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FABRICATION OF Cu_2O NANO CRYSTALS BY {111} PLANE-ORIENTED GROWTH

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Abstract

Cu_2O nano crystals were fabricated by reduction of $CuCl_2$ by hydrazine in presence of sodium dodecyl sulfate (SDS) as a capping ligand in alkaline medium. X-Ray Diffraction results indicated the appearance of single phase of Cu_2O possessing cubic crystal system with lattice parameter *a* of 4.263 nm. By using X-ray Photoelectron Spectroscopy, subsequently, analyzing the binding energy of Cu2p electron, the oxidation sate of copper element was proved to be +1. In presence of SDS, the Cu_2O crystals preferred to grow towards {111} plane-orientation. The SEM images showed the difference shapes and sizes of Cu_2O single crystals. Under certain conditions, the truncated cube or truncated octahedron was obtained. In these structures, {111} crystal planes were exposed around the surface of Cu_2O grains. The amount of hydrazine was considered as the most important factor for tuning the morphology of Cu_2O particles. The results of this study is hoped to uncover the exploiting ability of the potential advantages from {111} planes on the surface of Cu_2O single crystals.

Keywords. Cuprous oxide, oriented growth, truncated octahedron, truncated cube.

1. INTRODUCTION

Studies on the fabrication and application of nano-sized particles of cuprous oxide (Cu_2O) have attracted many research groups all over the world in recent years [1-3]. Cu_2O is a p-type semiconductor with a direct band gap of 2.0-2.2 eV [4] which is suitable for photovoltaic conversion, electronic devices, or fabrication of photocatalyst. Research group in Faculty of Chemistry, Hanoi University of Science, VNU-Hanoi has achieved various successes in the field of fabrication, size particle control, and utilization of Cu_2O nano particles as a catalyst for the photocatalytic degradation reaction of dyes under visible light [5, 6]. Up to now, most researches have reported Cu_2O crystallites with the sphere or parallelepiped shapes which are surrounded by {100} planes. These types of particles usually reveal electronic properties or catalytic activity not as good as those of particle possessing the {111} planes on the surface [7, 8]. Some reports notified the successful manufacture of Cu_2O with the surface that was preferred to growth towards {111} plane-orientation, in which Au, WO_3, MgO/Al_2O_3, *etc*. were used as directing agents for the surface growth [8-11]. In this study, we report the fabrication of Cu_2O nanoparticles coupled the control of oriented growth towards <111> directions without the utilization of surface growth directing agents. To the best of our knowledge, this is the first report in which the surface of Cu_2O particles are controllable towards to the {111} planes. The successful fabrication of Cu_2O material coupled {111} plane–developed surface will be hoped to uncover the exploiting ability of the potential advantages from {111} planes on the surface of Cu_2O single crystals in the field of photovoltaic conversion, electronic devices, and photocatalytic reactions.

2. EXPERIMENTAL

2.1. Materials

$CuCl_2.2H_2O$, NaOH, $N_2H_4.H_2O$, sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$, SDS), ethanol.

2.2. Fabrication of Cu_2O nanoparticles

In this study, the Cu_2O nanoparticles were fabricated based on the procedures that were

reported in the references [5, 6] with some modification aiming to suit purposes of the research. Typically, 9.5 mL of distilled water and 0.1 mL of 0.1 M $CuCl_2$ solution were introduced into a 50-mL beaker. The obtained mixture was stirred at room temperature by a magnetic stirrer set at 500 rpm. Subsequently, 0.087 g of SDS that served as a capping ligand was added and the mixture was kept at same conditions described above until SDS surfactant was dissolved completely. 0.25 mL of 1 M NaOH solution was poured before adding *V* mL (*V* = 0.15-0.65 mL) of 0.2 M hydrazine solution drop by drop into the beaker. After that, the mixture was annealed *ca.* 2 h aiming the reduction reaction occurred completely. The solid was separated from reaction mixture by centrifuge operated at 4000 rpm for 10 min, followed by washing with distilled water at least 3 times. Finally, the solid was dispersed in ethanol.

2.3. Techniques for characterizing materials

X-Ray Diffraction (XRD) patterns were recorded on a Bruker SIEMEN D5005 diffractometer using the CuK_α radiation, λ = 0.15406 nm with an X-ray generator working at 40 kV and 40 mA. The data were collected with 2θ = 10-70^o at scanning rate of 0.01^o min^{-1}. Scanning Electron Microscopy (SEM) images were observed on FEI Nova Nano SEM 450 Microscope operating at 5 kV. X-ray Photoelectron Spectroscopy (XPS) was measured on a Shimadzu Kratos AXISULTRA DLD spectrometer using Al target at 15 kV and 10 mA. The binding energies were calibrated with C 1s level (284.8 eV) as an internal standard reference. The binding energy of Cu2p electron was scanned with high resolution in range of 925-960 eV.

