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Synthesis and Optical Properties of Cu_2O and Au-Cu_2O Core-shell Particles

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Abstract: Cuprous oxide (Cu_2O) and Au-Cu_2O core-shell nanoparticles were successfully synthesized using the chemical reduction method. The morphology of the synthesized pure Cu_2Oparticles can be controlled by varying the amount of reducing agent $NH_2OH.HCl$. Due to their similar crystal structure and relatively small lattice mismatch Cu_2O particles are nucleated and locally undergo an epitaxial growth on the surface of the multi-faceted Au seed resulting in a stellated icosahedra Au-Cu_2O core-shell particle. The extinction spectrum of Cu_2O particles offew hundred-nm in size is dominated by light scattering, while that of the stellated icosahedra Au-Cu_2O core-shell particles exhibits the interband absorption of the Cu_2O shell only. The interband absorption peak undergoes a blue shift as the shell gets thinner. No prominent SPR of the Au nanocore was observed due to a rather thick Cu_2O shell.

Keywords: Cu_2O nanoparticle, Au-Cu_2O core-shell nanoparticle, Surface Plasmon Resonance (SPR).

1. Introduction

Cuprous oxide is one of the earliest discovered direct band gap semiconductor with a band gap energy of 2.1 *e*V [1, 2], which makes it a promising material for applications in various fields such as sensor [3], photocatalysis [4], photoactivated water splitting [5] and lithium ion batteries [6]. In the last decade, Cu_2O nanostructures have attracted significant attention because many interesting properties were enhanced greatly due to surface and quantum effects. Different micro and nanostructures of Cu_2O such as nanocube [7], octahedral [8] and other symmetrical structures have been synthesized and studied but nano-heterostructures of Cu_2O are only studied recently. Such heterostructures have shown many promising applications in photo-catalysis and electrochemical applications.

In this report, Cu_2O and Au-Cu_2O core-shell particles were synthesized by chemical reduction method. The synthesized samples were then subjected to characterizations such as XRD, FESEM, TEM and optical absorption analysis.

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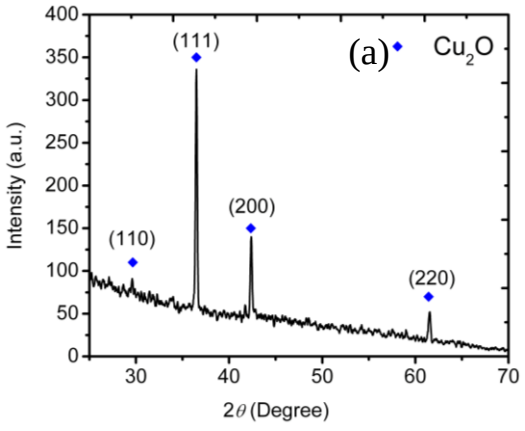
2. Experimental

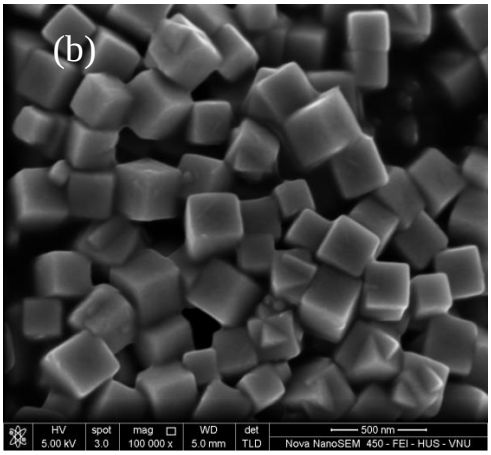
Spherical gold nanoparticles were synthesized and then used as the core for the fabrication of Au-Cu_2O core-shell particles. The synthesis procedure of the gold nanoparticles was reported in detail elsewhere [9]. Cu_2O and Au-Cu_2O core-shell nanoparticles were fabricated using the technique reported in [10-13]. In a typical synthesis procedure of Cu_2O particles, an amount of 0.87 g Sodium Dodecyl Sulfate (SDS - $C_{12}H_{25}NaO_4S$) was dissolved in (9.05 – *x*) ml of DI water. Volumes of 0.1 ml of 0.1 M $CuCl_2$, 0.25 ml of 1.0 M NaOH were then added under stirring. After introducing a volume of *x* ml of 0.2 M $NH_2OH.HCl$, the mixture was left undisturbed for an hour at room temperature. The as-synthesized samples were then centrifuged at 5000 rpm in 5 minutes and washed with ethanol to remove the surfactant. Finally, the collected precipitate was suspended in ethanol. Au-Cu_2O core-shell nanoparticles were synthesized in a similar procedure with a volume of 0.1 ml of gold nanospheres being added to the mixture just before introducing a volume of *x* ml of 0.2 M $NH_2OH.HCl$.

