SYNTHESIS OF COBALT/GOLD BIMETALLIC HOLLOW MICROSPHERES AND ITS OPTICAL PROPERTIES

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Introduction

Galvanic replacement reaction is a very simple and effective method to prepare the particles with hollow interior [1]. Herein, the formation of hollow bimetallic microspheres with nanostructures is achieved by a galvanic replacement reaction, as exemplified by the reaction between Co microspheres and $HAuCl_4$ to make Au/Co hollow microspheres.

Experimental

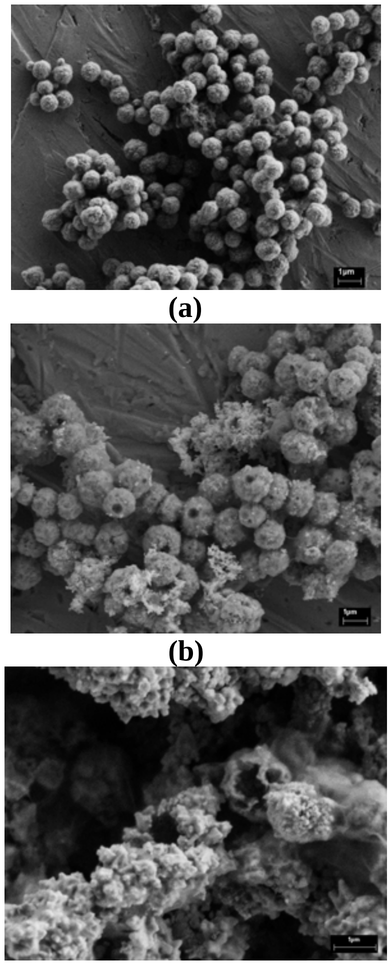
Cobalt particles were synthesized using the polyol process. Briefly: $CoCl_2.6H_2O$ (1mmol) was first dissolved in 40ml Ethylene Glycol (EG). The metal salt solution was subsequently added with 2 mmol of NaOH and 5 mmol of N_2H_4. This mixture was stir for 20 minutes before heated to the boiling point of EG. Cobalt particles were obtained after the mixture reflux for 30 minutes. Cobalt powder were collected by centrifuged and redispersed in the fresh EG with volume of 40 ml.

5 ml of $HAuCl_4$ (5mM) withdraw and injected into the cobalt suspension while stirring. The colour of the mixture gradually changed from yellow to pink. Mixture was stir for 1 hour. Finally the powders were obtained by centrifugation and washed several times with ethanol and keep in sample bottle for further characterizations. The procedures were repeated with 6 ml of $HAuCl_4$. These two samples were designated as GR 1 and GR 2 respectively.

X-ray Diffraction (XRD) was performed using D5000 siemens Diffractometer with a Cu-Kα (λ=0.154021 nm) radiation source. Micrographs were taken using Leo Supra 50 variable pressure field emission scanning electron microscope (SEM) and ZEISS Libra 120 transmission electron microscope (TEM). Electron Spectroscopic Imaging (ESI) was attached with TEM. UV visible (UV vis) measurement was conducted in the Perkin Elmer double beam spectrophotometer using a 10 mm optical path length quartz cuvette.

Results and Discussion

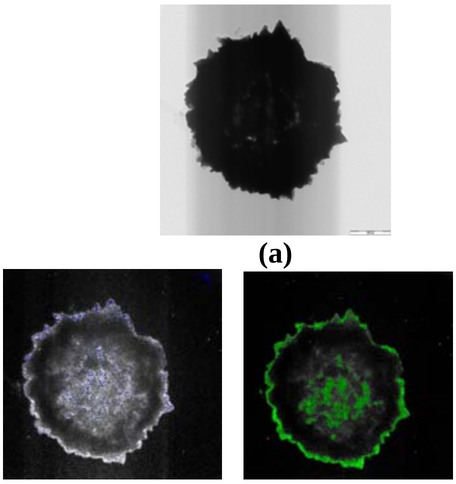
Fig.1 (a) shows the SEM micrograph for the cobalt particles prepared by polyol process and the particles that prepared through galvanic replacement were shown in the fig. 1 (b) and (c). It was clearly shows that some pinholes on the surface of the particles after galvanic replacement. This indicated that particles with hollow interior were formed.



