RI YU∗, JIYEON YUN∗, YOOJIN KIM∗,♯

SYNTHESIS AND CHARACTERIZATION OF SiO\textsubscript{2}, SnO\textsubscript{2} AND TiO\textsubscript{2} METAL OXIDE SHELLS COVERING Cu\textsubscript{2}O PARTICLES

In this work is described a means of improving the chemical stability of Cu\textsubscript{2}O@SiO\textsubscript{2}, Cu\textsubscript{2}O@SnO\textsubscript{2} and Cu\textsubscript{2}O@TiO\textsubscript{2} materials. The SiO\textsubscript{2}, SnO\textsubscript{2} and TiO\textsubscript{2} coated samples were stable from pH 3 to pH 10 for up to seven days. To determine the stability of the coated nanoparticles, and their colloidal solutions under acidic and basic conditions, colloidal nanoparticle solutions with various pH values were prepared and monitored over time. Details of the effect of variations in pH on the phase stability of core-shell type Cu\textsubscript{2}O were characterized using transmission electron microscopy and X-ray diffraction.

Keywords: Cu\textsubscript{2}O, metal oxide coating, pH value, SiO\textsubscript{2}, TiO\textsubscript{2}, SnO\textsubscript{2}

1. Introduction

Cuprous oxide (Cu\textsubscript{2}O) nanostructures are of considerable interest given their fundamental usefulness in many applications, including catalysis, pigment, and p-type semiconductor materials [1-2]. However, nano-sized Cu\textsubscript{2}O has an unstable oxidation state and low stability, which limits its use in certain applications. In general, Cu\textsubscript{2}O nanoparticles were transformed into CuO nanoparticles by treatment in a basic high pH solution: copper ions (Cu\textsuperscript{2+}) turned into Cu(OH)\textsubscript{2}\textsuperscript{−} in NaOH solution. The Cu(OH)\textsubscript{2}\textsuperscript{−} ions were then transformed into Cu\textsubscript{2}O particles by addition of an acid solution as oxidation catalyst [3-4]. To prevent oxidation and aggregation of the Cu\textsubscript{2}O particles, core-shell structures incorporation layers of inorganic materials were required. Silica (SiO\textsubscript{2}), like tin (IV) oxide (SnO\textsubscript{2}), is a suitable material for use as an optical coating due to its transparency in the visible range [5]. Silicon dioxide (SiO\textsubscript{2}), is an excellent inorganic modifier and has been widely investigated for its exceptional applications in the synthesis of nanostructures [6-7]. SiO\textsubscript{2} shells can significantly modify the qualities of the core materials due to physical properties that include such as optical capabilities, biocompatibility and environmental stability [6]. Another raw material, titanium oxide (TiO\textsubscript{2}), is a common choice for use as a photocatalyst due not only to its photocatalytic attributes, but also to its low cost [8-9]. Previously, great effort had been directed toward synthesis of core@TiO\textsubscript{2} structures [8]. For example, Caruso and co-workers introduced a layer-by-layer self-assembly strategy for coating TiO\textsubscript{2}, which was realized by surface electrostatic interactions [9]. In this work is described a means of improving the chemical stability of Cu\textsubscript{2}O@SiO\textsubscript{2}, Cu\textsubscript{2}O@SnO\textsubscript{2} and Cu\textsubscript{2}O@TiO\textsubscript{2} materials. SiO\textsubscript{2}, SnO\textsubscript{2} and TiO\textsubscript{2} coated samples were stable from pH 3 to pH 10 for up to 7 days. To determine the stability of the coated nanoparticles, and their colloidal solutions under acidic and basic conditions, colloidal nanoparticle solutions with various pH values were prepared and monitored over time.

2. Experimental procedure

2.1. Raw materials

The starting materials, copper (II) chloride dehydrate (CuCl\textsubscript{2}·2H\textsubscript{2}O, 99.99%), sodium hydroxide (NaOH,
2.2. Synthesis of Cu$_2$O nanoparticles

The experimental procedure is a modification of that in the literature.[10] CuCl$_2$·2H$_2$O (0.085 g) was dissolved in deionized water (50 mL). PVP (1.66 g) was dissolved in the mixture solution. Then 0.5 mL of NaOH aqueous solution (0.2 M) was dropped into the mixture solution heated to 60°C. After rapid stirring for 30 min, L-ascorbic acid solution (5 mL, 0.6 M) was introduced in the CuCl$_2$ solution. The color of the solution immediately changed from light green to yellow. The mixed solution was stirred again for 3 h at 55°C. After the reaction, the precipitates were collected by centrifugation.