The crystal structure of the synthesized samples was characterized by a Siemens D5005 XRD diffractometer. The morphologies of the synthesized nanoparticles were observed by a Nova nanoSEM 450, a JEOL JEM-1010 transmission electron microscopy (TEM), and a FEI Tecnai $G^2$20 FEG (HRTEM). The absorption spectra of the samples were measured at room temperature using a Shimadzu UV-Vis-2450PC spectrometer.

3. Results and discussion

Figure 1.a. shows a typical XRD pattern of the synthesized Cu_2O samples. The pattern exhibits four well-resolved diffraction peaks at 29.65°, 36.45°, 42.35° and 61.42° which can be indexed to those of the (110), (111), (200) and (220) planes of the fcc phase of cuprous oxide crystal structure (PDF 05-0667, ICDD). The lattice constant *a* was estimated to be 4.077 ± 0.002Å, which is in good agreement with the standard value of 4.079 Å given in PDF 05-0667, ICDD. Typical FESEM images of the Cu_2O particles synthesized by using different amount of reduction agent $NH_2OH.HCl$ are shown in Fig.1.b-d. The amount of reducing agent $NH_2OH.HCl$ plays an important role in shaping the Cu_2O particles. As the volume of 0.2 M $NH_2OH.HCl$ increases from 0.15 ml to 0.30 ml and 0.45 ml, the morphology of the Cu_2O particles changes from cubic to truncated cube and truncated octahedral, respectively, as shown in Fig.1.b-d. The average size of cubic, truncated cube and truncated octahedral Cu_2O particles was estimated using the FESEM images to be about 220 ± 20 nm, 200 ± 20 nm and 280 ± 18 nm, respectively.





