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SYNTHESIS AND CHARACTERIZATION OF SiO₂, SnO₂ AND TiO₂ METAL OXIDE SHELLS COVERING Cu₂O PARTICLES

SYNTEZA I CHARAKTERYSTYKA POWŁOK TLENKOWYCH SiO₂, SnO₂ I TiO₂ POKRYWAJĄCYCH CZĄSTKI Cu₂O

In this work is described a means of improving the chemical stability of Cu₂O@SiO₂, Cu₂O@SnO₂ and Cu₂O@TiO₂ materials. The SiO₂, SnO₂ and TiO₂ 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 Cu₂O were characterized using transmission electron microscopy and X-ray diffraction.

Keywords: Cu₂O, metal oxide coating, pH value, SiO₂, TiO₂, SnO₂

1. Introduction

Cuprous oxide (Cu₂O) 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 Cu₂O has an unstable oxidation state and low stability, which limits its use in certain applications. In general, Cu₂O nanoparticles were transformed into CuO nanoparticles by treatment in a basic high pH solution: copper ions (Cu²⁺) turned into Cu(OH)₂²⁻ in NaOH solution. The Cu(OH)₂²⁻ ions were then transformed into Cu₂O particles by addition of an acid solution as oxidation catalyst [3-4]. To prevent oxidation and aggregation of the Cu₂O particles, core-shell structures incorporation layers of inorganic materials were required. Silica (SiO₂), like tin (IV) oxide (SnO₂), is a suitable material for use as an optical coating due to its transparency in the visible range [5]. Silicon dioxide (SiO₂), is an excellent inorganic modifier and has been widely investigated for its exceptional applications in the synthesis of nanostructures [6-7]. SiO₂ 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 (TiO₂), 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@TiO₂ structures [8]. For example, Caruso and co-workers introduced a layer-by-layer self-assembly strategy for coating TiO₂, which was realized by surface electrostatic interactions [9]. In this work is described a means of improving the chemical stability of Cu₂O@SiO₂, Cu₂O@SnO₂ and Cu₂O@TiO₂ materials. SiO₂, SnO₂ and TiO₂ 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

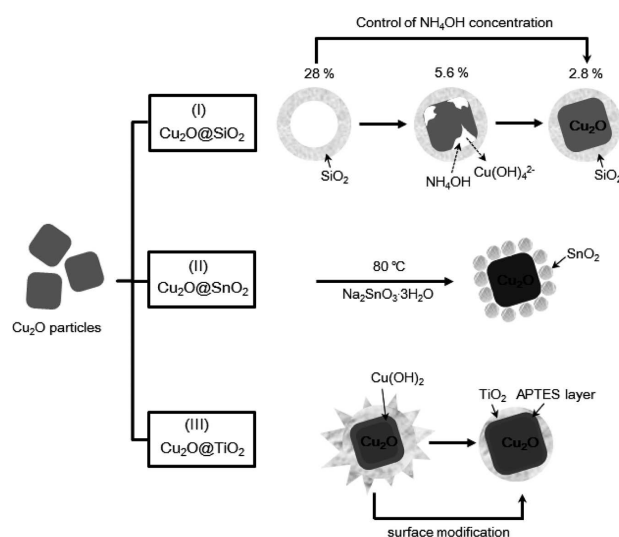


Fig. 1. Schematic illustration described the experimental process of metal oxide coating

2.1. Raw materials

The starting materials, copper (II) chloride dehydrate (CuCl₂·2H₂O, 99.99%), sodium hydroxide (NaOH,

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>98%), PVP ($M_w=40,000$), *L*-ascorbic acid, tetraethylorthosilicate (TEOS, 99.999%), ammonium hydroxide solution (NH_4OH , 28% solution in water, 99.99%), cetyltrimethyl ammonium bromide (CTAB, 99%), sodium stannate trihydrate ($\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, 95%) and titanium(IV) butoxide ($\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$, TBOT, 97%) were purchased from Aldrich. All the materials were used as received without further purification.

