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**SYNTHESIS AND CHARACTERIZATION OF SiO<sub>2</sub>, SnO<sub>2</sub> AND TiO<sub>2</sub> METAL OXIDE SHELLS COVERING Cu<sub>2</sub>O PARTICLES**

**SYNTEZA I CHARAKTERYSTYKA POWŁOK TLENKOWYCH SiO<sub>2</sub>, SnO<sub>2</sub> I TiO<sub>2</sub> POKRYWAJĄCYCH CZĄSTKI Cu<sub>2</sub>O**

In this work is described a means of improving the chemical stability of Cu<sub>2</sub>O@SiO<sub>2</sub>, Cu<sub>2</sub>O@SnO<sub>2</sub> and Cu<sub>2</sub>O@TiO<sub>2</sub> materials. The SiO<sub>2</sub>, SnO<sub>2</sub> and TiO<sub>2</sub> 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<sub>2</sub>O were characterized using transmission electron microscopy and X-ray diffraction.

*Keywords:* Cu<sub>2</sub>O, metal oxide coating, pH value, SiO<sub>2</sub>, TiO<sub>2</sub>, SnO<sub>2</sub>

**1. Introduction**

Cuprous oxide (Cu<sub>2</sub>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<sub>2</sub>O has an unstable oxidation state and low stability, which limits its use in certain applications. In general, Cu<sub>2</sub>O nanoparticles were transformed into CuO nanoparticles by treatment in a basic high pH solution: copper ions (Cu<sup>2+</sup>) turned into Cu(OH)<sub>2</sub><sup>2-</sup> in NaOH solution. The Cu(OH)<sub>2</sub><sup>2-</sup> ions were then transformed into Cu<sub>2</sub>O particles by addition of an acid solution as oxidation catalyst [3-4]. To prevent oxidation and aggregation of the Cu<sub>2</sub>O particles, core-shell structures incorporation layers of inorganic materials were required. Silica (SiO<sub>2</sub>), like tin (IV) oxide (SnO<sub>2</sub>), is a suitable material for use as an optical coating due to its transparency in the visible range [5]. Silicon dioxide (SiO<sub>2</sub>), is an excellent inorganic modifier and has been widely investigated for its exceptional applications in the synthesis of nanostructures [6-7]. SiO<sub>2</sub> 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<sub>2</sub>), 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<sub>2</sub> structures [8]. For example, Caruso and co-workers introduced a layer-by-layer self-assembly strategy for coating TiO<sub>2</sub>, which was realized by surface electrostatic interactions [9]. In this work is described a means of improving the chemical stability of Cu<sub>2</sub>O@SiO<sub>2</sub>, Cu<sub>2</sub>O@SnO<sub>2</sub> and Cu<sub>2</sub>O@TiO<sub>2</sub> materials. SiO<sub>2</sub>, SnO<sub>2</sub> and TiO<sub>2</sub> 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**

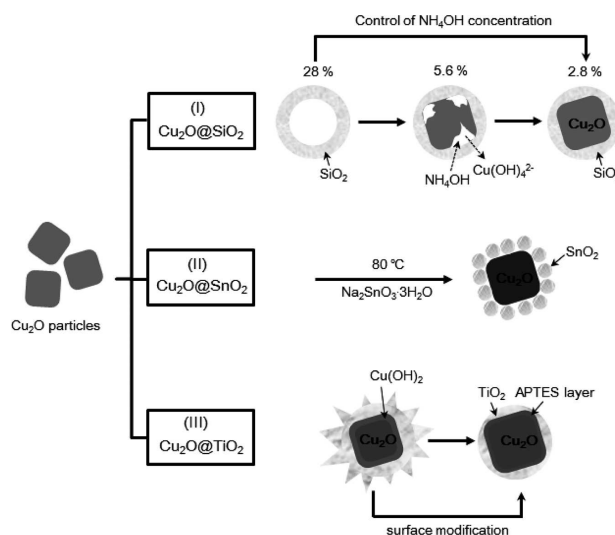


Fig. 1. Schematic illustration described the experimental process of metal oxide coating