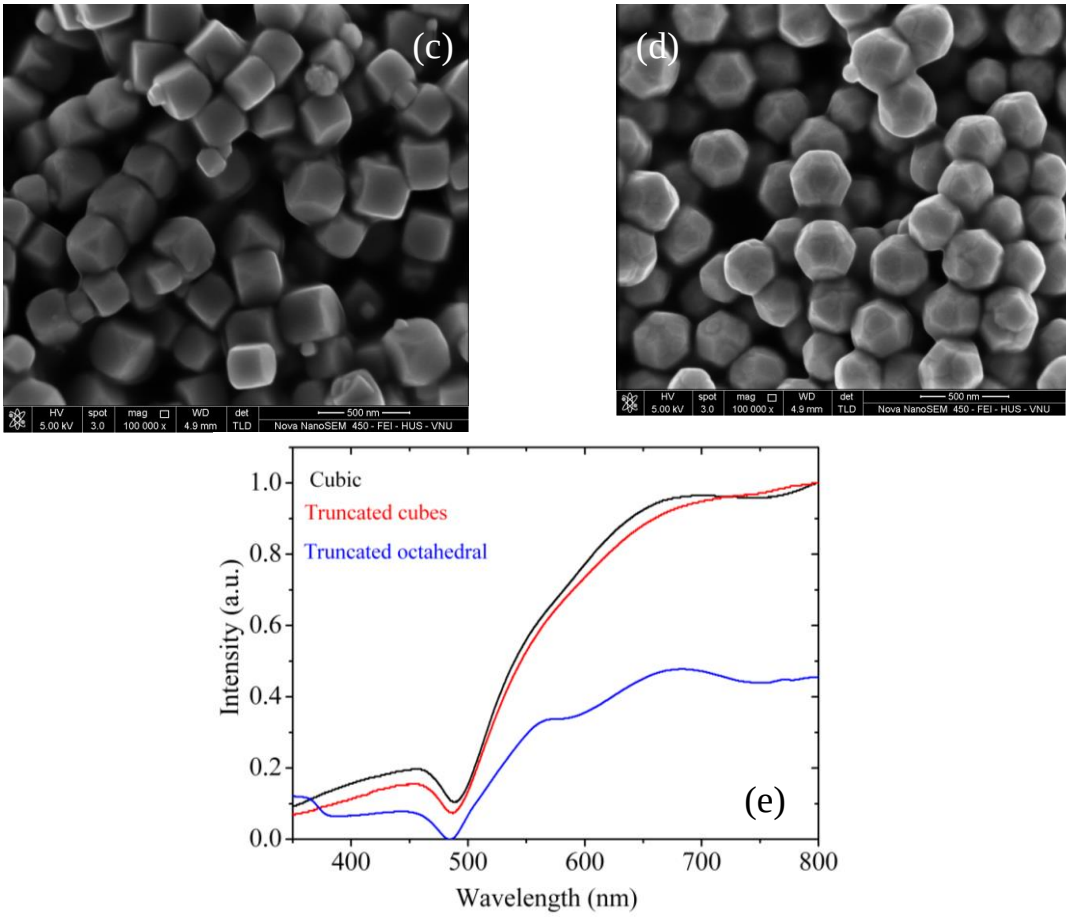


Fig. 1. The typical XRD patterns (a), FESEM images of Cu_2O synthesized using 0.15 ml (b), 0.30 ml (c) and 0.45 ml (d) of 0.2 M $NH_2OH.HCl$, extinction spectrum of the synthesized Cu_2O particles (e).

The extinction spectrum of the synthesized Cu_2O particle samples are shown in Fig.1.e. Due to a rather large size of Cu_2O particles, their extinction spectrum is dominated by strong and broad light scattering bands in the red and near infrared wavelength region. In the region below 500 nm, the extinction spectrum exhibits a broad excitation interband absorption band at around 550 nm [14]. The geometry-dependent nature of the optical property of the synthesized Cu_2O particles is evident as the extinction spectrum of the truncated octahedral Cu_2O particles is slightly deference from those of the cubic and truncated cube ones.

The synthesized gold nanoparticles were used as the core of the Au-Cu_2O core-shell nanoparticles. Figure 2.a-c show typical XRD pattern, TEM image and UV_Vis spectrum of the synthesized Au nanoparticles, respectively. The XRD pattern exhibits two diffraction peaks at 38.24^o and 44.45^o, which match well with the (111) and (200) diffraction peaks of the fcc phase of metallic gold structure (PDF 04-0784, ICDD). As shown in Fig.2.b., the synthesized Au nanoparticles seem to be quasi-spherical in shape and their average size was estimated to be 16.8 ± 1.9 nm. The UV_Vis spectrum of the synthesized Au nanoparticles exhibits only one absorption peak at about 520 nm corresponding to the dipole Surface Plasmon Resonance (SPR) of the symmetric spherical gold nanoparticles [9].

