Synthesis and Characterization of Nanocomposites Using the Nanoscale Laser Soldering in Liquid Technique

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ABSTRACT

We have synthesized Au/CuO and Au/ZnO nanocomposites using the laser soldering technique. Their UV-VIS absorption and transmission were observed and the results indicated that the bandgap energies of the Au/CuO and Au/ZnO are significantly lower than those of pure CuO and ZnO.

1 INTRODUCTION

Since catalytic and sensing properties of semiconductor and metal nanoparticles (NPs) can be greatly enhanced if they are made in the form of nanocomposites, synthesis and characterization of such materials have attracted considerable attention recently. Commonly, metal nanocomposites can be prepared using simultaneous chemical reduction of metal salts or laser vaporization of metal alloys. The chemical reduction method needs harmful chemicals. The laser vaporization can offer the possibility of preparing clean nanoparticles but the technique suffers from low yields.

In this study we report the use of the laser ablation in liquid technique to prepare Au/CuO and Au/ZnO nanocomposites. The technique is based on laser irradiation of a solution containing previously prepared nanoparticles of two types: one type of particles that do not absorb the laser energy, and the other that have a strong absorption band whose energy coincides with the photon energy of the laser. The particles of the former type will be unheated and remain in their solid phase. The particles of the latter type can be heated above their melting point and melted to form nanocomposites with the remaining solid particles. With this approach, Au/Fe_3O_4 [1], Au/Pt [2], Au/TiO_2[3], Au/Ag [4], and Au/SnO_2 [5], Au/Ag and Co/Mo [6] have been successfully synthesized.

2 EXPERIMENT

We first prepared, in separate vessels, Au, CuO, and ZnO nanoparticles by laser ablating gold, copper, and zinc targets, respectively, submerged in water containing 0.1 % by weight chitosan. A picture of the present experiment is shown in Fig.1. The laser beam, (0.265 J/cm^2 at 1064 nm, 10 Hz rep rate and 5.5 ns pulse duration) from a single-mode, Q-switched Nd-Yag laser was horizontally aligned 10 mm below the liquid surface and the metal target was located at 50 mm from the cell window facing the laser.

Figure 1. A picture of the laser ablation apparatus

Two mixed solutions were prepared: one contains Au-CuO and the other contains Au-ZnO by simply mixing the previously prepared suspensions together. The mixed solutions were then irradiated by 532 nm laser pulses of 0.09 J/cm^2 continuously for 20 minutes. Since the gold particles had a strong plasmon absorption band near 520 nm, they were heated, melted to form alloys with CuO, and ZnO nearby. The synthesized nanocomposites were carefully sampled for UV-VIS spectroscopy characterization using an OceanOptics CHEMUSB4000 UV/VIS/NIR spectrometer

For the alloying process mentioned above to be effective, Au nanoparticles must be in contact or in a very close proximity with CuO, and ZnO nanoparticles. The latter requires high particle density. The problem with using high particle density is that, the penetration length of the laser beam is short and many Au particles might remain unheated. To avoid such the problem, we used suspensions with low particle density and the mixed solutions were stirred at 65 RPM for 2 hours to bring the Au particles into contact with CuO and ZnO particles before being irradiated.

3 RESULTS AND DISCUSIONS

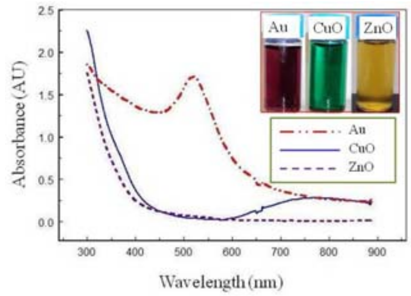

Figure 2. UV-VIS spectra of Au, CuO, and ZnO

Typical Au, CuO, and ZnO nanoparticles suspensions and their corresponding UV-VIS absorption spectra are shown in Fig. 2. The absorption spectrum of ZnO nanoparticles was significant in the wavelength region that is shorter than 450 nm and it decays quickly toward the longer range. The absorption here can be attributed to the direct/indirect transition of the ZnO electrons from the interbands residing in the deep level of the valence band. For Au and CuO suspensions, such similar transitions were observed. In addition, we also observed two intense abruption peaks: one occurred at about 520 nm for Au nanoparticles and the other around 750 nm for CuO nanoparticles. These absorption peaks can be attributed to the transition of the electrons of these materials from the upper levels of the valence band. This is also known as surface plasmon resonance peak which arises from the coherent oscillation of the Au electrons and CuO electrons by the interacting electromagnetic field.