**2.1. Raw materials**

The starting materials, copper (II) chloride dehydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O, 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 ( $\text{NH}_4\text{OH}$ , 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 $\text{Cu}_2\text{O}$ 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  $\text{CuCl}_2$  aqueous solution. Then 0.5 mL of  $\text{NaOH}$  aqueous solution (0.2 M) was dropped into  $\text{CuCl}_2$  solution heated to  $60^\circ\text{C}$ . After rapid stirring for 30 min, *L*-ascorbic acid solution (5 mL, 0.6 M) was introduced in the  $\text{CuCl}_2$  solution. The color of the solution immediately changed from light green to yellow. The mixed solution was stirred again for 3 h at  $55^\circ\text{C}$ . 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  $\text{Cu}_2\text{O}$  nanoparticles were synthesized by following a modified literature method. [3,11]  $\text{Cu}_2\text{O}$  (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  $\text{NH}_4\text{OH}$  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  $\text{NH}_4\text{OH}$  (purchased at 28% from Aldrich) using D.I. water. A 14% (diluted)  $\text{NH}_4\text{OH}$  solution was prepared by mixing 0.5 mL  $\text{NH}_4\text{OH}$  and 0.5 mL D.I. water. In the same way, to make 2.8% diluted  $\text{NH}_4\text{OH}$  solution, prepared  $\text{NH}_4\text{OH}$  (0.1 mL) and D.I. water (0.9 mL). The aqueous  $\text{NH}_4\text{OH}$  solution (28% ammonia) was diluted with five times its volume with water to make a diluted  $\text{NH}_4\text{OH}$  solution (2.8% ammonia). When the higher concentration of  $\text{NH}_4\text{OH}$  solution was used, the color of the solution more rapidly turned from sky blue to yellow. The  $\text{NH}_4\text{OH}$  solution at concentrations of 2.8, 14 and 28% resulted in the same reaction time. Diluted  $\text{NH}_4\text{OH}$  solution (50  $\mu\text{L}$ ) was added to the mixed solution and then stirred for 15 min. TEOS (30  $\mu\text{L}$ ) was then introduced into the mixed solution. The silica-coated  $\text{Cu}_2\text{O}$  particles obtained after 4 h were collected by means of centrifugation and dried in a vacuum at room temperature.

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

The  $\text{SnO}_2$ -coated  $\text{Cu}_2\text{O}$  nanoparticles were synthesized by a modification of a method from the literature.[5] The  $\text{Cu}_2\text{O}$  (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  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$  (10 mmol) was added in the  $\text{Cu}_2\text{O}$  nanoparticle solution. The reaction was continued for 24h at  $80^\circ\text{C}$ . 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  $\text{TiO}_2$  shells of the core-shell structures were prepared via the sol-gel method [9]. The  $\text{Cu}_2\text{O}$  (75 mg) nanoparticles were dispersed in absolute ethanol (100 mL), and mixed with concentrated  $\text{NH}_4\text{OH}$  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  $45^\circ\text{C}$  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  $50^\circ\text{C}$ .

## 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

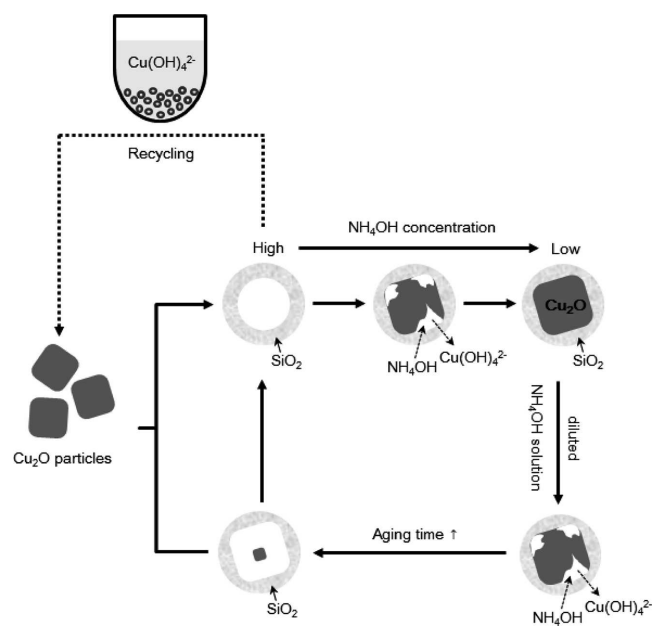


Fig. 2. Schematic illustration described the  $\text{SiO}_2$  coating experimental process

The octahedral  $\text{Cu}_2\text{O}$  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  $\text{Cu}_2\text{O}$  surfaces has rarely been synthesized, because  $\text{Cu}_2\text{O}$  was etched out in the aqueous  $\text{NH}_4\text{OH}$  solution use to provide the conventional silica coating. The selective etching of the  $\text{Cu}_2\text{O}$  core in a dilute  $\text{NH}_4\text{OH}$  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  $\text{SiO}_2$  particles. Thus, the cuprous oxide ( $\text{Cu}_2\text{O}$ ) particles were used as templates to produce the hollow silica particles.