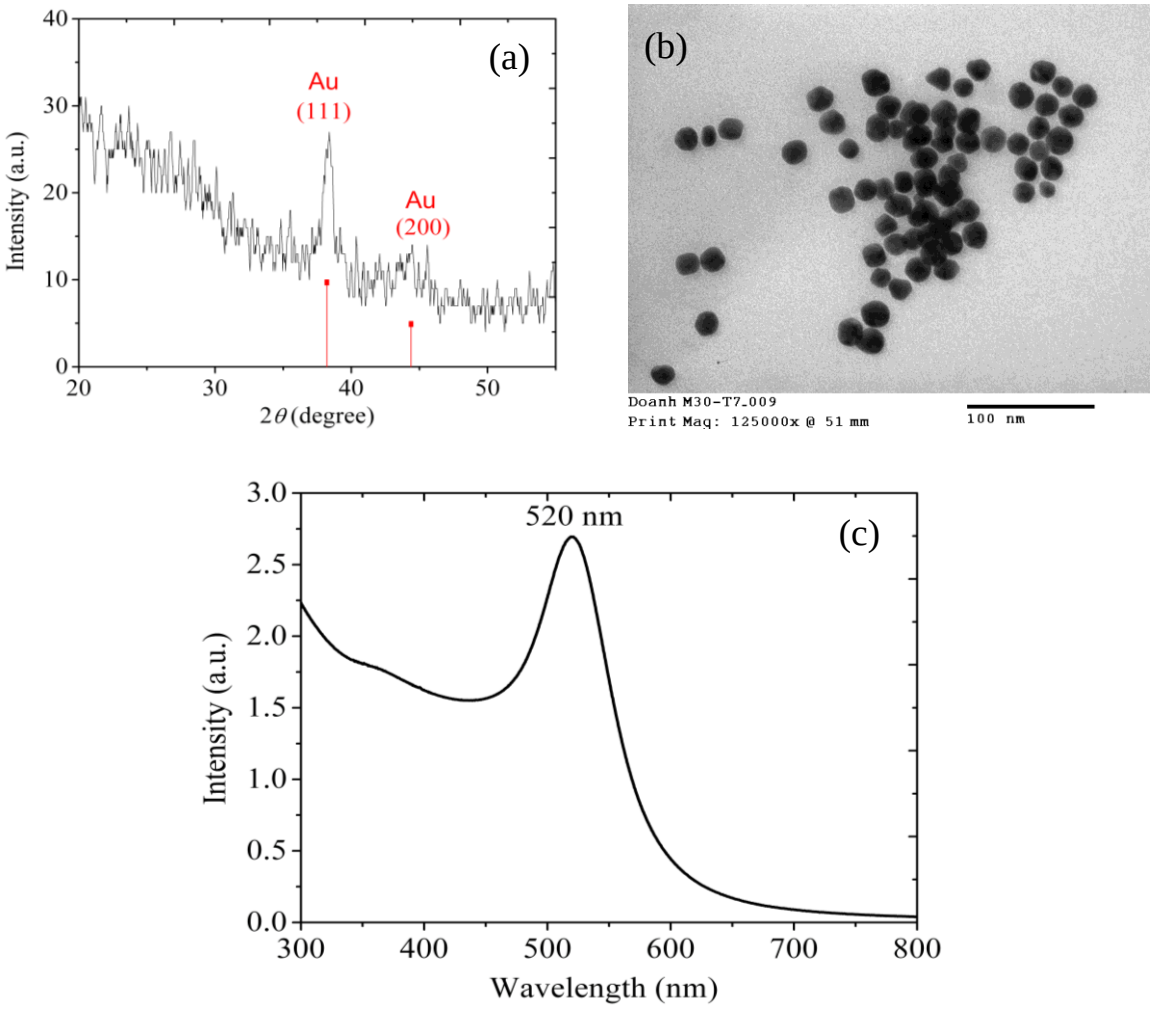
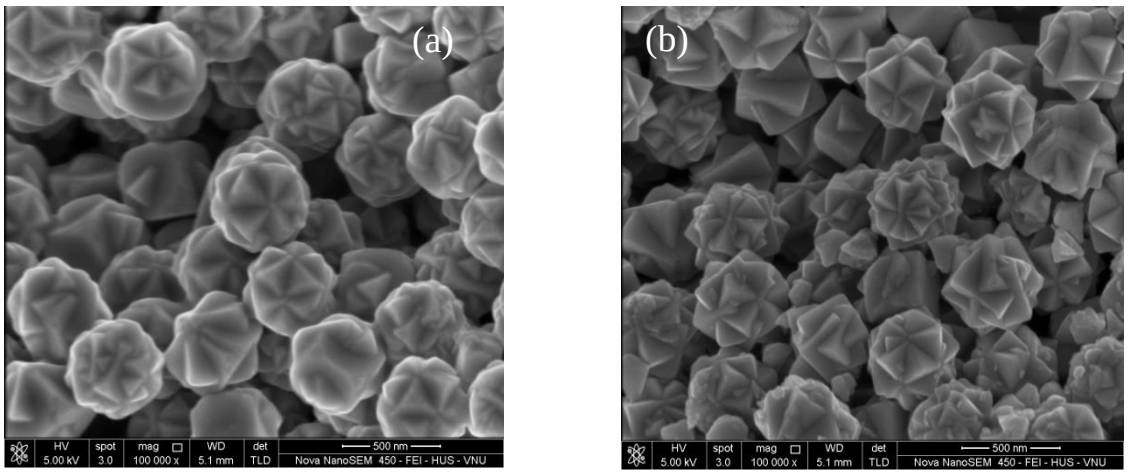


Fig. 2. The typical XRD patterns (a), TEM image (b), and UV_Vis spectrum (e) of the synthesized Au nanoparticles.



