

# Preparation of nanosize copper recycled from an electroplating wastewater

C.-H. Huang<sup>\*</sup>, H. Paul Wang<sup>\*\*</sup> and I.-W. Sun<sup>\*\*\*</sup>

<sup>\*</sup>Department of Environmental Engineering, National Cheng Kung University  
Tainan, Taiwan, p5894109@mail.ncku.edu.tw

<sup>\*\*</sup>Department of Environmental Engineering and Sustainable Environmental Research Center, National  
Cheng Kung University, Tainan, Taiwan, wanghp@mail.ncku.edu.tw

<sup>\*\*\*</sup>Department of Chemistry, National Cheng Kung University, Tainan, Taiwan,  
iwsun@mail.ncku.edu.tw

## ABSTRACT

To better utilize copper recovered from an electroplating (EP) wastewater, a simple method of preparing valuable nanoparticles has been developed in the present work. Experimentally, about 40-50% of copper in the wastewater can be chelated with  $\beta$ -cyclodextrin ( $\beta$ -CD). The  $\beta$ -CD-Cu<sup>2+</sup> complex was dried at 373 K for 24 hours and carbonized at 573 K for at least two hours to obtain the nanosize metallic copper (Cu) encapsulated in the carbon shells (Cu@C). The images observed by transmission electron microscopy (TEM) also indicate that the size of Cu in the Cu@C is in the range of 10-60 nm. The component fitted X-ray absorption near edge structure (XANES) spectra suggest that the chelated Cu<sup>2+</sup> is reduced to form Cu as the hydroxyl groups of the  $\beta$ -CD are oxidized to H<sub>2</sub>O vapor during carbonization. By extended X-ray absorption fine structure (EXAFS) spectroscopy, it is found that the average coordination number (CN) of Cu in the Cu@C nanoparticles decreases along with the decrease of the size of Cu, i.e. the CN of the nanosize Cu (23 nm) is reduced to 8 comparing to 12 of the bulky Cu.

**Keywords:** copper, electroplating wastewater, nanoparticles, XANES, EXAFS

## 1 INTRODUCTION

Electroplating (EP) wastewater generally contains high concentrations of copper (typically 300-3,000 ppm) [1, 2]. To recover copper from the EP wastewater, chemical precipitation, adsorption, membrane filtration, electro-coagulation, and bio-treatment have been widely used [3-5]. However, these processes are not economically and environmentally attractive. In the separate experiments, we found that Cu<sup>2+</sup> in the chemical mechanical polishing (CMP) wastewater was chelated with cyclodextrins [6]. Remarkably, Cu(II) ions chelated with  $\beta$ -CD molecules to which hydroxyl groups have been appended may be reduced and encapsulated in the carbon shell during carbonization of the CD-Cu<sup>2+</sup> complex at the temperature of 573 K. Nanosize-controllable Cu@C particles can, therefore, be synthesized via this simple method.

The Cu@C nanoparticles have been used in enhanced efficiency of a dye-sensitized solar cell (DSSC). A small amount (0.08%) of the Cu@C nanoparticles dispersed in an ionic liquid ([bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]) which is used as a DSSC electrolyte can increase its electrolyte conductivity by several fold [7]. Furthermore, deposition of the nanosize copper (Cu) encapsulated carbon thin film onto the counter electrode of a DSSC can increase the efficiency by 50% if compared with the relatively expensive Pt electrode [8].

Molecule-scale data of select elements in the complex matrix can be obtained by X-ray absorption spectroscopy [9]. By X-ray absorption near edge structure (XANES) or extended X-ray absorption fine structure (EXAFS) spectroscopy, it has been found that the main As species in ground water of the blackfoot disease area are As<sub>2</sub>O<sub>5</sub> and As(V)-HS [10]. The nanosize CuO in the CMP wastewater can be extracted and forms CuO clusters in the mesopores of MCM-41 as observed by XANES [11]. The CuO cluster in the micropores of ZSM-5 or ZSM-48 also played important roles in catalytic decomposition of 2-chlorophenol and reduction of NO [12, 13]. Thus, the main objective of this work was to investigate the feasibility of recovery of copper from an EP wastewater for preparing relatively high-value Cu@C core-shell nanoparticles. In addition, the Cu nanoparticles in the size range of 23-57 nm were also synthesized under the pH values of 1.0-2.3. Speciation of copper in the Cu@C formation process was also studied by XANES and EXAFS.