3. RESULTS AND DISCUSSION

Synthesis conditions and some preliminary characteristics of obtained samples were listed in Table 1. In spite of the different amounts of hydrazine, all four entries gave similar red-colored solids with same chemical composition, *vide infra*.

In order to determine the crystal structure, and therefore the phase composition of obtained solids, all samples were inspected by X-ray diffraction. The XRD patterns of all fabricated samples exhibited four distinguishable diffraction peaks observed at 2θ of 29.7^o, 36.4^o, 42.3^o, and 61.3^o. These peaks were assigned to (110), (111), (200), and (220) planes which are the characteristics of cubic crystal system of cuprous oxide, Cu_2O. The lattice constant of this system was also calculated with *a* of 4.263 nm that coincide with the reference lattice parameter (*a* = 4.2696 nm) of Cu_2O (05-0667 JCPDS). All peaks on the XRD patterns belonged to the Cu_2O phase proved the single phase nature of all prepared samples.

Table 1: Notation and some characteristics of Cu_2O nano-sized samples fabricated with different amounts of reductant

Sample	Amount of hydrazine (mmol)	Color of solid	Phase composition*
N1	1.5×10^{-2}	Red	Cu_2O
N2	2.5×10^{-2}	Red	Cu_2O
N3	4.5×10^{-2}	Red	Cu_2O
N4	6.5×10^{-2}	Red	Cu_2O

Reaction conditions: H_2O (9.5 mL), 0.1 M $CuCl_2$ solution (0.1 mL), SDS (0.087 g), 1 M NaOH solution (0.25 mL), * Determined by powder X-ray diffraction technique.

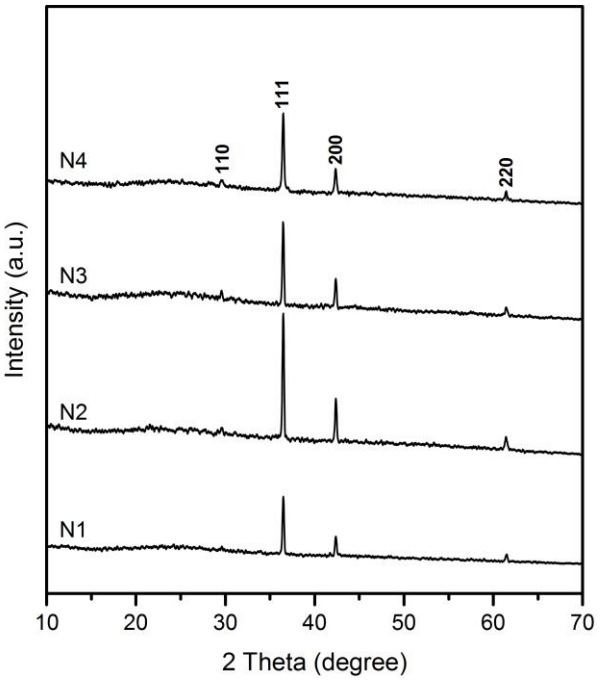

Fig. 1: XRD patterns of Cu_2O nanoparticle samples

Table 2: Interplanar spacings d_{hkl} (nm) and lattice constant* *a* (nm) of Cu_2O

Sample	d_{110}	d_{111}	d_{200}	d_{220}	*a*
N1	3.018	2.460	2.131	1.506	4.263
N2	3.016	2.461	2.131	1.507	4.263
N3	3.020	2.461	2.131	1.507	4.264
N4	3.015	2.461	2.132	1.507	4.263

* Lattice parameter *a* of cubic crystal system is calculate by following formula: $a^2=d^2\times(h^2+l^2+l^2)$

