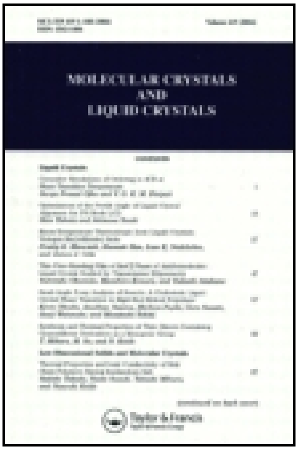

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Preparation and Characterization of Cu-SiO_2 Nanocomposite

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Preparation and Characterization of Cu–SiO_2 Nanocomposite

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Cu–SiO_2 nanocomposites have been studied to achieve hybrid structures at room temperature without an inert atmosphere. First, SiO_2 nanoparticles were synthesized by the sol-gel method. Second, SiO_2 nanoparticles deposited with copper (Cu–SiO_2) were prepared by the reaction of the SiO_2 nanoparticles and copper chloride at room temperature for 6 hrs with catalyst and without catalyst, respectively. Results showed that the SiO_2 nanoparticles with about 90 nm diameters were covered with Cu nanoparticles. The Cu–SiO_2 nanocomposites were investigated with TEM, energy dispersive X-ray spectroscopy analysis (EDS), and X-ray photoelectron spectroscopy (XPS).

Keywords: binding energy; Cu–SiO_2 nanocomposite; SiO_2 nanoparticle; Stöber method

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INTRODUCTION

Novel optical effects are expected by appropriately arranging metal particles on the surface of insulating cores of spherical shape, so as to compose, on a nanometer scale, core-shell or hybrid structures [1,2]. Optical resonance from near infrared to the visible range may be tuned by adjusting the core size, shell thickness and type of metal and core material [3,4]. Core-shell or hybrid structures have been intensively studied very recently, in particular since such structures exhibit peculiar properties which make them attractive for applications in optical and biological sensors and in optoelectronics [5,6]. In all coating methods, the monolayer cover is important, as the chemistry is specific to the shell. The monolayer route to oxide-shell materials is rather involved and required multistep process, and scale-up is difficult. To this purpose, oxide nanospheres of nearly equal size, offering great flexibility of composition, are well suited [7]. While on planar substrates a number of vacuum-based deposition methods may be utilized, including physical and chemical vapor deposition, laser ablation and cluster beam deposition, and also thin coating techniques, the situation is different with non-planar substrates because of their peculiar geometry. The aim of producing core-shell or hybrid structures requires one to achieve a high nucleation but low growth rate, so as to obtain a high number density of metal nanoparticles without the formation of aggregates. Cu–SiO_2 nanocomposites are synthesized by using well-known Stöber method at low temperature route for coating SiO_2 nanoparticle slurry with $CuCl_2$. The usefulness of copper as an antimicrobial agent has been known for a long time. It is an effective agent with low toxicity, which is especially important in the topical antibacterial treatment [8,9]. In this study, we report the characterization of well-dispersed Cu–SiO_2 nanocomposite, and an XPS study of Cu–SiO_2 nanocomposite including the prepared SiO_2 nanoparticles. The shape and morphology were investigated with TEM. The ratios of components were investigated with EDS.

EXPERIMENTALS

Silica nanoparicles were synthesized according to the well-known Stöber method by hydrolysis and condensation of tetraethoxysliane (TEOS, Aldrich Co., 98%, 0.5 mol) in a mixture of ethanol (1 L) with water (1 mol), using ammonia (1 mol) as catalyst to initiate the reaction. The size of silica nanoparticles is controlled by the molar ratio of TEOS, water and ammonia. The synthesis starts with mixing and stirring of the components, requires about 6 hrs reaction time.

TABLE 1 Experimental Details and EDS Analysis

	Reactant (mol)			Atomic%		
Materials	SiO$_2$	CuCl$_2$	NH$_3$	O	Si	Cu
Cu–SiO$_2$-1	0.167	0.075	–	65.97	31.56	2.48
Cu–SiO$_2$-2	0.167	0.150	–	64.64	31.87	3.49
Cu–SiO$_2$-3	0.167	0.300	–	59.71	31.44	8.85
Cu–SiO$_2$-4	0.167	0.075	0.026	65.89	23.21	10.90
Cu–SiO$_2$-5	0.167	0.150	0.053	59.87	26.71	13.61
Cu–SiO$_2$-6	0.167	0.300	0.105	54.25	29.73	16.02

