

Preparation of M@Cu₂O (M= Au, Ag, Pd) Core-Shell Nanocrystals by a Facile Citrate-Chelating Approach

Yin-Kai Lin and Yung-Jung Hsu*

*E-mail: yhsu@cc.nctu.edu.twDepartment of Materials Science and Engineering,
National Chiao Tung University
1001 University Road, Hsinchu, Taiwan 30010, Republic
of China

The interactions between each of the components of hybrid nanostructures may induce enhanced and novel functions which had not been previously achieved. [1-3]. Interests in preparation of heterostructures are driven not only by the synthetic challenges but also by the potential enhanced functionalities. For example, the coupling of plasmonic metal with semiconductor in hybrid metal/semiconductor structures allows fine tunes to be made to the resulting light absorptions. Especially, metal/semiconductor structures are effective in improving charge separation, a vital component in photocatalytic process [4-5].

Cuprous oxide (Cu₂O) is a typical p-type direct bandgap semiconductor with a bandgap energy of 2.17 eV. Cu₂O not only has a large light absorption coefficient but also is an environment-friendly material. The core-shell structures of Au@Cu₂O have achieved much success in recent years. Most of the reported synthetic procedures however involved the use of environmentally harmful surfactants [6] or the need of relatively harsh reaction conditions [7], which may further hinder the applicability of the products. As a result, creation of a more effective, environmentally benign approach from which one can obtain Au@Cu₂O core-shell nanocrystals has been imperative. In this study, we developed a citrate-chelating approach which is simple and effective to synthesize Au@Cu₂O core-shell nanocrystals. This method shows great robustness in reproducibility and can be extended to prepare other core-shell nanocrystals such as Ag@Cu₂O and Pd@Cu₂O.

The synthesis was based on the chelating capability of citrate which efficiently binds Cu²⁺ to Au surface by forming Cu²⁺-citrate complex. Note that Au particles (with the size of about 15 nm) were first prepared by the typical citrate reduction method. The surface-attached citrate molecules of Au particles can then bind Cu²⁺ to enable the coating of Cu₂O upon the addition of reducing agent, ascorbic acid. Interestingly, when other metal particles derived from citrate reduction method (such as Ag and Pd) were employed, nanocrystals with well-defined core-shell structures were still grown, demonstrating the generality of the current synthetic route to core-shell nanocrystals. Figure 1 shows the typical SEM images of the products. The as-obtained core-shell nanocrystals had a uniform size 50-70 nm and a polyhedral shape similar to pure Cu₂O. The corresponding TEM image (Figure 2) and XRD pattern (Figure 3) confirms the core-shell structures and the compositions of the products. The core-shell nanocrystals of M@Cu₂O may find potential applications in plasmonics, photocatalysis as well as gas-sensing.

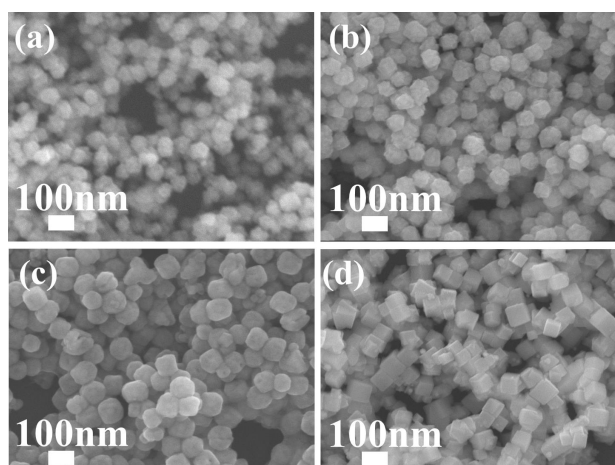


Figure 1. SEM images of (a) pure Cu₂O, (b) Au@Cu₂O, (c) Ag@Cu₂O, and (d) Pd@Cu₂O nanocrystals.

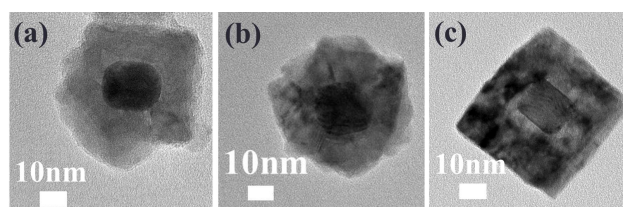


Figure 2. TEM images of (a) Au@Cu₂O, (b) Ag@Cu₂O, (c) Pd@Cu₂O.

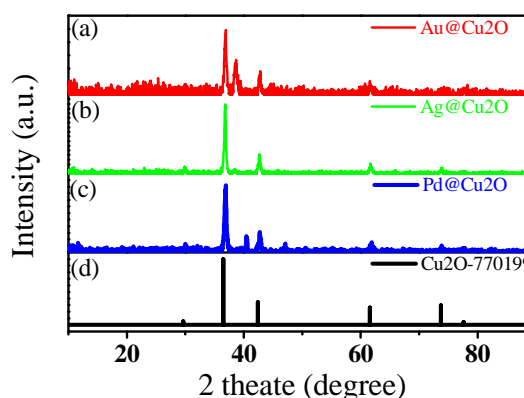


Figure 3. XRD patterns of (a) Au@Cu₂O, (b) Ag@Cu₂O, (c) Pd@Cu₂O, and (d) reference Cu₂O.

References

- [1]. S. Kim, B. Fisher, H. J. Eisler and M. Bawendi, *J. Am. Chem. Soc.*, 2003, 125, 11466.
- [2]. J. T. Zhang, Y. Tang, L. Weng and M. Ouyang, *Nano Lett.*, 2009, 9, 4061.
- [3]. J. Choi, Y. Jun, S. Yeon, H. C. Kim, J.-S. Shin and J. Cheon, *J. Am. Chem. Soc.*, 2006, 128, 15982.
- [4]. P. Li, Z. Wei, T. Wu, Q. Peng and Y. D. Li, *J. Am. Chem. Soc.*, 2011, 133, 5660.
- [5]. C.-H. Kuo, Y.-C. Yang, S. Gwo and M. H. Huang, *J. Am. Chem. Soc.*, 2011, 133, 1052.
- [6]. C.-H. Kuo, T.-E. Hua, and M. H. Huang, *J. Mater. Chem.*, 2012, 22, 719-724
- [7]. D.-Y. Liu, S.-Y. Ding, H.-X. Lin, B.-J. Liu, Z.-Z. Ye, F.-R. Fan, B. Ren, and Z.-Q. Tian., *J. Phys. Chem. C* 2012, 116, 4477-4483.