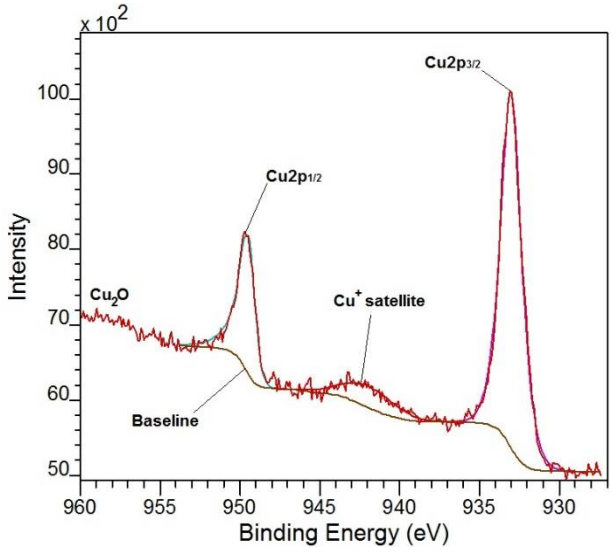

Fig. 2: Narrow-scan Cu2p XPS spectrum of Cu_2O sample

To further study oxidation state of copper element existed in the solids, we used X-ray Photoelectron Spectroscopy. Data were collected from 925-960 eV that covered the binding energy of Cu2p. The C1s peak was used as an internal reference to correct position of others. The narrow-scan Cu2p XPS spectrum indicated that binding energies of $Cu2p_{3/2}$ and $Cu2p_{1/2}$ were 933.01 eV and 949.44 eV, respectively. These values are characteristics of oxidation state of +1 of copper element. The deconvolution result showed only one component peak for $Cu2p_{3/2}$ or $Cu2p_{1/2}$. This demonstrated the unique oxidation state (+1) of copper. Furthermore, at position of 941.95 eV was shake-up peak that was assigned to $Cu2p_{3/2}$ satellite band. This binding energy band owned the weak intensity characterizing for oxidation number +1 of Cu. This peak does not appear on the XPS spectrum of Cu, while should possess very strong intensity in the case of Cu^{2+} [12]. Once again, the unique existence of +1 oxidation state was confirmed.

When varying the amount of reductant (hydrazine), the crystallites of Cu_2O were preferred to growth in different directions yielding the grains with various shapes and sizes. The scanning electron micrographs (SEM) (Fig. 3), exhibited the cube shape for N1 sample, truncated cube one for N2, and truncated octahedron one for N3, while the morphology of Cu_2O particles in sample was not uniform and clear. 3D models and the orientation of faces of Cu_2O truncated cube and truncated octahedron crystallites were shown in Fig. 4.