2.3. Synthesis of the Cu$_2$O@SiO$_2$ particles

Silica-coated Cu$_2$O nanoparticles were synthesized by following a modified literature method.[3, 11] Cu$_2$O (12 mg) nanoparticles were re-dispersed in a mixed solution of ethanol (9 mL) and DI water (12 mL) by ultrasonication for 5 min. CTAB (15 mg) was added in the mixture solution. When higher concentration of NH$_4$OH solution was used, the color of the solution more rapidly turned from sky blue to yellow. In order to slow the hydrolysis reaction, we made diluted NH$_4$OH (purchased at 28% from Aldrich) using DI water. A 14% (diluted) NH$_4$OH solution was prepared by mixing 0.5 mL NH$_4$OH and 0.5 mL DI water. The aqueous NH$_4$OH solution (0.28% ammonia) was diluted with five times its volume with water to make a diluted NH$_4$OH solution (2.8% ammonia). When the higher concentration of NH$_4$OH solution was used, the color of the solution more rapidly turned form sky blue to yellow. The NH$_4$OH solution at concentrations of 2.8, 14 and 28% resulted in the same reaction time. Diluted NH$_4$OH solution (50 μL) was added to the mixed solution and then stirred for 15 min. TEOS (30 μL) was then introduced into the mixed solution. The silica-coated Cu$_2$O particles obtained after 4 h were collected by means of centrifugation and dried in a vacuum at room temperature.

2.4. Synthesis of the Cu$_2$O@SnO$_2$ particles

The SnO$_2$-coated Cu$_2$O nanoparticles were synthesized by a modification of a method from the literature.[5] The Cu$_2$O (0.2 g) nanoparticles were re-dispersed in 100 mL of DI water by ultrasonication for 5 min. A 1.0 mL aliquot of an aqueous solution of Na$_2$SnO$_3$·3H$_2$O (10 mmol) was added in the Cu$_2$O nanoparticle solution. The reaction was continued for 24 h at 80°C. A dark red solution was obtained immediately. The solution was cooled to room temperature and centrifuged (8,000 rpm for 10 min). The resulting precipitate was collected and dried in a vacuum at room temperature.

2.5. Synthesis of the Cu$_2$O@TiO$_2$ particles

The uniform porous TiO$_2$ shells of the core-shell structures were prepared via the sol-gel method [9]. The Cu$_2$O (75 mg) nanoparticles were dispersed in absolute ethanol (100 mL), and mixed with concentrated NH$_4$OH solution (0.3 mL, 1.4 wt%) with stirring for 15 min. Afterward, 0.7 mL of TBOT (titanium butoxide) was added drop-wise over 5 min, and the reaction was allowed to proceed for 24 h at 45°C with under continuous mechanical stirring. The resultant products were separated and collected, followed by washing three times each with deionized water and ethanol. Then, the obtained powders were dried overnight at 50°C.

2.6. Characterization

The prepared samples were characterized by X-ray diffraction (XRD, Rigaku D/max 2500v/pc). The morphologies of the samples were examined using a scanning electron microscope (SEM, JEOL-6710F) and a transmission electron microscope (TEM, TEM-2010, JEOL, Kyoto, Japan) with an acceleration voltage of 200 kV.

3. 3. Results and discussion

![Fig. 2. Schematic illustration described the SiO$_2$ coating experimental process](image-url)

The octahedral Cu$_2$O particles were coated with silica, producing Cu$_2$O@SiO$_2$ core-shell particles (Fig. 2) via the sol-gel coating process in a basic aqueous solution. Silica coating on Cu$_2$O surfaces has rarely been synthesized, because Cu$_2$O was etched out in the aqueous NH$_4$OH solution use to provide the conventional silica coating. The selective etching of the Cu$_2$O core in a dilute NH$_4$OH solution started to generate empty space in the core, and further etching produced Cu$_2$O@SiO$_2$ yolk-shell particles and finally led to hollow SiO$_2$ particles. Thus, the cuprous oxide (Cu$_2$O) particles were used as templates to produce the hollow silica particles.
A one-pot process for synthesis of Cu$_2$O particles to hollow silica particles was made possible simply by adjusting the concentration of ammonia in the reaction batch. The etched Cu$_2$O exists in the form of Cu(NH$_3$)$_2^{2+}$. The etched solution was recycled to produce Cu$_2$O particles again, making the process environment-friendly.