A one-pot process for synthesis of  $\text{Cu}_2\text{O}$  particles to hollow silica particles was made possible simply by adjusting the concentration of ammonia in the reaction batch. The etched  $\text{Cu}_2\text{O}$  exists in the form of  $\text{Cu}(\text{NH}_3)_4^{2+}$ . The etched solution was recycled to produce  $\text{Cu}_2\text{O}$  particles again, making the process environment-friendly.

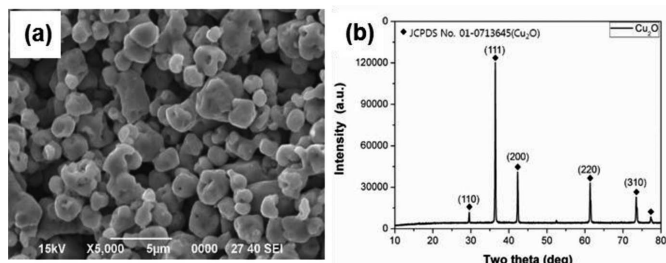


Fig. 3. (a) SEM image of prepared  $\text{Cu}_2\text{O}$  particles and (b) XRD data of  $\text{Cu}_2\text{O}$  particles

Fig. 3 shows an SEM image and XRD data of the  $\text{Cu}_2\text{O}$  particles. The average size of the  $\text{Cu}_2\text{O}$  particles was  $\sim 300 \pm 45$  nm. The XRD patterns in Fig. 3b shows that the  $\text{Cu}_2\text{O}$  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  $\text{Cu}_2\text{O}$  particles. The TEM images showed  $\text{SiO}_2$ ,  $\text{SnO}_2$  and  $\text{TiO}_2$ -coated  $\text{Cu}_2\text{O}$  NPs having a  $\text{SiO}_2$  layer 10 nm thick, of which the  $\text{Cu}_2\text{O}$  particle was covered by a layer of small ( $\sim 2$ -3

nm)  $\text{SnO}_2$  particles. (see Fig. 4a and 4b) The silica coating was successfully prepared by reducing the  $\text{NH}_4\text{OH}$  concentration. After coating with the silica layer, the average particle size increased to  $\sim 240 \pm 70$  nm. (Fig. 4a) Because the etching of  $\text{Cu}_2\text{O}$  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 ( $\text{pH} = 12.8$ ) are the keys to stable production of core-shell particles. Therefore, we used the 5 times diluted  $\text{NH}_4\text{OH}$  solution (5.6%) as a catalyst for silica coating. In the case of the  $\text{TiO}_2$  layer, the  $\text{Cu}_2\text{O}$  particles were modified by APTES but the  $\text{TiO}_2$  shell thickness could not be confirmed. On the other hand, the  $\text{TiO}_2$  coating was irregular on the surface of  $\text{Cu}_2\text{O}$  particles when carried out without surface modification. However, even without modification,  $\text{TiO}_2$ -coated  $\text{Cu}_2\text{O}$  particles were synthesized by adjusting the concentration and amount of  $\text{NH}_4\text{OH}$ . See Fig. 5 for the details of the effect of  $\text{NH}_4\text{OH}$  concentration on the  $\text{Cu}_2\text{O}$  core during the  $\text{TiO}_2$  coating process. TEM images of  $\text{TiO}_2$ -coated  $\text{Cu}_2\text{O}$  particles extracted in 28% and 1.4%  $\text{NH}_4\text{OH}$  solution, respectively, after reaction times of 4h. (Fig. 5) The  $\text{TiO}_2$  surface is not flat at the higher  $\text{NH}_4\text{OH}$  concentration (28%) because the hydrolysis reaction between TBOT and  $\text{NH}_4\text{OH}$  is too fast. (Fig. 5a) When the concentration was lowered to 1.4%,  $\text{TiO}_2$  coated the surface of the  $\text{Cu}_2\text{O}$  particles, but Fig. 5b reveals that some isolated  $\text{TiO}_2$  particles also formed in the coating solution. In response, the amount of 1.4%  $\text{NH}_4\text{OH}$  solution was reduced to 20 vol%. As a result, a  $\text{TiO}_2$  shell was successfully coated onto the  $\text{Cu}_2\text{O}$  surface.