The UV-VIS spectra of the mixed Au- ZnO nanoparticles suspensions and Au-CuO nanoparticles suspensions before and after being irradiated by 532 nm laser pulses are shown in Fig. 3. The results shown here indicated that, before irradiation the absorption spectra of the mixed suspensions exhibited a similar behavior to that of the absorption spectra that would be obtained by summing the individual absorption spectrum shown in Fig. 2. The two plasmon peaks were seen to be slightly broadened but they still located at the same locations as those shown in Fig. 2. After irradiation, however, the plasmon peak due to Au nanoparticles almost disappeared indicating a significant spectral change of the suspensions after it was irradiated. Similar spectral changes were also reported by Kawaguchi et al. [1] on gold/iron oxide nanocomposites, Mafune et al. [2] on the laser nanosoldering of Au-Pt nanoparticles, and Fazio et al. [3] on the the formation of Au/TiO_2 nanostructures. In our case, the spectral change must be due to the fact that, during irradiation, the gold nanoparticles were heated, melted, and different structured nanocomposites are formed when the melted gold got soldered to the ZnO as well as CuO nanoparticles. Otherwise, if the gold nanoparticles were just simply fractured into smaller sizes due to 532 nm irradiation, a sharper and blue-shifted plasmon peak would have been seen in the absorption spectrum.

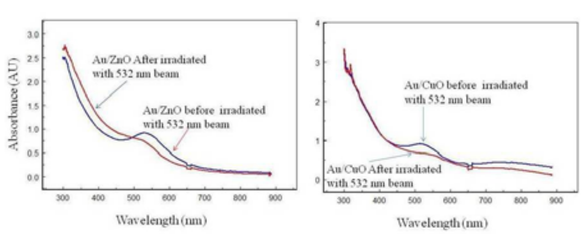

Figure 3. UV-VIS absorption spectra of Au-CuO, Au-ZnO nanoparticles suspensions before and after irradiation by 532 nm laser pulses

The optical bandgap energies of ZnO, CuO. Au/ZnO, and Au/CuO nanocomposites are calculated using the Tauc equation as $(\alpha h\nu)^n = h\nu - Eg$. Where α is the aborption coefficient, h is the Planck constant, ν is the incident photon frequency, Eg is the energy bandgap, and n is the exponent that determines the type of the electronic transition and its values of ½ representing the indirect transition and 2 for direct transition. In Fig. 4 we plotted $(\alpha h\nu)^2$ versus $h\nu$ and obtained a perfect linear relationship between $(\alpha h\nu)^2$ and the incident photon energy $h\nu$. This indicates that the optical bandgaps of these nanoparticles are due to a direct allowed transition. The optical bandgap energies are determined from the intercept of the straight line with the $h\nu$-coordinate. The result shown here indicates that the bandgap energies for ZnO and CuO could be reduced significantly if they are made in the form of nanocomposites.

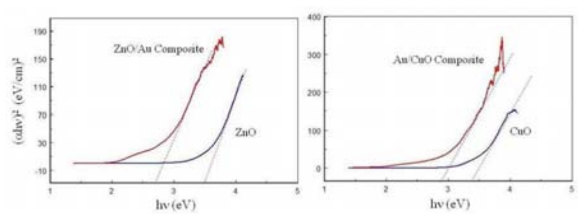

Figure 4. Bandgap energies of CuO and ZnO nanoparticles and Au/CuO and Au/ZnO nanocomposites

4 CONCLUSIONS

We have conducted a study on the synthesis of metal nanocomposites by using the laser soldering in liquid technique. Our results on Au/CuO and Au/ZnO showed that the bandgap energies of CuO and ZnO can be tuned and significantly reduced if these metal oxides are fused with gold in the form of nanocomposites.

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