(a) (b) (c)

Fig. 1 SEM micrographs for (a) pure cobalt particles (b) GR1 and (c) GR 2.

To further confirm the particles synthesized are hollow microspheres, TEM was employed. TEM image for the sample GR 2 was shown in fig. 2 (a), the contrast between the edge and the center of the particle suggests that it is a hollow structure. In order to confirm the composition of these microspheres, ESI was conducted and shown in fig. 2 (b) and (c).



(a)

(b) (c)

Fig. 2 (a) TEM for the sample with hollow structure, and ESI for the same sample (b) blue colour for element cobalt and (c) green colour for element gold. This proven that the shell is a mixture of gold and cobalt.

However, according to Leonardo and co-workers [2], ESI is suitable for thin samples, typically less than 50nm. Therefore, the particular particle with a diameter of around 700m is considered too large for the ESI. The part that colour can not be filled is due to the limitation of ESI. Nevertheless, result still can be obtained in the thinner part i.e. in the center and the edge of the particle.

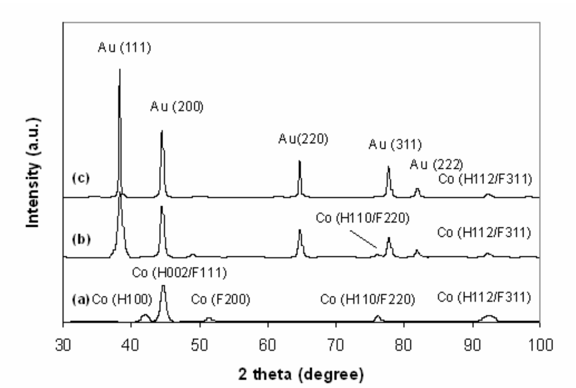


Fig. 3 XRD patterns of (a) cobalt particles (b) GR 1 and (c) GR 2. (H=HCP; F=FCC)

The XRD patterns of the powders were shown in fig. 3. Both face center cubic (F) and hexagonal (H) phases are found to presented in the same cobalt sample. For the hollow microspheres after galvanic replacement, there are five diffraction peaks can be assigned to (111), (200), (220), (311), and (222) planes which is belong to cubic phase Au particles. However, other peaks that located at about 92° and 76° also can be observed in the sample GR1 and GR2. These peaks are belonging to FCC and HCP cobalt. This further support that the microspheres with hollow interior are composed gold and cobalt particles.

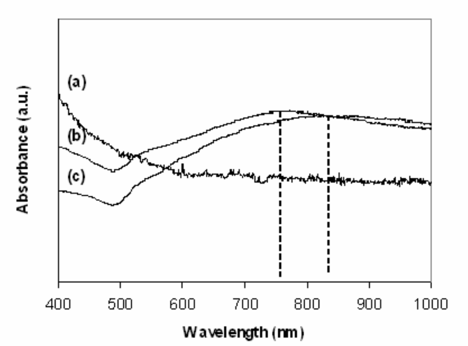


Fig. 4 UV vis spectrum of (a) cobalt particles (b) GR 1 and (c) GR 2.

The optical absorption spectrum of the hollow Au/Co spheres was shown in Fig. 4. Typical absorption peak for solid gold particles located at around 520nm. However the hollow spheres shows peak around 750 nm, and red shifted to around 830nm when the gold ions increased in the reaction. The shift of the peak might be due to hollow structure and many larger Au particles formed on the surface of the microspheres. The broadening of the absorption peak is due to the increase of the variation of Au concentration in the Au/Co particles when more gold ions were added in the solution during the reaction [3].

Conclusion

Au/Co bimetallic hollow spheres were successfully synthesized. The optical properties have been investigated. With the tunable optical properties and the present of the magnetic cobalt in the shell, these hollow particles may have some potential applications in reusable catalyst and optical sensor.

References

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