The separated products were dried at temperature below 100°C for 2 hrs [10]. To synthesize Cu–SiO$_2$ nanocomposite, the specified amounts of copper chloride (CuCl$_2$, Aldrich Co., 97%) as Table 1 were added to SiO$_2$ nanoparticle slurry, which was prepared by 0.167 mol of SiO$_2$ nanoparticles dispersed in water. The products were filtered and purified by washing with ethanol, and then dried at room temperature for 2 hrs. Finally, Cu–SiO$_2$ nanocomposites were obtained. TEM examinations of the samples were carried out on a HITACHI H-7500 (low-resolution) and a JEOL JEM 2010 (high-resolution) TEM. TEM samples were prepared on the 400 mesh copper grid coated with carbon. EDS study of the sample was carried out on a Scanning Electron Microscope HITACHI S-2400. The chemical analysis on the elements was recorded on an XPS (MUTILAB 2000). The samples were compressed into a pellet of 2 mm thickness and then mounted on a sample holder by utilizing double-sided adhesive tape for XPS analysis. The sample holder was then placed into a fast entry air load-lock chamber without exposure to air and evacuated under vacuum ($< 10^{-6}$ Torr) overnight. Finally, the sample holder was transferred to the analysis chamber for XPS study. The base pressure inside the analysis chamber was usually maintained at better than 10^{-10} Torr. Binding energy was referenced to the C1s line at 284.6 eV from adventitious carbon.

RESULTS AND DISCUSSION

The influence of amount of copper chloride was shown in Figure 1. Figure 1 shows TEM images of Cu–SiO$_2$ nanocomposite. TEM image shows that Cu nanoparticles were deposited on the surface of SiO$_2$ nanoparticles. To optimize the fixing ratio of Cu nanoparticles on SiO$_2$, we controlled the ratio of CuCl$_2$. As the ratio of CuCl$_2$ was

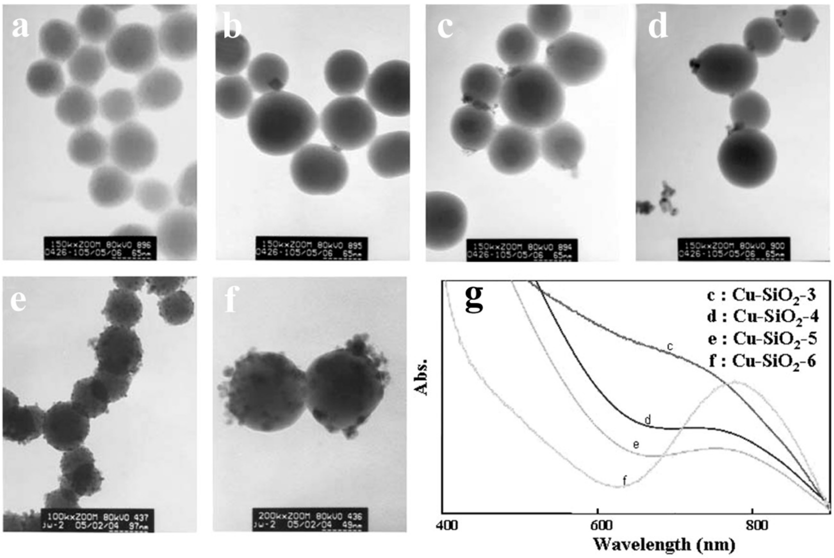


FIGURE 1 TEM images of Cu–SiO$_2$ nanocomposites. (a) Cu–SiO$_2$-1, (b) Cu–SiO$_2$-2 (c) Cu–SiO$_2$-3, (d) Cu–SiO$_2$-4, (e) Cu–SiO$_2$-5, and (f) Cu–SiO$_2$-6. (g) UV-vis spectra of Cu–SiO$_2$ nanocomposites.