## 2 EXPERIMENTAL SECTION

The EP wastewater was sampled from an ultimate wastewater mixing tank of a copper electroplating process in Taiwan. The wastewater generally contains about 400 ppm of copper.  $\beta$ -CD (WAKO, 97%) was used to chelate copper ions in the EP wastewater or CuSO<sub>4</sub>·5H<sub>2</sub>O (RDH, 99%). At the CD/Cu molar ratio of 0.063, the CD-Cu<sup>2+</sup> complex was dried at 373 K for 24 hours, washed by distilled water and filtrated with a 0.2  $\mu$ m filter to remove unchelated copper, and carbonized under high purity nitrogen (99.99%) at 573 K for at least two hours to yield the nanosize Cu encapsulated in the carbon shell (Cu@C).

Concentration of copper in the EP wastewater, CD-Cu<sup>2+</sup> complex, and Cu@C was analyzed by induced coupling plasma-optical emission spectroscopy (ICP-OES) (JOBIN YVON, Ultima 2000). Chemical structure of the samples was characterized by X-ray diffraction spectroscopy (XRD) (BRUKER, D8 Advanced) scanned from 10 to 80° (2θ) at a scan rate of 3°/min using CuKα radiation (40 kV, 40 mA). Images of the nanosize Cu@C were studied by transmission electron microscopy (TEM) (PHILIPS, CM-200) having an accelerating voltage of 200 kV. The EXAFS spectra of copper in the samples were collected on the Wiggler BL17C beamline at the Taiwan National Synchrotron Radiation Research Center. The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 8.0 simulation programs [14]. The component fittings of model compounds in the complexation solutions were deduced by using the least-square fittings of the XANES spectra.

### 3 RESULTS AND DISCUSSION

About 369 ppm of copper and a small amount of zinc (41 ppm), manganese (1.8 ppm), nickel (0.3 ppm), and lead (0.02 ppm) were found in the EP wastewater. Copper in the EP wastewater was chelated with β-CD at the β-CD/Cu ratio of 0.063. At the pH values of 1.0-2.3, 6.5-44% of copper can be recovered from the EP wastewater (see Table 1). Note that under the pH value of 1.0, a high-purity Cu@C can be obtained by carbonization of the β-CD-Cu<sup>2+</sup> complex.

The component fitted XANES spectra in Fig. 1 show that the main copper compound in the EP wastewater is CuSO<sub>4</sub>. After chelation of Cu<sup>2+</sup> with β-CD in the EP wastewater and dried at 373 K, about 6% of β-CD-Cu<sup>2+</sup> complex are formed. As the pH value of the EP wastewater is decreased to 2.0, the fraction of the β-CD-Cu<sup>2+</sup> complex is increased to 34%. At the pH value of 1.0, the fraction of β-CD-Cu<sup>2+</sup> complex is 50% and a small amount of Cu<sub>2</sub>O (2%) is also found.

Figure 2 shows the XRD patterns of carbonized samples at the β-CD/Cu ratio of 0.063. Note that CuSO<sub>4</sub> is the main copper compound in the EP wastewater (Fig. 2(a)). After carbonization of the β-CD-Cu<sup>2+</sup> complex at 573 K, metallic copper encapsulated in the carbon shells is observed in Fig. 2(b)-(d). Copper in the β-CD-Cu<sup>2+</sup> complex is reduced to yield Cu as the hydroxyl groups of the β-CD are oxidized to H<sub>2</sub>O vapor during carbonization. Note that the XRD peaks of Cu become broadened, suggesting the existence of nanosize Cu. The average crystalline sizes of Cu calculated with the Scherrer equation [15] using the full width at half maximum of the Cu(111) (2θ = 43.3°) peak are 23-57 nm. It is clear that smaller Cu in the Cu@C can be prepared from the CD-Cu<sup>2+</sup> complex under a low pH value.

Table 1: Copper in the electroplating wastewater chelated with β-CD for synthesis of Cu@C nanoparticles.

Copper source	CD/Cu molar ratio	pH value at chelation	% chelated <sup>a</sup>	Purity (%) of product Cu@C <sup>b</sup>
EP	0	2.3	-	-
EP	0.063	2.3	6.5	19
EP	0.063	2.0	36	78
EP	0.063	1.0	44	99

<sup>a</sup>: determined by ICP-OES; <sup>b</sup>: determined by XANES.