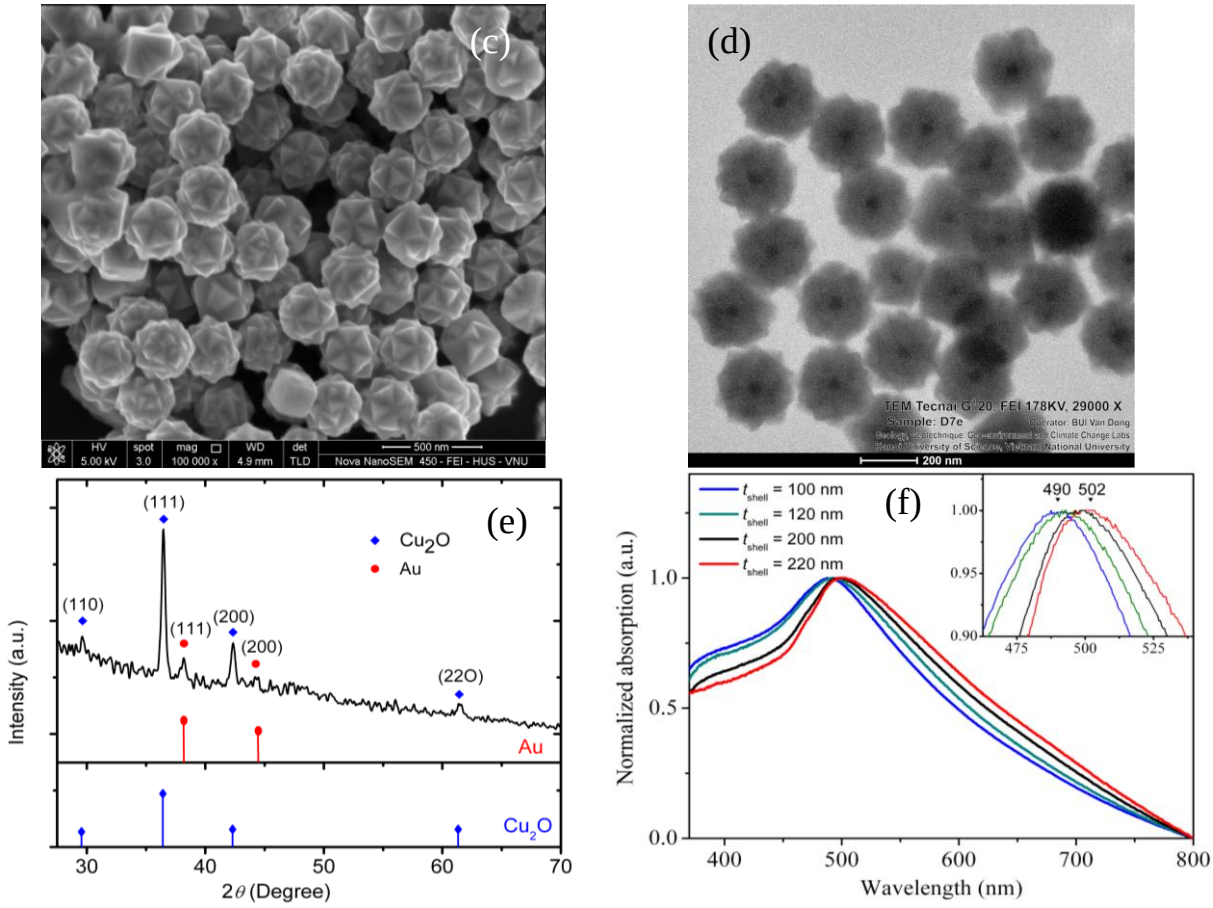


Fig 3. The typical FESEM images of Au-Cu_2O core-shell particles with different shell thickness t_{shell} of 220 nm (a), 200 nm (b) and 120 nm (c), TEM image of Au-Cu_2O core-shell particles with shell thickness t_{shell} of 100 nm (d), the XRD patterns (e) and extinction spectrum (f) of the synthesized Au-Cu_2O core-shell particles.