Fig. 3. (a) SEM image of prepared Cu$_2$O particles and (b) XRD data of Cu$_2$O particles

Fig. 3 shows an SEM image and XRD data of the Cu$_2$O particles. The average size of the Cu$_2$O particles was \(~300\pm45\) nm. The XRD patterns in Fig. 3b shows that the Cu$_2$O particles have octahedron structures and that the XRD peaks were correctly indexed to the face-centered-cubic (FCC) crystal structure (JCPDS No. 78-2076). Fig. 4 shows TEM images of various metal-oxide coated Cu$_2$O particles. The TEM images showed SiO$_2$, SnO$_2$ and TiO$_2$-coated Cu$_2$O NPs having a SiO$_2$ layer 10 nm thick, of which the Cu$_2$O particle was covered by a layer of small (~2-3 nm) SnO$_2$ particles. (see Fig. 4a and 4b) The silica coating was successfully prepared by reducing the NH$_4$OH concentration. After coating with the silica layer, the average particle size increased to \(~240\pm70\) nm. (Fig. 4a) Because the etching of Cu$_2$O and the coating of silica is competitive in this process, fast coating of silica in the early stage and high pH of the reaction medium (pH = 12.8) are the keys to stable production of core-shell particles. Therefore, we used the 5 times diluted NH$_4$OH solution (5.6%) as a catalyst for silica coating. In the case of the TiO$_2$ layer, the Cu$_2$O particles were modified by APTES but the TiO$_2$ shell thickness could not be confirmed. On the other hand, the TiO$_2$ coating was irregular on the surface of Cu$_2$O particles when carried out without surface modification. However, even without modification, TiO$_2$-coated Cu$_2$O particles were synthesized by adjusting the concentration and amount of NH$_4$OH. See Fig. 5 for the details of the effect of NH$_4$OH concentration on the Cu$_2$O core during the TiO$_2$ coating process. TEM images of TiO$_2$-coated Cu$_2$O particles extracted in 28% and 1.4% NH$_4$OH solution, respectively, after reaction times of 4h.(Fig. 5) The TiO$_2$ surface is not flat at the higher NH$_4$OH concentration (28%) because the hydrolysis reaction between TBOT and NH$_4$OH is too fast. (Fig. 5a) When the concentration was lowered to 1.4%, TiO$_2$ coated the surface of the Cu$_2$O particles, but Fig. 5b reveals that some isolated TiO$_2$ particles also formed in the coating solution. In response, the amount of 1.4% NH$_4$OH solution was reduced to 20 vol%. As a result, a TiO$_2$ shell was successfully coated onto the Cu$_2$O surface.

Fig. 4. TEM images of (a) SiO$_2$-coated Cu$_2$O particles, (b) SnO$_2$-coated Cu$_2$O particles and (c) TiO$_2$-coated Cu$_2$O particles

Fig. 5. TEM images of TiO$_2$-coated Cu$_2$O particles by adjusting concentration and amount of NH$_4$OH. (a) 28% NH$_4$OH (0.3mL), (b) 1.4% diluted NH$_4$OH (0.3mL), (c) 1.4% diluted NH$_4$OH (0.03mL)
The Cu$_2$O etched away in the NH$_4$OH solution is expected to form Cu(OH)$_2$ according to following equation [4].

$$\text{Cu}_2\text{O} + \text{NH}_4\text{OH} \rightarrow 2[\text{Cu(NH}_3\text{)}_2]^2+ + 4\text{OH}^-$$  \hspace{1cm} (1)

$$(\text{Cu(NH}_3)_2)^2+ + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2 + 4\text{NH}_3$$  \hspace{1cm} (2)

$$\text{Cu(OH)}_2 + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2^2-$$  \hspace{1cm} (3)

The amount of NH$_4$OH is an important factor in the formation of the SiO$_2$ and TiO$_2$ shells. To cover Cu$_2$O particles with covering such as TiO$_2$ and SiO$_2$, it is necessary to make use of diluted NH$_4$OH solution.

In Fig. 6, EDS confirmed the formation of TiO$_2$-coated Cu$_2$O particles. Fig. 6 suggests the existence of Cu (yellow), O (red) and Ti (orange) elements in the Cu$_2$O@TiO$_2$ point section. The EDS results for O and Ti confirm the formation of TiO$_2$ layers, as indicated by the TEM photograph in Fig. 6.