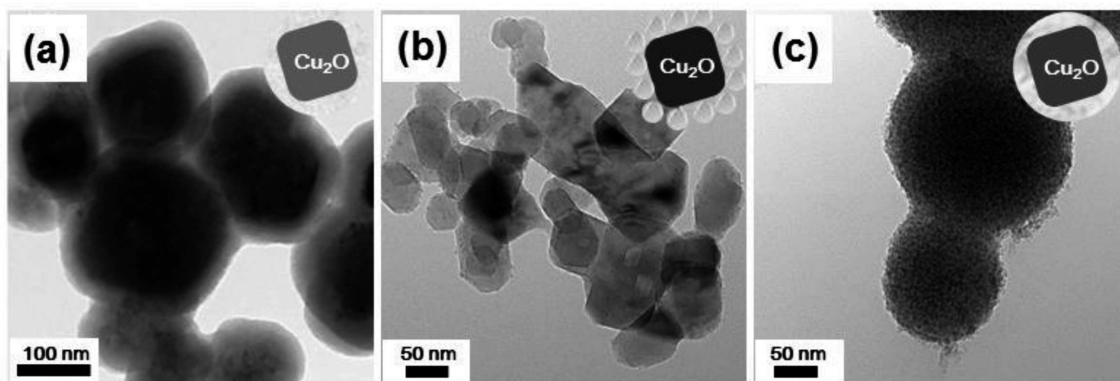


Fig. 4. TEM images of (a)  $\text{SiO}_2$ -coated  $\text{Cu}_2\text{O}$  particles, (b)  $\text{SnO}_2$ -coated  $\text{Cu}_2\text{O}$  particles and (c)  $\text{TiO}_2$ -coated  $\text{Cu}_2\text{O}$  particles

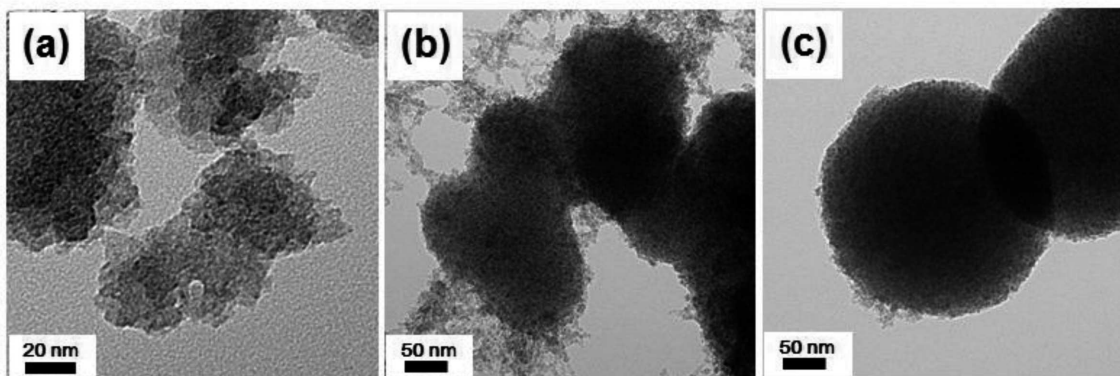
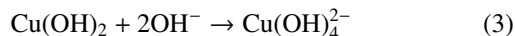
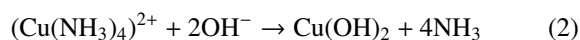
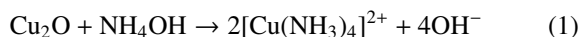


Fig. 5. TEM images of  $\text{TiO}_2$ -coated  $\text{Cu}_2\text{O}$  particles by adjusting concentration and amount of  $\text{NH}_4\text{OH}$ . (a) 28%  $\text{NH}_4\text{OH}$  (0.3mL), (b) 1.4% diluted  $\text{NH}_4\text{OH}$  (0.3mL), (c) 1.4% diluted  $\text{NH}_4\text{OH}$  (0.03mL)



The  $\text{Cu}_2\text{O}$  etched away in the  $\text{NH}_4\text{OH}$  solution is expected to form  $\text{Cu}(\text{OH})_4^{2-}$  according to following equation [4].