2.2. Synthesis of Cu_2O nanoparticles

The experimental procedure is a modification of that in the literature.[10] $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.085 g) was dissolved in deionized water (50 mL). PVP (1.66 g) was dissolved in CuCl_2 aqueous solution. Then 0.5 mL of NaOH aqueous solution (0.2 M) was dropped into CuCl_2 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 $\text{Cu}_2\text{O}@\text{SiO}_2$ particles

Silica-coated Cu_2O nanoparticles were synthesized by following a modified literature method. [3,11] Cu_2O (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_4OH 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_4OH (purchased at 28% from Aldrich) using D.I. water. A 14% (diluted) NH_4OH solution was prepared by mixing 0.5 mL NH_4OH and 0.5 mL D.I. water. In the same way, to make 2.8% diluted NH_4OH solution, prepared NH_4OH (0.1 mL) and D.I. water (0.9 mL). The aqueous NH_4OH solution (28% ammonia) was diluted with five times its volume with water to make a diluted NH_4OH solution (2.8% ammonia). When the higher concentration of NH_4OH solution was used, the color of the solution more rapidly turned from sky blue to yellow. The NH_4OH solution at concentrations of 2.8, 14 and 28% resulted in the same reaction time. Diluted NH_4OH 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_2O particles obtained after 4 h were collected by means of centrifugation and dried in a vacuum at room temperature.

2.4. Synthesis of the $\text{Cu}_2\text{O}@\text{SnO}_2$ particles

The SnO_2 -coated Cu_2O nanoparticles were synthesized by a modification of a method from the literature.[5] The Cu_2O (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 $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ (10 mmol) was added in the Cu_2O nanoparticle solution. The reaction was continued for 24h 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 $\text{Cu}_2\text{O}@\text{TiO}_2$ particles

The uniform porous TiO_2 shells of the core-shell structures were prepared via the sol-gel method [9]. The Cu_2O (75 mg) nanoparticles were dispersed in absolute ethanol (100 mL), and mixed with concentrated NH_4OH 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

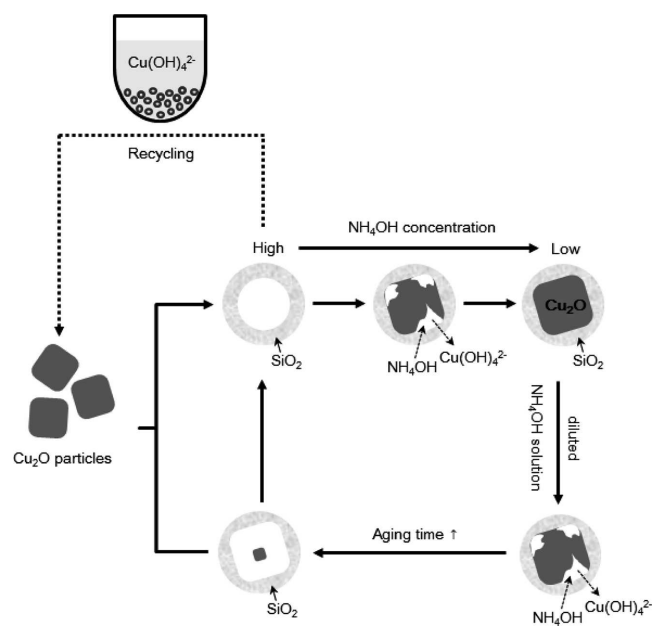


Fig. 2. Schematic illustration described the SiO_2 coating experimental process

The octahedral Cu_2O particles were coated with silica, producing $\text{Cu}_2\text{O}@\text{SiO}_2$ core-shell particles (Fig. 2) via the sol-gel coating process in a basic aqueous solution. Silica coating on Cu_2O surfaces has rarely been synthesized, because Cu_2O was etched out in the aqueous NH_4OH solution use to provide the conventional silica coating. The selective etching of the Cu_2O core in a dilute NH_4OH solution started to generate empty space in the core, and further etching produced $\text{Cu}_2\text{O}/\text{SiO}_2$ yolk-shell particles and finally led to hollow SiO_2 particles. Thus, the cuprous oxide (Cu_2O) particles were used as templates to produce the hollow silica particles.

A one-pot process for synthesis of Cu_2O particles to hollow silica particles was made possible simply by adjusting the concentration of ammonia in the reaction batch. The etched Cu_2O exists in the form of $\text{Cu}(\text{NH}_3)_4^{2+}$. The etched solution was recycled to produce Cu_2O particles again, making the process environment-friendly.

