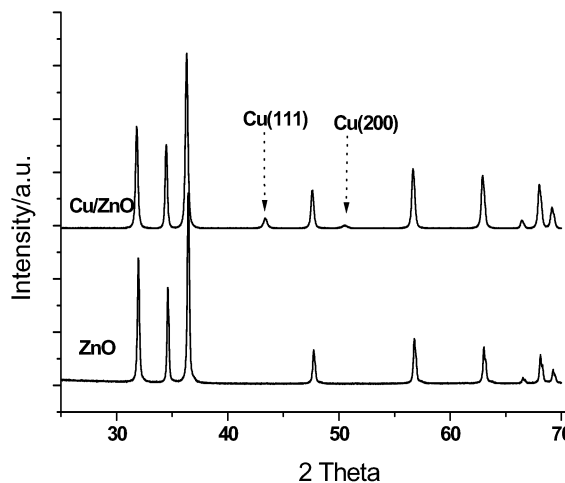


Fig. 1 XRD spectra of nano-ZnO and Cu/ZnO prepared from photo-reduction of $[\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$ on nano-ZnO in methanol solution.

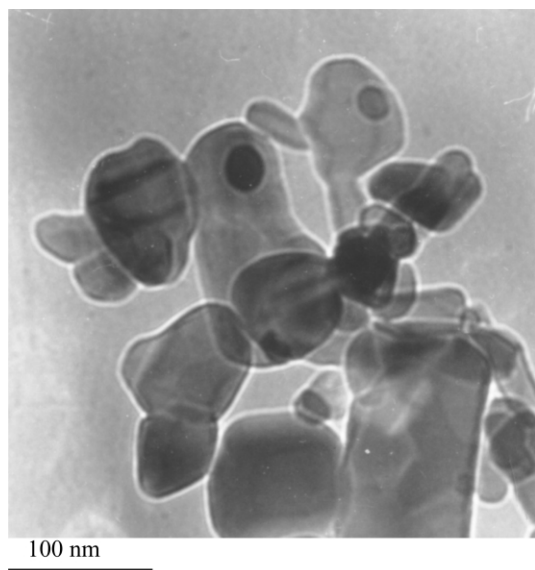


Fig. 2 TEM image of a Cu/ZnO sample prepared from photo-deposition of $[\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$ on ZnO in methanol solution.

in Fig. 2. Only the characteristic peaks of Cu, Zn and Au (from the gold TEM sample grid) species were detected. A typical EDX spectrum is illustrated in Fig. 3, which clearly shows the co-existence of Cu and Zn in the sample, indicating the formation of nano-Cu on the nano-ZnO surface though it is very difficult to distinguish the Cu particles from ZnO by our TEM study.

The synthesized metallic Cu particles are easily oxidized after being exposed to air. On oxidation the red sample turned gray with formation of Cu_xO species. The gray Cu_xO species were easily reduced back to the red nano-Cu species in methanol or ethanol upon irradiation with UV light for a few minutes. Neither CuO nor Cu_2O were directly detected by XRD in our study, indicating the possibility of formation of XRD inactive amorphous Cu_2O and CuO species.

ZnO is a typical n-type semiconductor with a band gap of about 3.2 eV, which absorbs impinging photons with energies

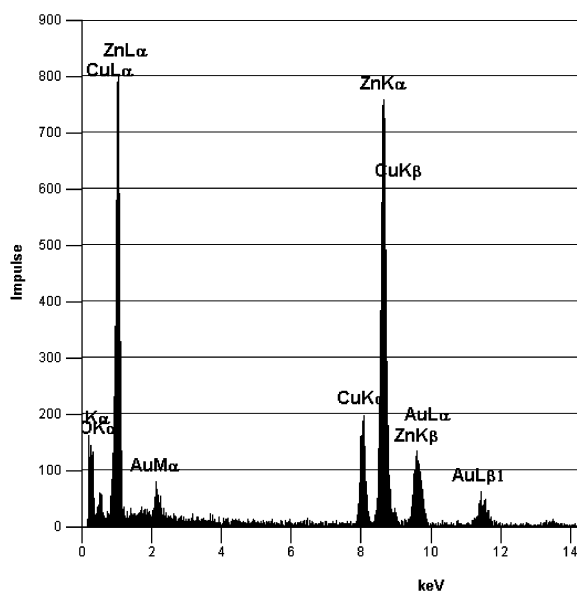


Fig. 3 EDX spectrum of a Cu/ZnO sample prepared from photo-deposition of $[\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$ on ZnO in methanol solution.