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

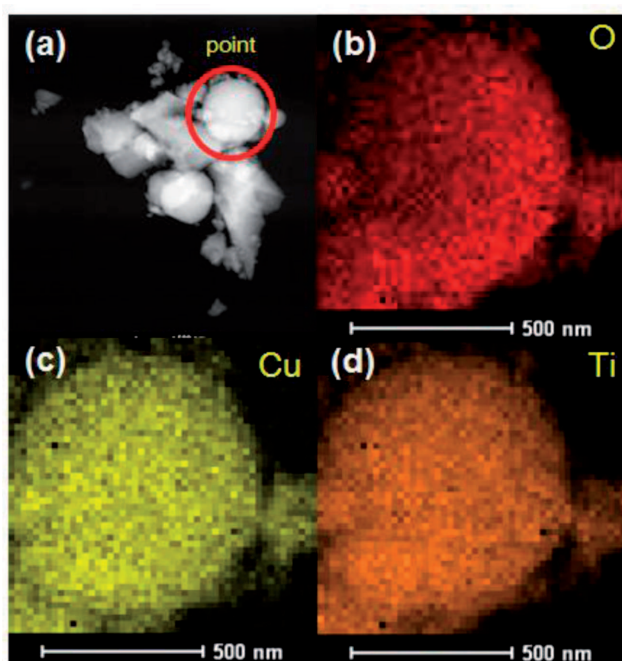


Fig. 6. Energy Dispersive X-ray Spectroscopy (EDS) mapping of elements in  $\text{TiO}_2$ -coated  $\text{Cu}_2\text{O}$ ; (a)  $\text{TiO}_2$ -coated  $\text{Cu}_2\text{O}$  image, (b) O-K, (c) Cu-K, (d) Ti-K

In Fig. 6, EDS confirmed the formation of  $\text{TiO}_2$ -coated  $\text{Cu}_2\text{O}$  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  $\text{TiO}_2$  layers, as indicated by the TEM photograph in Fig. 6.

Photographs of colloidal  $\text{Cu}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{SnO}_2$  and  $\text{TiO}_2$ -coated  $\text{Cu}_2\text{O}$  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  $\text{SiO}_2$ -coated  $\text{Cu}_2\text{O}$  particles displayed good dispersion. The  $\text{SiO}_2$ -coated  $\text{Cu}_2\text{O}$  solution exhibited no more color change than did the  $\text{SnO}_2$ -coated  $\text{Cu}_2\text{O}$  solution. On the other hand, the  $\text{TiO}_2$ -coated  $\text{Cu}_2\text{O}$  solution changed to a green color at all pH values. No color or phase change occurred for the  $\text{Cu}_2\text{O}$  dispersion solution during  $\text{Cu}_2\text{O}$  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,  $\text{Cu}_2\text{O}$  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].

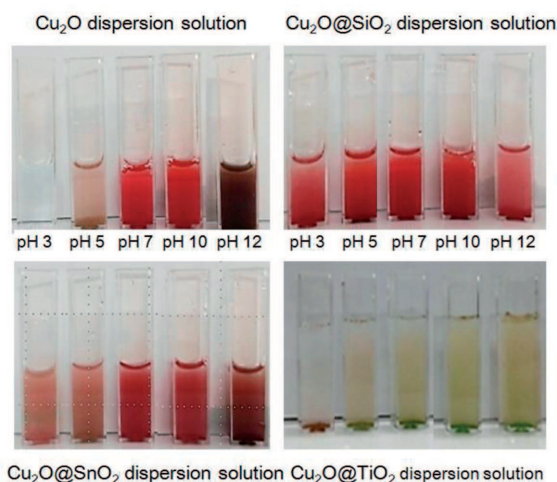
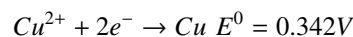


Fig. 7. Photograph of  $\text{SiO}_2$ ,  $\text{SnO}_2$  and  $\text{TiO}_2$ -coated  $\text{Cu}_2\text{O}$  solution at various pH values



Under alkaline conditions, the formation of  $\text{Cu}_2\text{O}$  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  $\text{Cu}_2\text{O}$  in HCl and NaOH solution is expected to form  $\text{CuCl}_2$  and  $\text{Cu}(\text{OH})_2$  in accordance with the following reaction [12].