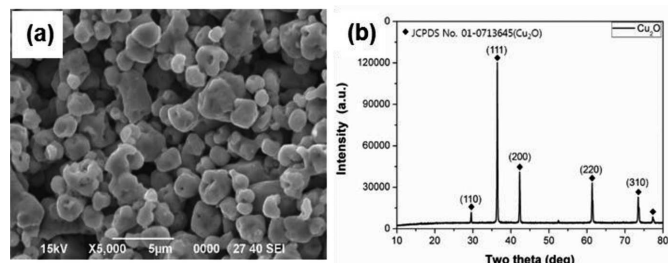


Fig. 3. (a) SEM image of prepared Cu_2O particles and (b) XRD data of Cu_2O particles

Fig. 3 shows an SEM image and XRD data of the Cu_2O particles. The average size of the Cu_2O particles was $\sim 300 \pm 45$ nm. The XRD patterns in Fig. 3b shows that the Cu_2O 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_2O particles. The TEM images showed SiO_2 , SnO_2 and TiO_2 -coated Cu_2O NPs having a SiO_2 layer 10 nm thick, of which the Cu_2O 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_4OH concentration. After coating with the silica layer, the average particle size increased to $\sim 240 \pm 70$ nm. (Fig. 4a) Because the etching of Cu_2O 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 ($\text{pH} = 12.8$) are the keys to stable production of core-shell particles. Therefore, we used the 5 times diluted NH_4OH solution (5.6%) as a catalyst for silica coating. In the case of the TiO_2 layer, the Cu_2O 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_2O particles when carried out without surface modification. However, even without modification, TiO_2 -coated Cu_2O particles were synthesized by adjusting the concentration and amount of NH_4OH . See Fig. 5 for the details of the effect of NH_4OH concentration on the Cu_2O core during the TiO_2 coating process. TEM images of TiO_2 -coated Cu_2O particles extracted in 28% and 1.4% NH_4OH solution, respectively, after reaction times of 4h. (Fig. 5) The TiO_2 surface is not flat at the higher NH_4OH concentration (28%) because the hydrolysis reaction between TBOT and NH_4OH is too fast. (Fig. 5a) When the concentration was lowered to 1.4%, TiO_2 coated the surface of the Cu_2O 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_4OH solution was reduced to 20 vol%. As a result, a TiO_2 shell was successfully coated onto the Cu_2O surface.

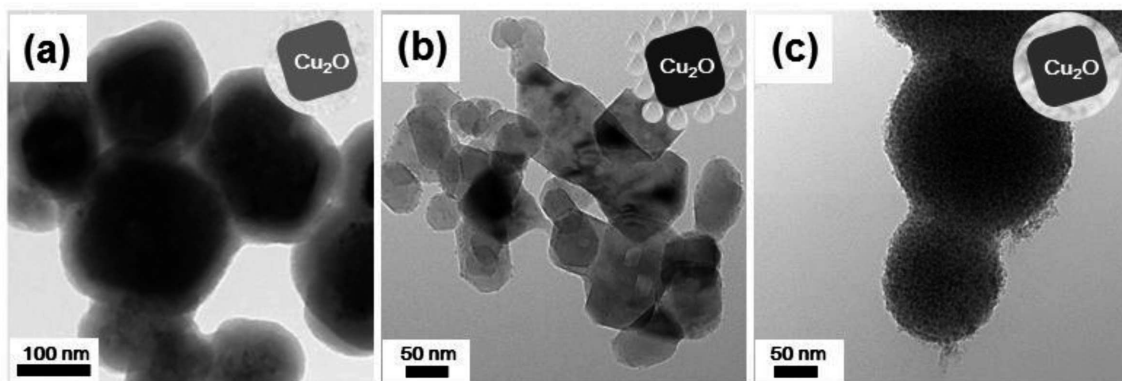


Fig. 4. TEM images of (a) SiO_2 -coated Cu_2O particles, (b) SnO_2 -coated Cu_2O particles and (c) TiO_2 -coated Cu_2O particles