increased, the size of Cu nanoparticles deposited on the surface of SiO$_2$ was increased. At low concentration of CuCl$_2$ (0.075 mol), the concentration of Cu nanoparticles deposited on the surface of SiO$_2$ nanoparticle was very low, but at high concentration of CuCl$_2$ (0.3 mol), Cu nanoparticles was clearly shown. In the presence of catalyst, Cu nanoparticles were more deposited on the surface of SiO$_2$ nanoparticles and the size of Cu nanoparticles was lager than that without catalyst in Figure 1. Despite low concentration of catalyst, Cu nanoparticles were easily deposited on the surface of SiO$_2$ nanoparticle compared to Cu nanoparticles prepared without catalyst. In high concentration of catalyst, Cu nanoparticles were easily deposited on the surface of SiO$_2$ nanoparticles. Alkaline condition produced strong nucleophiles via deprotonation of hydroxo ligands (Eq. 1) and then electrophilic material like metal reacted with nucleophilic part (Eq. 2) [11].

$$\mathrm{Si-OH + B^-(NH_3) \rightarrow SiO^- + BH} \tag{1}$$

$$\mathrm{2(SiO^-) + Cu^{2+} \rightarrow 2(SiO)Cu} \tag{2}$$

The Cu deposition process we employed is considered to be sensitive to the configuration of terminal groups on the SiO$_2$ surface, since such surface groups obviously provide the capability required for the reduction of Cu ions. Terminal OH groups usually form on the oxide surface by dissociative adsorption of water molecules, depending on their coordination symmetry. Accordingly, nanocomposite may form by auto-reduction of noble metal ions with oxide surfaces. The efficiency of the surface mediated reduction process can be decreased with consumption of hydroxyl groups and generation of surface charging. The schematic diagram for tentative mechanism of Cu deposition on the surface SiO_2 nanoparticle is illustrated in Figure 2.

UV-vis spectrum of Cu–SiO_2 nanocomposite was also shown in Figure 1g. UV-vis spectra of Cu–SiO_2 nanocomposite showed absorption band at 776 nm where as that of Cu nanoparticles prepared showed the $\lambda_{\max}$ at about 590 nm. This absorption band was rather broad and red-shifted compared with the plasmon absorption band of Cu nanoparticle. The position and shape of the plasmon absorption of copper nanoparticles were strongly dependent on the particle size, dielectric medium, and surface-adsorbed species. This was concerned with red-shifted absorption band of Cu–SiO_2 [12]. In low concentration of $CuCl_2$, there was only shoulder part in UV-vis spectrum, but in high concentration, a sharp is shown at 776 nm. As the concentration of $CuCl_2$ goes to high, the optical property is easily observed at about 800 nm because of typical optical property of Cu nanoparticles.

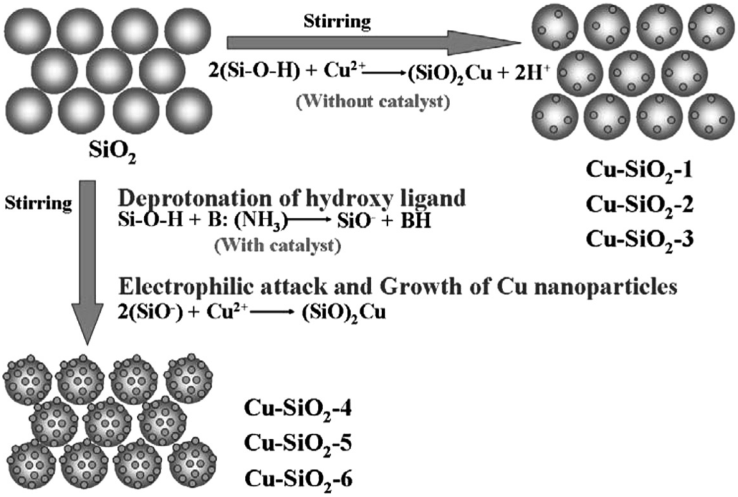
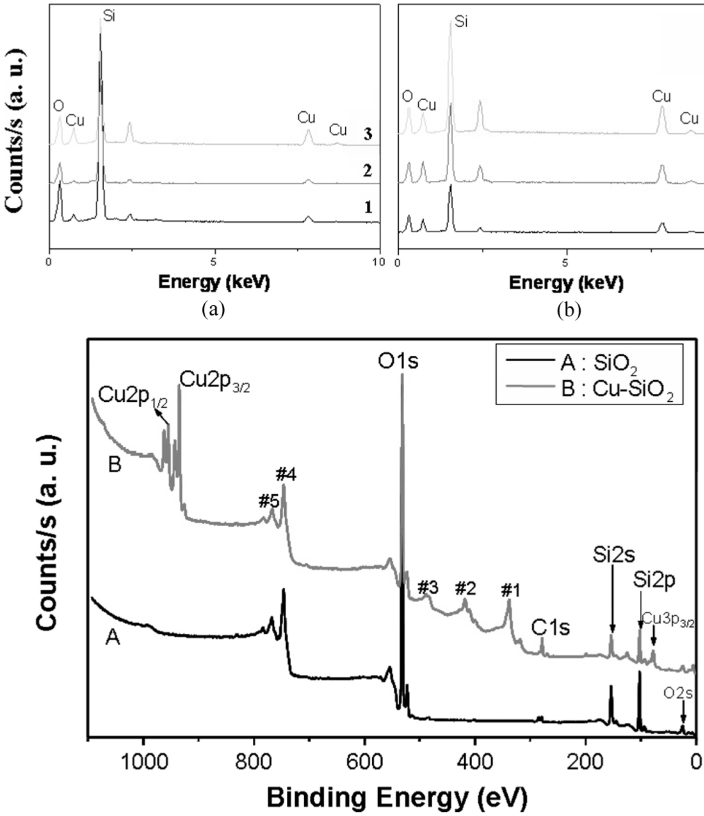