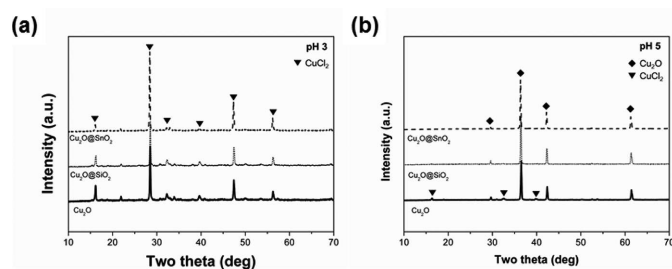
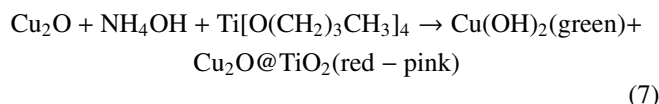
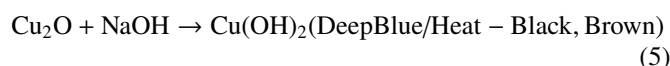
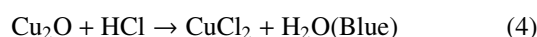
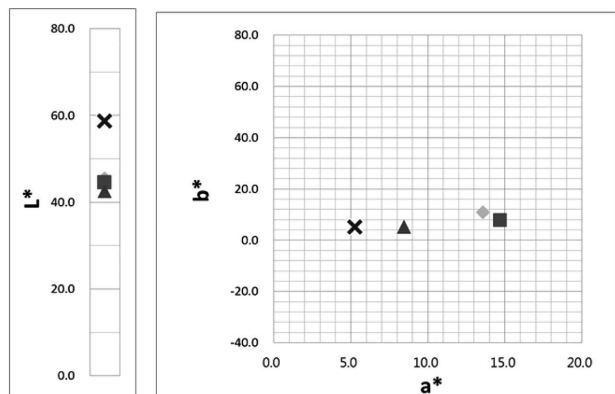


Fig. 8. XRD data of  $\text{Cu}_2\text{O}$  and various metal oxide-coated  $\text{Cu}_2\text{O}$  under acidic conditions: (a) pH 3 values, (b) pH 5 values

Fig. 8 shows the XRD pattern of  $\text{Cu}_2\text{O}$  and various metal oxide-coated  $\text{Cu}_2\text{O}$  under acidic conditions. Some  $\text{Cu}_2\text{O}$  particles transformed into  $\text{CuCl}_2$  at pH 5.(Fig. 8b) XRD data

confirmed that metal oxide-coated Cu<sub>2</sub>O nanoparticles were not changed at pH 5. All Cu<sub>2</sub>O nanoparticles with metal oxide coating were not changed at pH 5. Non-coated Cu<sub>2</sub>O samples formed CuCl<sub>2</sub> at pH 5. Finally, all samples were changed to CuCl<sub>2</sub> at pH 3. (Fig. 8a)



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

Fig. 9. CIE Lab values of (a) Cu<sub>2</sub>O, (b) SiO<sub>2</sub>-coated Cu<sub>2</sub>O, (c) SnO<sub>2</sub>-coated Cu<sub>2</sub>O and (d) TiO<sub>2</sub>-coated Cu<sub>2</sub>O

The color of the Cu<sub>2</sub>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<sub>2</sub>O particles and metal oxide-coated Cu<sub>2</sub>O particles. The CIE  $L^*a^*b^*$  colorimetric parameters for Cu<sub>2</sub>O after ceramic coating with SiO<sub>2</sub>, SnO<sub>2</sub> or TiO<sub>2</sub> are also given in Fig. 9. For another important red pigment (Fe<sub>2</sub>O<sub>3</sub>), the  $a^*$  value was 23 but Cu<sub>2</sub>O red pigment produced a relatively low  $a^*$  value. However, the SiO<sub>2</sub>-coated Cu<sub>2</sub>O, in particular, exhibits an increased  $a^*$  value indicating an increase in Cu<sub>2</sub>O@SiO<sub>2</sub>(□). On the other hand, there was a small decrease in  $a^*$  values of the SnO<sub>2</sub>(△) and TiO<sub>2</sub>(×)-coated samples.

#### 4. Conclusions

In summary, we have successfully synthesized metal oxide-coated Cu<sub>2</sub>O particles with SiO<sub>2</sub>, SnO<sub>2</sub> and TiO<sub>2</sub>. The preparation of Cu<sub>2</sub>O@SiO<sub>2</sub> 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<sub>4</sub>OH solution. The pH stability of SiO<sub>2</sub> and SnO<sub>2</sub>-coated Cu<sub>2</sub>O particles in solution was similar to that of TiO<sub>2</sub>-coated Cu<sub>2</sub>O particles in acidic solution. Our studies found that the SiO<sub>2</sub> and SnO<sub>2</sub>-coated Cu<sub>2</sub>O particles in solution were more stable at pH 5 than at pH 3. On the other hand, TiO<sub>2</sub>-coated Cu<sub>2</sub>O particles in solution changed to a green color at all pH values.

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