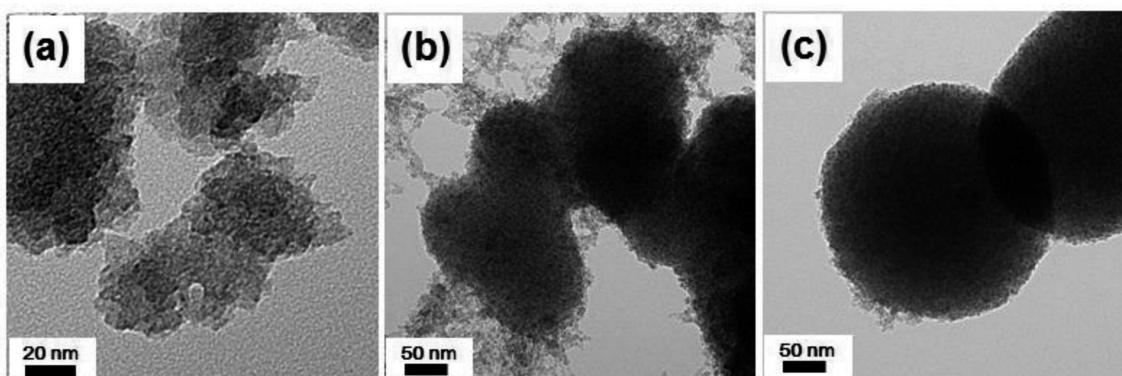
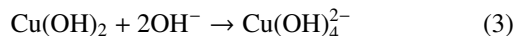
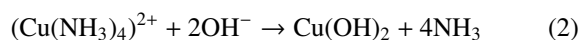
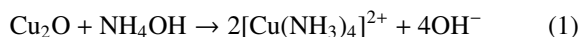


Fig. 5. TEM images of TiO_2 -coated Cu_2O particles by adjusting concentration and amount of NH_4OH . (a) 28% NH_4OH (0.3mL), (b) 1.4% diluted NH_4OH (0.3mL), (c) 1.4% diluted NH_4OH (0.03mL)

The Cu_2O etched away in the NH_4OH solution is expected to form $\text{Cu}(\text{OH})_4^{2-}$ according to following equation [4].



The amount of NH_4OH is an important factor in the formation of the SiO_2 and TiO_2 shells. To cover Cu_2O particles with covering such as TiO_2 and SiO_2 , it is necessary to make use of diluted NH_4OH solution.

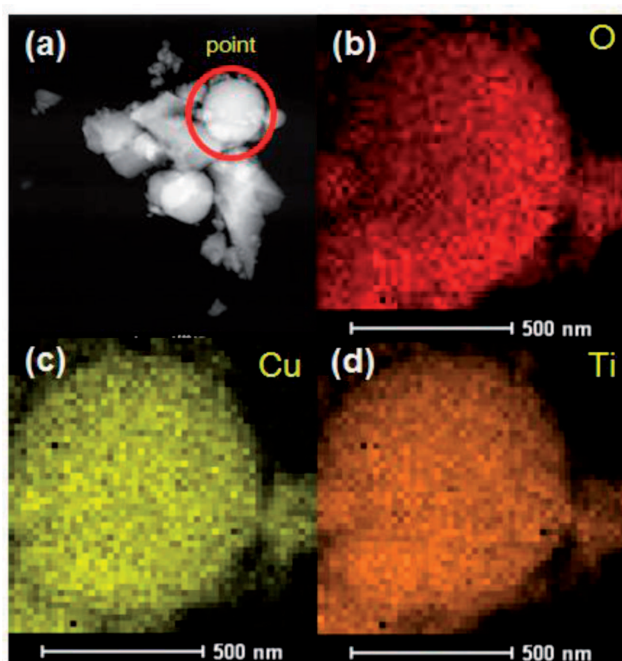


Fig. 6. Energy Dispersive X-ray Spectroscopy (EDS) mapping of elements in TiO_2 -coated Cu_2O ; (a) TiO_2 -coated Cu_2O image, (b) O-K, (c) Cu-K, (d) Ti-K

In Fig. 6, EDS confirmed the formation of TiO_2 -coated Cu_2O particles. Fig. 6 suggests the existence of Cu (yellow), O (red) and Ti (orange) elements in the $\text{Cu}_2\text{O}@\text{TiO}_2$ 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.