The Cu$_2$O crystals can be etched in acids so that only nanoparticle-aggregated spheres and octahedra were grown at pH greater than 7 and less than 12. Maintaining a steady pH in the solution during the whole reaction process favors the Ostwald ripening of nanoparticle aggregations, thus forming truncated octahedra with smooth surfaces [13].

$$\text{Cu}^+ + e^- \rightarrow \text{Cu} \hspace{1cm} E^0 = 0.521\text{V}$$

$$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \hspace{1cm} E^0 = 0.342\text{V}$$

$$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \hspace{1cm} E^0 = 0.153\text{V}$$

Under alkaline conditions, the formation of Cu$_2$O is preferred due to the larger reducing potential of Cu(OH)$_2$/Cu compared to Cu(OH)$_2$/Cu (Reactions 9-11). The Cu$_2$O in HCl and NaOH solution is expected to form CuCl$_2$ and Cu(OH)$_2$ in accordance with the following reaction [12].

$$\text{Cu}_2\text{O} + \text{HCl} \rightarrow \text{CuCl}_2 + \text{H}_2\text{O(Blue)}$$  \hspace{1cm} (4)

$$\text{Cu}_2\text{O} + \text{NaOH} \rightarrow \text{Cu(OH)}_2(\text{DeepBlue}/\text{Heat} - \text{Black}, \text{Brown})$$  \hspace{1cm} (5)

$$\text{Cu(OH)}_2 + \text{NaOH} \rightarrow \text{CuO(Black)}$$  \hspace{1cm} (6)

$$\text{Cu}_2\text{O} + \text{NH}_4\text{OH} + \text{Ti(O(CH}_2)_3\text{CH}_3\text{)}_4 \rightarrow \text{Cu(OH)}_2(\text{green}) + \text{Cu}_2\text{O@TiO}_2(\text{red} - \text{pink})$$  \hspace{1cm} (7)

$$(\text{DeepBlue})$$

Fig. 7 shows the XRD pattern of Cu$_2$O and various metal oxide-coated Cu$_2$O at acidic condition: (a) pH 3 values, (b) pH 5 values.

Fig. 8 shows the XRD pattern of Cu$_2$O and various metal oxide-coated Cu$_2$O under acidic conditions. Some Cu$_2$O particles transformed into CuCl$_2$ at pH 5.
confirmed that metal oxide-coated Cu$_2$O nanoparticles were not changed at pH 5. All Cu$_2$O nanoparticles with metal oxide coating were not changed at pH 5. Non-coated Cu$_2$O samples formed CuCl$_2$ at pH 5. Finally, all samples were changed to CuCl$_2$ at pH 3. (Fig. 8a)

Fig. 9. CIE Lab values of (a) Cu$_2$O, (b) SiO$_2$-coated Cu$_2$O, (c) SnO$_2$-coated Cu$_2$O and (d) TiO$_2$-coated Cu$_2$O

The color of the Cu$_2$O particles and core-shell structure was assessed on the grounds of $L^*$, $a^*$ and $b^*$ parameters, calculated from diffuse reflectance spectra, using the method recommended by the Commission Internationale de l’Eclairage (CIE). In this method the parameter $L^*$ represents the brightness of the sample; a positive $a^*$ value represents red, a negative value indicates green. It is said that red pigments show a higher red color tone with increasing $a^*$. Fig. 9 shows the CIE $L^*a^*b^*$ values of the non-coated Cu$_2$O particles and metal oxide-coated Cu$_2$O particles. The CIE $L^*a^*b^*$ colorimetric parameters for Cu$_2$O after ceramic coating with SiO$_2$, SnO$_2$ or TiO$_2$ are also given in Fig. 9. For another important red pigment (Fe$_2$O$_3$), the $a^*$ value was 23 but Cu$_2$O red pigment produced a relatively low $a^*$ value. However, the SiO$_2$-coated Cu$_2$O, in particular, exhibits an increased $a^*$ value indicating an increase in Cu$_2$O@SiO$_2$($\bigsquare$). On the other hand, there was a small decrease in $a^*$ values of the SnO$_2$($\triangle$) and TiO$_2$(×)-coated samples.

4. Conclusions

In summary, we have successfully synthesized metal oxide-coated Cu$_2$O particles with SiO$_2$, SnO$_2$ and TiO$_2$. The preparation of Cu$_2$O@SiO$_2$ particles via the well-known sol-gel process was performed for the first time by controlling the hydrolysis reaction using different reaction times and concentrations of NH$_4$OH solution. The pH stability of SiO$_2$ and SnO$_2$-coated Cu$_2$O particles in solution was similar to that of TiO$_2$-coated Cu$_2$O particles in acidic solution. Our studies found that the SiO$_2$ and SnO$_2$-coated Cu$_2$O particles in solution were more stable at pH 5 than at pH 3. On the other hand, TiO$_2$-coated Cu$_2$O particles in solution changed to a green color at all pH values.

Acknowledgements

This work was supported by Innovation Development Program, funded by the Small and Medium Business Administration (SMBA, Korea).

REFERENCES


Received: 20 November 2014.