A novel synthesis of Co Au nanoparticles and characterization

Zhihui Ban, C. J. O'Connor

Advanced Materials Research Institute University of New Orleans, New Orleans, LA, USA, zban2@uno.edu

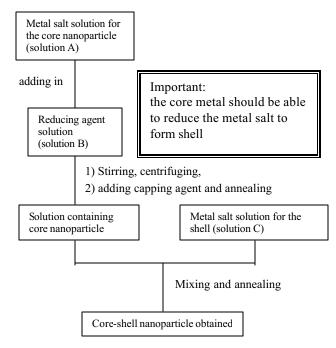
ABSTRACT

A homogeneous non-aqueous solution reactions method has been developed to prepare gold-coated cobalt (Co@Au) nanoparticles. After the samp le was washed with 8% HCl. XRD (X-Ray Diffraction), TEM (transmission electron microscopy), and magnetic measurements SQUID (Superconducting Quantum Interference Device) are utilized to characterize the nanocomposites. XRD shows the pattern of sample, which is only responding to gold. TEM results show that the average size of Co@Au nanoparticles is about 10 nm and we can find core-shell structure of the sample. SQUID results show that the particles are ferromagnetic materials at 300K. So the goldcoated cobalt nanoparticles (Co@Au) can be successfully prepared by the homogeneous non-aqueous approach. This kind of core-shell materials is stable in acid condition, which would give many opportunities for bio-application.

Keywords: core-shell structure, cobalt, gold, non-aqueous method, magnetic materials

1 INTRODUCTION

A combination of nanotechnologies and biosciences will be one of the leading areas of research and development in the 21st century; magnetic nanoparticles will certainly play an extremely important role. However, as the particle size decreases, the reactivity of the particle increases, and the magnetic properties are influenced more by surface effects[1]. So far the passivation of magnetic nanoparticles (? - Fe₂O₃, Co, Fe, et. al.) by another inert layer (SiO₂, gold, polymer et. al.) has been developed[2-7]. However, the nonmetallic layer potentially reduces the magnetic properties of the magnetic nanoparticles. Gold has become a favored coating material because of a simple synthetic procedure and its chemical functionality[8]. The presence of the diamagnetic coating passivates the magnetic core thus protecting the magnetic properties without having a pronounced effect on the magnetic properties. The presence of the diamagnetic coating allows for a surface that can be derivatized to allow for greater versatility while not reducing the magnetic properties. It is expected that iron nanoparticles can avoid being oxidized and maintain their magnetic properties (such as coercivity or blocking temperature) by gold coating. The reverse micelles method for synthesis of Fe@Au nanoparticles had been developed by our group(9). Here, in this paper, we will present another novel method for synthesis the gold-coated cobalt nanoparticles, which can be stable in acid condition. The idea of the method is using reducing agents (Na, K, Li) to reduce MLn (M = Fe, Co, Ni; L = Cl, Br; n = 2, 3) to form metallic core nanoparticles, and then using the surface of metallic core particles to reduce Au^{3+} to form gold coated metallic nanoparticles, as shown in scheme 1.



scheme 1. the reaction route to synthesize core-shell nanoparticles.

2 EXPERIMENT

The reduction reactions were performed in solutions of polar aprotic solvents. 2 mmol of CoCl₂ were dissolved in NMPO (1-Methyl-2-Pyrrolidinone) to form blue solution (Designated as solution A). 4 mmols of Na were dissolved in NMPO with 4 mmols of naphthalene to form a dark green solution (Designated as solution B). 0.6 mmol of dehydrated HAuCl₄ was dissolved in NMPO (Designated as solution C). The solution A was added into solution B quickly with intensive stirring at room temperature. The color of reaction system changed to dark brown immediately. The mixture was further stirred for two hours and then centrifuged to remove the sodium chloride. A small amount of capping agent, 4-benzylpyridine, was then

put into the solution. Heated and refluxed at 165 °C for 3 hours. After cooled down to 60 °C, the obtained black mixture was added with solution C, then stirring and heat to 125 °C for 4 hours and get light blue solution. After that the reaction solution was centrifuged to get black paste. All the above operations are done in glove box. The sample was then washed with EtOH, 8% HCl solution, water and EtOH for three times, respectively. After dried in vacuum, the product was characterized with SQUID, XRD, and redispersed into hexane for TEM observation.