Photographs of colloidal Cu_2O , SiO_2 , SnO_2 and TiO_2 -coated Cu_2O solutions at various pH values are shown in Fig. 7. The photographs were taken approximately 24 h after the pH values were adjusted with HCl and NaOH. Over the pH range 5-10, the SiO_2 -coated Cu_2O particles displayed good dispersion. The SiO_2 -coated Cu_2O solution exhibited no more color change than did the SnO_2 -coated Cu_2O solution. On the other hand, the TiO_2 -coated Cu_2O solution changed to a green color at all pH values. No color or phase change occurred for the Cu_2O dispersion solution during Cu_2O synthesis at pH 7 and pH 10. The reduction reaction was enhanced under alkaline conditions, leading to formation of nanoparticle-aggregated spheres and octahedra, truncated octahedra, and cuboctahedra at pH >7). The as-formed nanoparticles aggregated in order to decrease their surface energy, due to the considerable decrease of pH in the reaction process. In addition, Cu_2O 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].

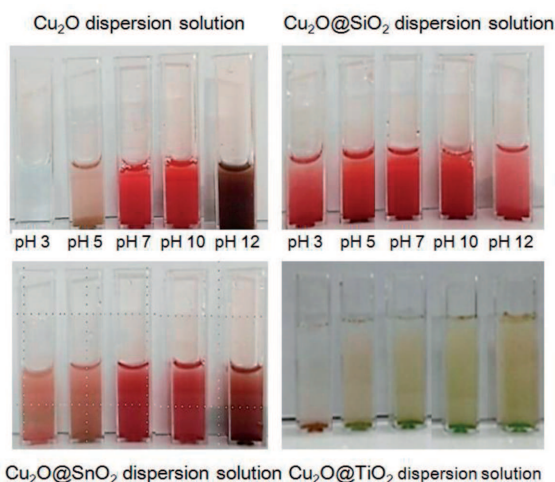
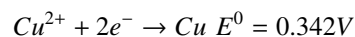


Fig. 7. Photograph of SiO_2 , SnO_2 and TiO_2 -coated Cu_2O solution at various pH values



Under alkaline conditions, the formation of Cu_2O is preferred due to the larger reducing potential of $\text{Cu}(\text{OH})_2/\text{Cu}_2\text{O}$ compared to $\text{Cu}(\text{OH})_2/\text{Cu}$ (Reactions 9-11). The Cu_2O in HCl and NaOH solution is expected to form CuCl_2 and $\text{Cu}(\text{OH})_2$ in accordance with the following reaction [12].

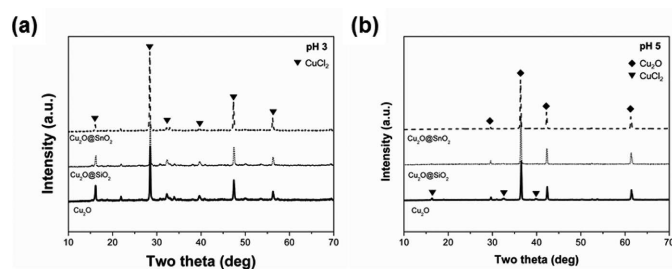
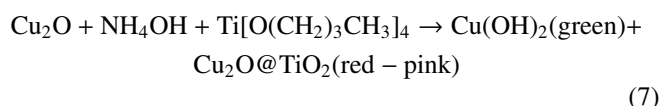
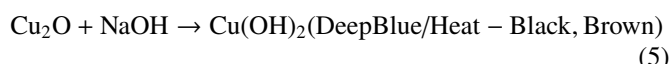
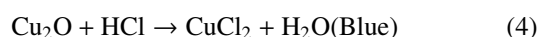
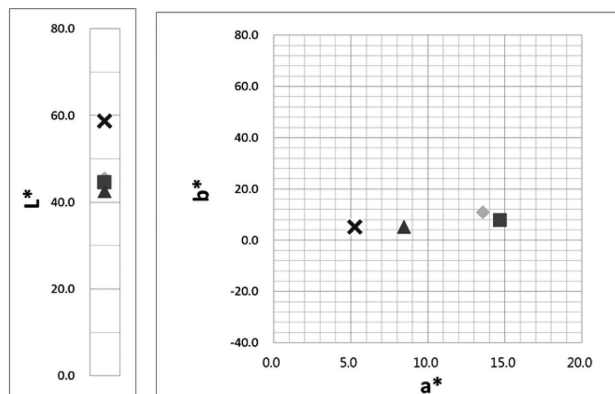


Fig. 8. XRD data of Cu_2O and various metal oxide-coated Cu_2O under acidic conditions: (a) pH 3 values, (b) pH 5 values