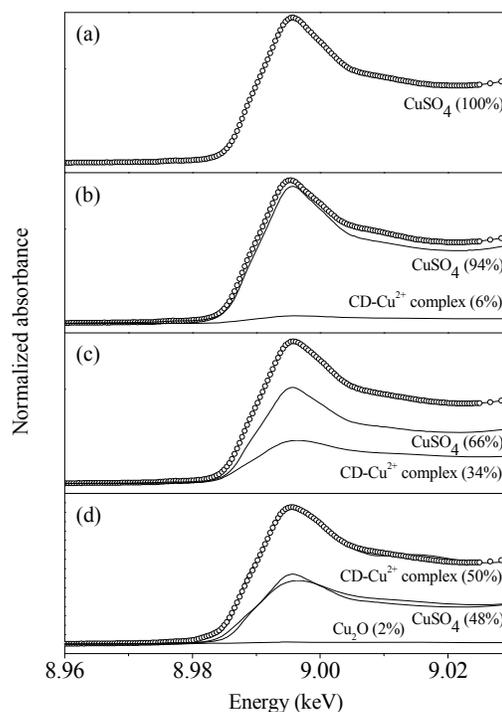


Figure 1: XANES spectra of copper (a) in the EP wastewater and chelated with β-CD at the β-CD/Cu molar ratio of 0.063 under the pH values of (b) 2.3, (c) 2.0, and (d) 1.0.

The images of the nanosize Cu encapsulated in the amorphous carbon shells can be observed by TEM shown in Fig. 3. Without the perturbation of other metal ions in the EP wastewater, in the CuSO<sub>4</sub> solution, the as-synthesized Cu@C nanoparticles have a narrow size distribution between 10-20 nm (shown in Fig. 3(a)). On the contrary, Cu recovered from the EP wastewater has a relatively wide size distribution of 10-60 nm (Fig. 3(b)). Under a low pH value of 1.0, the size distribution of Cu is in the range of 10-30 nm.

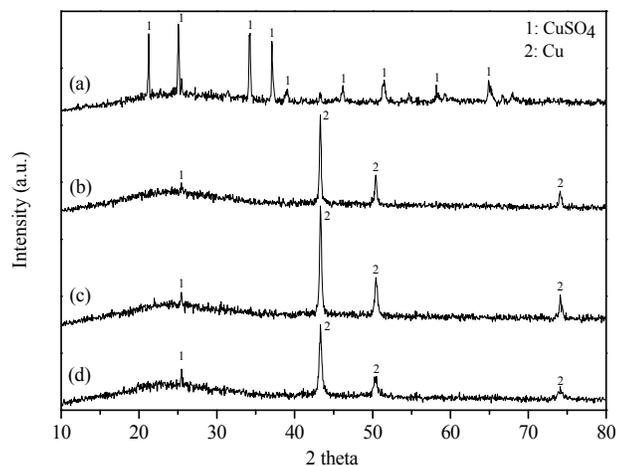


Figure 2: XRD patterns of copper (a) in the EP wastewater and the Cu@C synthesized by carbonization of the  $\beta$ -CD-Cu<sup>2+</sup> complexes (at the  $\beta$ -CD/Cu molar ratio of 0.063) obtained from chelation of copper in the EP wastewater under the pH values of (b) 2.3 (c) 2.0, and (d) 1.0.

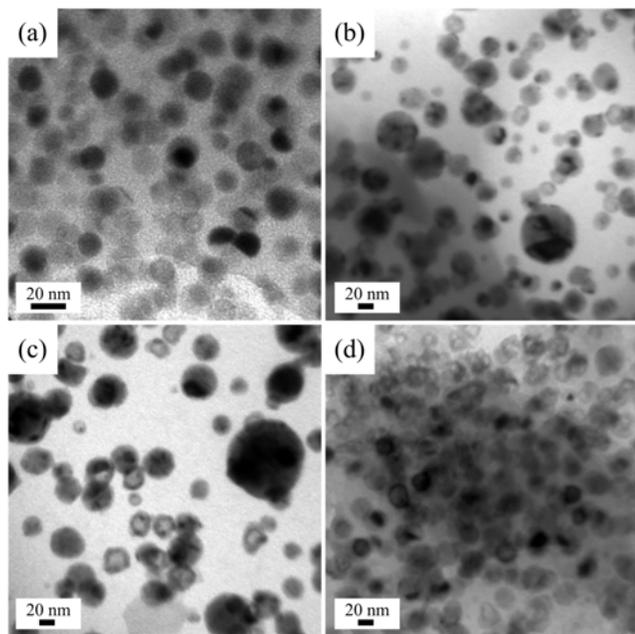


Figure 3: TEM images of the Cu@C nanoparticles synthesized from (a) CuSO<sub>4</sub> and EP wastewater under the pH values of (b) 2.3, (c) 2.0, and (d) 1.0 at the  $\beta$ -CD/Cu molar ratio of 0.063.