equal or higher than the band gap to form pairs of negative electrons and positive holes. The photo-excited electrons reduce the Cu^{2+} inside the precursor to the Cu^0 state, while the positive holes oxidize the solvent methanol, which consequently results in the completion of the reaction. Since reduction or oxidation of any substrate over a photo-excited semiconductor surface depends on the band gap and redox potential of related half-reactions, our concept may be applied for other soluble or volatile organometallic precursors with suitable redox potentials of half-reactions to produce corresponding nano-metal particles over a ZnO surface. In addition, TiO_2 (P-25, mixture of anatase and rutile) was also tested in our study by the same reaction conditions as those for nano-ZnO. Metallic Cu was formed as expected indicating a common mechanism for photo-induced reduction of organometallic precursors on suitable semiconductor surfaces in non-aqueous media. Methanol plays a very important role in the photo-reaction. One-electron oxidation of the solvent methanol can take place during the photoreaction to yield strongly reducing α -hydroxyl radicals which in turn can act as strong reductants for Cu(II) and then greatly speed up the reaction.

It is worthy to note that $[\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$ is a typical volatile precursor for chemical vapor deposition to deposit Cu films. Its structure may be molecularly tailored to meet the various demands of special utilizations. Since photo-reaction over semiconductor surfaces usually takes place by several steps including adsorption and surface reaction, it should be possible to fine-tune the final Cu/ZnO product by optimizing the pre-adsorption steps, by modifying the precursor properties, as well as by changing the reaction conditions, *e.g.* light intensity, temperature, concentration, reaction time, solvent, *etc.* Moreover, these liquid–solid phase reaction steps will be similar as those in the gas–solid phase by continually flowing the mixture of volatile precursor and methanol vapor. Our recent preliminary work on this gas–solid phase reaction also shows the formation of Cu on ZnO. The details of this reaction are still under investigation.

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Notes and references

- P. L. Hansen, J. B. Wagner, S. Helveg, J. R. Rostrup-Nielsen, B. S. Clausen and H. Topsøe, *Science*, 2002, **295**, 15.
- G. Meitzner and E. Iglesia, *Catal. Today*, 1999, **53**, 433.
- G. J. Millar, I. H. Holm, P. J. R. Uwins and J. Drennan, *J. Chem. Soc., Faraday Trans.*, 1998, **94**(4), 593.
- H. L. Castricum, H. Bakker, B. Linden and E. K. Poels, *J. Phys. Chem. B.*, 2001, **105**, 7928.
- K. T. Lim, H. S. Hwang, M. S. Lee, G. D. Lee, S.-S. Hong and K. P. Jonston, *Chem. Commun.*, 2002, 1528.
- Jeffery C. S. Wu, I-H Tseng and W.-C. Chang, *J. Nanoparticle Res.*, 2001, **3**, 113.
- H. Natter and R. Hempelmann, *J. Phys. Chem.*, 1996, **100**, 19525.
- S. Ikeda, K. Akamatsu and H. Nawafune, *J. Mater. Chem.*, 2001, **11**, 2919.
- A. Fukuoka, Y. Sakamoto, S. Guan, S. Inagaki, N. Sugimoto, Y. Fukushima, K. Hirahara, S. Iijima and M. Ichikawa, *J. Am. Chem. Soc.*, 2001, **123**, 3373.
- J.-M. Herrmann, J. Disdier and P. Pichat, *J. Catal.*, 1988, **113**, 7.
- J. Hambrock, R. Becker, A. Birkner, J. Weiss and R. A. Fischer, *Chem. Commun.*, 2002, 68.
- H. Parala, A. Devi, R. Bhakta and R. A. Fischer, *J. Mater. Chem.*, 2002, **12**, 1625.
- J. Hambrock, K. Merz, S. Rabe, A. Birkner, A. Wohlfart, R. A. Fischer and M. Driess, *J. Mater. Chem.*, Submitted.
- S. C. Goel, K. S. Kramer, M. Y. Chiang and W. E. Buhro, *Polyhedron*, 1990, **9**, 611.