Fig. 8 shows the XRD pattern of Cu_2O and various metal oxide-coated Cu_2O under acidic conditions. Some Cu_2O particles transformed into CuCl_2 at pH 5. (Fig. 8b) XRD data

confirmed that metal oxide-coated Cu₂O nanoparticles were not changed at pH 5. All Cu₂O nanoparticles with metal oxide coating were not changed at pH 5. Non-coated Cu₂O samples formed CuCl₂ at pH 5. Finally, all samples were changed to CuCl₂ at pH 3. (Fig. 8a)



	L^*	a^*	b^*
(a) Cu ₂ O (◇)	45.50	13.59	10.78
(b) Cu ₂ O@SiO ₂ (□)	44.47	14.69	7.84
(c) Cu ₂ O@SnO ₂ (△)	42.52	8.47	5.09
(d) Cu ₂ O@TiO ₂ (X)	58.70	5.26	5.15

Fig. 9. CIE Lab values of (a) Cu₂O, (b) SiO₂-coated Cu₂O, (c) SnO₂-coated Cu₂O and (d) TiO₂-coated Cu₂O

The color of the Cu₂O 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 Cu₂O particles and metal oxide-coated Cu₂O particles. The CIE $L^*a^*b^*$ colorimetric parameters for Cu₂O after ceramic coating with SiO₂, SnO₂ or TiO₂ are also given in Fig. 9. For another important red pigment (Fe₂O₃), the a^* value was 23 but Cu₂O red pigment produced a relatively low a^* value. However, the SiO₂-coated Cu₂O, in particular, exhibits an increased a^* value indicating an increase in Cu₂O@SiO₂(□). On the other hand, there was a small decrease in a^* values of the SnO₂(△) and TiO₂(×)-coated samples.

4. Conclusions

In summary, we have successfully synthesized metal oxide-coated Cu₂O particles with SiO₂, SnO₂ and TiO₂. The preparation of Cu₂O@SiO₂ 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 NH₄OH solution. The pH stability of SiO₂ and SnO₂-coated Cu₂O particles in solution was similar to that of TiO₂-coated Cu₂O particles in acidic solution. Our studies found that the SiO₂ and SnO₂-coated Cu₂O particles in solution were more stable at pH 5 than at pH 3. On the other hand, TiO₂-coated Cu₂O particles in solution changed to a green color at all pH values.

Acknowledgements

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REFERENCES

- [1] J.Y. Ho, M.H. Huang, J. Phys. Chem. C **113**, 14159 (2009).
- [2] J.T. Zhang, J.F. Liu, Q. Peng, X. Wang, Y.D. Li, Chem. Mater. **18**, 867 (2006).
- [3] Y. Kim, J.H. Pee, J.H. Chang, K. Choi, K.J. Kim, D.Y. Jung, Chem. Lett. **38**, 842 (2009).
- [4] J.C. Park, J. Kim, H. Kwon, H. Song, Adv. Mater. **21**, 803 (2009).
- [5] S.H. Lee, I. Rusakova, D.M. Hoffman, A.J. Jacobson, T.R. Lee, ACS Appl. Mater. Interfaces **5**, 2479 (2013).
- [6] X. Su, J. Zhao, X. Zhao, Y. Guo, Y. Zhu, Z. Wang, Nanotechnology **19**, 365610 (2008).
- [7] R. Yu, K. Choi, J.H. Pee, Y. Kim, J. Kor. Powd. Met. Inst. **20**, 210 (2013).
- [8] J.Y. Kim, J.M. Byun, J.Y. Kim, Y.D. Kim, J. Kor. Powd. Met. Inst. **21**, 119 (2014).
- [9] W. Li, J. Yang, Z. Wu, J. Wang, B. Li, S. Feng, Y. Deng, F. Zhang, D. Zhao, J. Am. Chem. Soc. **134**, 11864 (2012).
- [10] F. Caruso, X. Shi, R.A. Caruso, A. Susha, Adv. Mater. **13** 740 (2001).
- [11] Q. Hua, D. Shang, W. Zhang, K. Chen, S. Chang, Y. Ma, Z. Jiang, J. Yang, W. Huang, Langmuir **27**, 665 (2011).
- [12] R. Yu, Y. Kim, J.H. Pee, K.J. Kim, W. Kim, J. Nanosci. Nanotechnol. **11**, 6283 (2011).
- [13] K. Chen, D. Xue, Cryst. Eng. Comm. **14**, 8068 (2012).