Generally, surface to total atoms ratios are negligible in the bulky state but significantly effective in a nanometer scale. Surface atoms have a less CN compared to the inner atoms. The average CN of a select metal may decrease along with the decrease of its crystalline sizes. By EXAFS spectroscopy (see Table 2), it is found that the average CN of Cu in the Cu@C nanoparticles (36 nm) decreases from 12  $\rightarrow$  9 and further decreases to 8 for the smaller Cu@C (23 nm).

Table 2: Structure parameters of copper in Cu@C nanoparticles recovered from the electroplating wastewater.

Copper source	CD/Cu molar ratio	Cu size (nm)	pH	R ( $\text{\AA}$ )	CN	$\sigma^2$ ( $\text{\AA}^2$ )
Cu foil	-	-	-	2.53	12.3	0.008
EP	0.063	57	2.3	2.53	11.6	0.009
EP	0.063	36	2.0	2.53	9.4	0.009
EP	0.063	23	1.0	2.53	7.7	0.008

## 4 CONCLUSIONS

About 40-50% of copper in the EP wastewater can be recovered by chelation with  $\beta$ -CD for preparation of valuable Cu@C nanoparticles. Size controllable Cu@C nanoparticles can be synthesized at the pH value range of 1.0-2.3. The average CN of Cu in the Cu@C nanoparticles decreases along with the decrease of its particle sizes. The CN of the nanosize Cu (23 nm) is reduced (12  $\rightarrow$  8) compared to its bulk state.

This work exemplifies a valuable core-shell nanoparticles can be recovered from a wastewater. In addition, a better understanding of the nanoparticles in molecular scale is also obtained.

## 5 ACKNOWLEDGMENT

This research was supported by the Taiwan National Science Council, Bureau of Energy and the Excellence Project of the National Cheng Kung University. We also thank Professor J.-F. Lee of the Taiwan National Synchrotron Radiation Research Center for his experimental assistances.

## REFERENCES

- [1] L. Monser and N. Adhoum, *Sep. Purif. Technol.*, 26, 137, 2002.
- [2] S. Venkatesan and K. Begum, *Asia-Pac. J. Chem. Eng.*, 3, 387, 2008.
- [3] T. A. Kurniawan, G. Y. S. Chan, W. H. Lo and S. Babel, *Chem. Eng. J.*, 118, 83, 2006.
- [4] I. Heidmann and W. Calmano, *J. Hazard. Mater.*, 152, 934, 2008.
- [5] Y. J. Li, X. P. Zeng, Y. F. Liu, S. S. Yan, Z. H. Hu and Y. M. Ni, *Sep. Purif. Technol.*, 31, 91, 2005.
- [6] C. H. Huang, H. P. Wang, J. E. Chang and E. M. Eyring, *Chem. Comm.*, 31, 4663, 2009.
- [7] F. L. Chen, I. W. Sun, H. P. Wang and C. H. Huang, *J. Nanomater.*, 472950, 2009.
- [8] C. H. Huang, H. P. Wang and C. Y. Liao, *J. Nanosci. Nanotechnol.*, 10, 1, 2010.
- [9] H. L. Huang, H. P. Wang, G. T. Wei, I. W. Sun, J. F. Huang and Y. W. Yang, *Environ. Sci. Technol.*, 40, 4761, 2006.

- [10] H. C. Wang, H. P. Wang, C. Y. Peng, H. L. Liu and H. L. Huang, *B. Environ. Contam. Tox.*, 71, 798, 2003.
- [11] H. L. Huang and H. P. Wang, *J. Electron Spectrosc.*, 144, 307, 2005.
- [12] K. S. Lin and H. P. Wang, *J. Phys. Chem. B*, 105, 4956, 2001.
- [13] Y. J. Huang, H. P. Wang and J. F. Lee, *Chemosphere*, 50, 1035, 2003.
- [14] E. A. Stern, M. Newville, B. Ravel, Y. Yacoby and D. Haskel, *Physica B*, 209, 117, 1995.
- [15] H. Borchert, E. V. Shevehenko, A. Robert, I. Mekis, A. Kornowski, G. Grubel and H. Weller, *Langmuir*, 21, 1931, 2005.