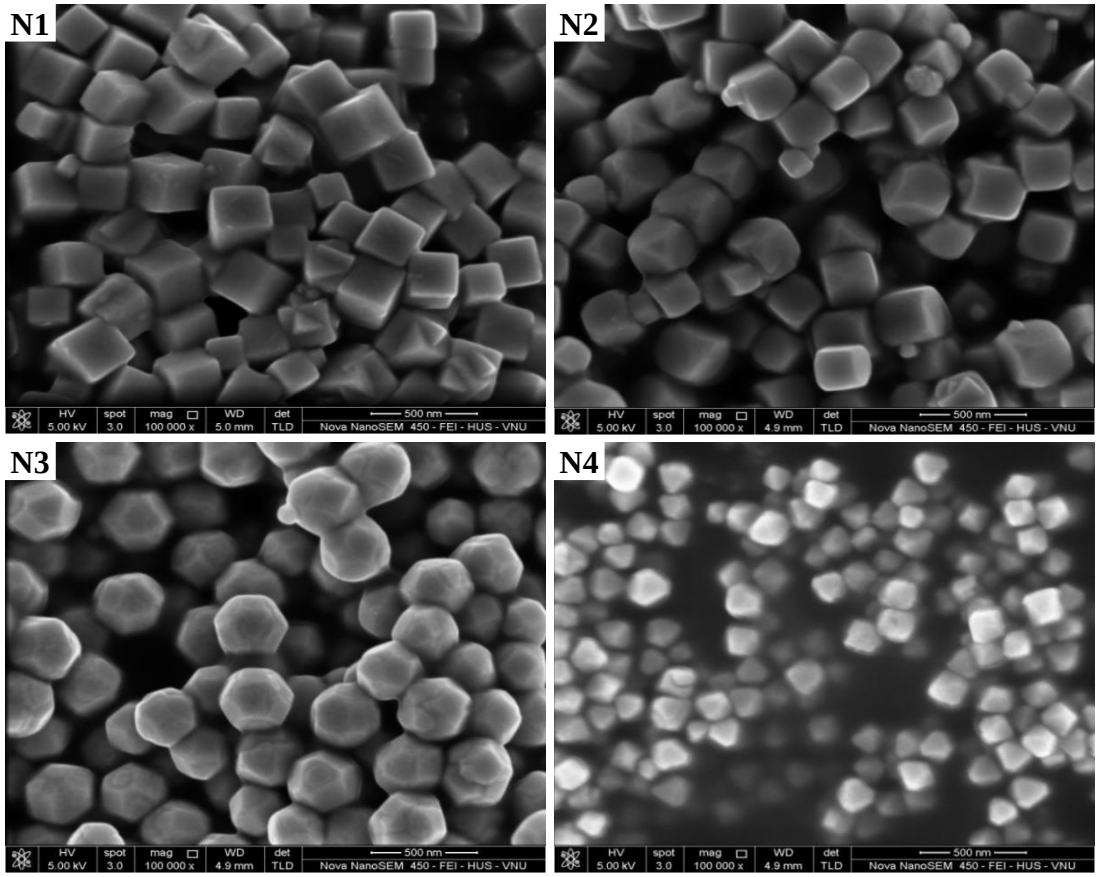

Fig. 3: SEM images of Cu_2O samples fabricated with different amount of reductant

Contrary to the cube shape in which the {111} planes exist within the volume of Cu_2O crystallites, in both truncated cube and truncated octahedron types, {111} planes are exposed on the surface of Cu_2O particles. According to the results of previous researches [7, 8], the planes surrounding surface of Cu_2O cube crystallites were {100}. However, this type showed electronic properties and catalytic activity weaker than expected. If the proportion of the Cu_2O crystallite surface covered by {111} planes increases, the material will reveal better electronic and catalytic activities compared with the crystallites surrounded by {100} planes. In the previous literatures, to fabricate the Cu_2O with {111}-plane-developed surface, authors usually prepare core-shell type in which the core was Au or WO_3, and the shell was Cu_2O. In our study, by using SDS as the capping ligand and controlling the amount of reductant, the Cu_2O crystallites surrounded by {111} planes with different morphologies were formed directly without using directing agents.

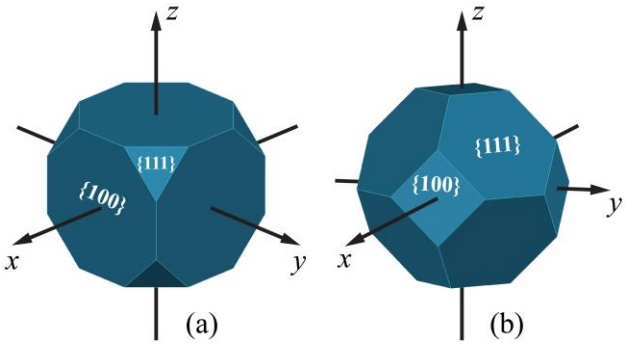

Fig. 4: 3D models and the orientation of Cu_2O crystallites with (a) truncated cube shape, and (b) truncated octahedron shape

The difference in morphology of Cu_2O crystallites was assumed to be result of the difference in the developing way of crystallite surface. We supposed that, normally, capping ligand binds strongly with the atoms on {111} planes. This phenomenon prevents the development of crystallite towards <111> directions. Consequently, when using smaller amount of reductant, the reduction occurred slowly leading to the crystallite growth towards <100> directions to form Cu_2O particles covered by {100} planes or had cube shape (sample N1, Fig. 3). When raising gradually the amount of reductant, besides the development towards <100> directions, the crystallites simultaneously grew towards <111> directions leading to the appearance of both {100} and {111} planes on the surface of Cu_2O particles (N2 and N3 samples, Fig. 3). Depending on the amount of reductant, the development preferred <100> to <111> directions or vice versa. If the growth was stronger towards <100> directions, the Cu_2O crystallites with truncated cube shape were formed (N2, Fig. 3). In the opposite case, the result was truncated octahedron shape (N3, Fig. 3). However, if the amount of reductant increased too much, the development of crystallite became uncontrollable (the capping ligand would not protect the as-synthesized Cu_2O seeds), leading to the Cu_2O crystallites with difference shapes and sizes (N4, Fig. 3).

4. CONCLUSION

Nano-sized particles of Cu_2O were fabricated successfully by reduction method in a basic solution using hydrazine and SDS as a reductant and capping ligand, respectively. All solids possessed single phase of Cu_2O. Oxidation state of copper element existed in all samples was confirmed to be +1 by XPS analysis. By varying the amount of hydrazine, the fabricated samples had different morphologies, in which Cu_2O crystallites preferred to grow towards {111} plane-orientation to form truncated cube or truncated octahedron particles with uniform size. The success in fabrication of Cu_2O crystallite surrounded by {111} planes is hoped to open the exploiting ability the outstanding electronic properties and catalytic activity of {111} planes in the fields of photovoltaic conversion and photocatalytic reaction.

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