FIGURE 2 The tentative mechanism of Cu deposition on the surface of SiO_2 nanoparticle with and without catalyst.

We obtained remarkable EDS spectra of Cu nanoparticles. Figure 3a and b show the EDX spectra of Cu–SiO_2 nanocomposites excited by an electron beam (20 kV). Peaks for the elements of O, Si and Cu were observed at 0.5249 ($O_{k\alpha1}$), 1.73998 ($Si_{k\alpha1,2}$), 1.83594 ($Si_{k\beta1}$), 0.9297 ($Cu_{L\alpha1,2}$), 0.9498 ($Cu_{L\beta1}$), 8.04788 ($Cu_{k\alpha1,2}$) and 8.90529 ($Cu_{k\beta1}$), respectively. There is silica and copper atom in EDS spectra. Accordingly, from the EDX spectra we could confirm that the nanoparticles in TEM images are silica-copper hybrid nanoparticles. The atomic% of elements is shown in Table 1. The composition of Cu increases as



(a) (b)

(c)

FIGURE 3 EDS spectra of Cu–SiO_2 nanocomposites (a) without and (b) with catalyst. (1:Cu–SiO_2-1, 2:Cu–SiO_2-2, 3:Cu–SiO_2-3, 4:Cu–SiO_2-4, 5:Cu–SiO_2-5 and 6:Cu–SiO_2-6), and (c) XP spectra survey of SiO_2 and Cu–SiO_2 nanocomposites (#1:Cu L_3VV, #2:Cu $L_3M_{23}V$, #3:Cu $L_{23}M_{23}M_{23}$, #4:O $KL_{22}L_{23}$, and #5:O KL_1L_{23}).

increasing the CuCl$_2$ concentrations. The chemical states of elements in pure SiO$_2$ and Cu–SiO$_2$ nanocomposites are checked by XPS. Figure 3 c shows the representative survey XP spectra of pure SiO$_2$ and Cu deposited on the surface of SiO$_2$ nanoparticles. The resulting Si2p spectrum shows one peak at binding energy of 102.80 eV in agreement with accepted binding energy value for SiO$_2$. The peaks at about 933.10 and 953.10 eV are attributed to Cu2p$_{3/2}$ and Cu2p$_{1/2}$, respectively. The shake-up peak of Cu2p$_{3/2}$ is also observed at about 941.50 eV. Goodman et al. reported that the shake-up peak of Cu2p$_{3/2}$ was caused by the Cu^{2+} state, and the observed XP spectra of Cu are attributed to Cu^{+} and Cu^{2+} states by curve fitting parameters [13].

CONCLUSIONS

Silica coated with copper nanoparticles was prepared at room temperature. This method is well suited for preparing Cu metal nanoparticle coatings on the surface of silica nanoparticle to achieve particulate coatings. The amount of catalyst is superior to that of CuCl$_2$ because NH$_3$ produced strong nucleophiles via deprotonation of hydroxo ligands and then electrophilic material like metal reacted with nucleophilic part. In case of controlling amount of CuCl$_2$, Cu nanoparticles are not evenly deposited on the surface of SiO$_2$ nanoparticles, but in case of controlling amount of catalyst, Cu nanoparticles are evenly deposited on the surface of SiO$_2$ nanoparticles.

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