3 RESULTS AND DISCUSSIONS

3.1 TEM RESULTS

Figure 1 shows the morphology of gold coated cobalt nanoparticles. The magnification is 400K and the scale bar is 20 nm. The core-shell structure (Co@Au) can be observed in the image. Mean core size of the nanoparticles is ca. 6 nm with shells of ca. 2 nm thick (as shown in the two small figures in figure 1. From the TEM results, we can see that the size distribution is not very well, some small size particles should be gold particles.

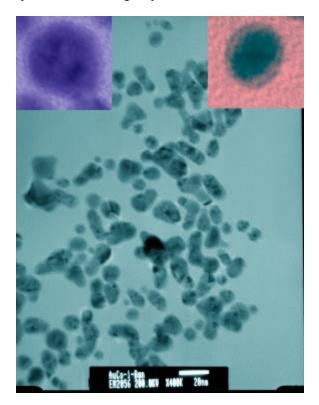


Figure 1 TEM results for Co@Au sample

3.2 XRD RESULTS

The XRD pattern of Co@Au nanoparticles is shown in Figure 2. In the result, there are only the diffraction peaks

which correspond to PDF card of Au (4-784). The diffractions attributed to cobalt cannot be observed probably due to the overlap with gold or amorphous of cobalt. But the magnetic property of the product as shown in Figure 3 shows the existence of pure cobalt. And in the XRD result, Cobalt oxides cannot be found, which would suggest that the cobalt was coated with gold very well.

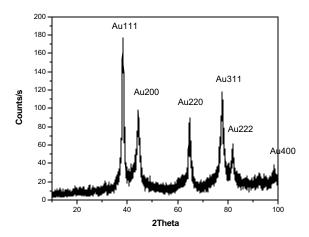


Figure 2 XRD pattern for the Co@Au sample

3.3 MAGNETIC PROPERTIES

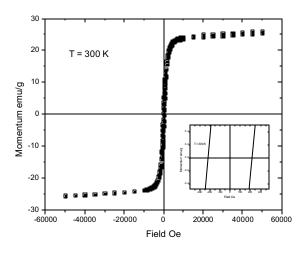


Figure 3 Hysterisis cure for Co@Au sample at 300 K

The SQUID results of the product shows that it is a ferromagnetic material with coercivity of 220 Oe (as shown in figure 3). The magnetic saturation is about 25 emu/g. If we consider the composition of the product obtained from EDS (including gold) and weight loss of TGA (which is organic materials), the magnetic saturation can be converted to over 140 emu/g. This indicates nanoparticles of Co coated completely with gold shell had been synthesized successfully.

4 CONCLUSIONS

Gold-coated cobalt nanoparticles (Co@Au) can be successfully prepared by the homogeneous non-aqueous approach. The Co@Au nanoparticles can be stable in both water and acid conditions, which would provide a wide range of opportunities for biosensors and biosciences. The method presented in this paper also could be used in making core-shell nanoparticles with other compositions.

REFERENCES

- 1. F. Bodker, S. Morup, and S. Linderoth, Phys. Rev. ett. 72, 282 (1994).
- 2. C. Pathmamnoharan and A. P. Philipse, J. Colloid Interface Sci. 205, 340 (1998).
- 3. D. V. Szabo and D. Vollath, Adv. Mater. 11, 1313 (1999).
- E. E. Carpenter, C. T. Seip, and C. J. O'Connor, J. Appl. Phys. 8, 5184 (1999).
- 5. Kinoshita, T.; Seino, S.; Okitsu, K.; Nakayama, T.; Nakagawa, T.; Yamamoto, T. A., J Alloys and Compounds 359(1-2), 46(2003).
- 6. Carpenter, E. E.; Calvin, S.; Stroud, R. M.; Harris, V. G., Chem of Mater, 15(17), 3245 (2003).
- 7. Teng, Xiaowei; Black, Donald; Watkins, Neil J.; Gao, Yongli; Yang, Hong., Nano Letters, 3(2), 261(2003).
- 8. M. Brust, D. Bethell, D. J. Schi!rin, and C. J. Kiely, Adv. Mater. 7, 795 (1995).
- 9. O'Connor, Charles J.; Carpenter, Everett E.; Sims, Jessica Ann. (USA). U.S. Pat. 2002068187