The morphology of the synthesized Au-Cu_2O core-shell nanoparticles was examined using the FESEM and TEM images. Figures 3.a-d show typical FESEM and TEM image of Au-Cu_2O core-shell particles synthesized by using different amount of reduction agent $NH_2OH.HCl$. The actual shape of Au nanoparticles has a strong influence on shaping the morphology of the Cu_2O shell [10]. Although the Au nanoparticles appeared as quasi-spherical particles, they are best described as multi-facetedtruncated particles [9]. Due to the similar crystal structure and relatively small lattice mismatch of 4.5 % between cuprous oxide and gold, Cu_2O particles are nucleated and then locally undergo an epitaxial growth only on the surface of the Au seed resulting in a rough shell of Cu_2O [11-14]. The SEM images, shown in Figs.2.a-c., reveal the stellated icosahedra morphology of the synthesized Au-Cu_2O particles. The TEM image shown in Fig.3.d. clearly indicates that all the particles possess the core-shell structure with only one Au core at the center covered entirely by a rough Cu_2O shell. No particle with multiple cores or coreless was observed. The average thickness t_{shell} of the Cu_2O shell of the synthesized Au-Cu_2O core-shell particle samples shown in Figs.3.a-d. was estimated to be 220.0 ± 7.0 nm, 200.0 ±7.0 nm, 120.0 ± 8.0 nm and 100.0 ± 8.0 nm, respectively.

Figure 3.e. shows a typical XRD pattern of the synthesized Au-Cu_2O core-shell particles. The pattern exhibits several well-resolved diffraction peaks. The diffraction peaks at 29.62 ^{o}, 36.46^o, 42.34^o and 61.42^o can be indexed to those of the (110), (111), (200) and (220) planes of the fcc phase of cuprous oxide crystal structure (PDF 05-0667, ICDD), respectively. The other diffraction peaks at 38.21^o and 44.40^o match well with the (111) and (200) diffraction peaks of the fcc phase of metallic gold structure (PDF 04-0784, ICDD). Since the Cu2O shell is in order of a few hundred-nm thick covering entirely the Au nanocore of about 16.8 ± 1.9 nm in diameter, the intensities of the diffraction peaks of Cu_2O shell are much stronger than those of Au nanocores.

The optical properties of the synthesized Au-Cu_2O core-shell particles were investigated by using the UV_Vis spectrum. Figure 3.f. shows the absorption spectrum of the synthesized Au-Cu_2O core-shell particles. The spectrum exhibits typical interband absorption band of Cu_2O shell without any sharp excitonic absorption peak. As the thickness t_{shell} of the Cu_2O shell decreases from about 220 nm to 100 nm, the interband absorption peak undergoes a blue shift from 502 nm to 490 nm in good agreement with the results reported elsewhere [15]. No prominent Surface Plasmon Resonance (SPR) absorption peak of Au nanoparticles is observed due to the fact that the Cu_2O shell thickness t_{shell} is too thick.

4. Conclusions

Cu_2O and Au-Cu_2O core-shell particles were successfully synthesized using chemical reduction method. The amount of reducing agent $NH_2OH.HCl$ has a significant influence on the morphology of the Cu_2O particles. By varying the amount of $NH_2OH.HCl$, several morphologies of the Cu_2O particles such as cube, truncated cube and truncated octahedral can be precisely fabricated. The extinction spectrum of Cu_2O particles of several hundred-nm in size is dominated by light scattering in the red and near infrared region.

Due to their similar crystal structure and relatively small lattice mismatch of 4.5%, Cu_2O particles are nucleated and then locally undergo an epitaxial growth on the surface of the multi-faceted Au seed resulting in a rough shell of Cu_2O. Only the characteristic interband absorption band of the Cu_2O shell is observed in the absorption spectrum of the synthesized Au-Cu_2O core-shell particles. The absorption band undergoes a blue shift from 502 nm to 490 nm as the shell thickness decreases from 220 nm to 100 nm. Au-Cu_2O core-shell particles with a much thinner shell would be necessary to investigate the SPR of Au nanocores.

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