Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 2, No. 2 (2013), 379-384

International Journal of Bio-Inorganic Hybrid Nanomaterials

Structural and Optical Behavior of Cu Doped Au Nanoparticles Synthesized by Wet-Chemical Method

Parivash Mashayekhi[1*], Nazanin Farhadyar[2]

[1] *Ph.D. Students, Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran*

[2] *Assistant Professor, Department of Chemistry, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran*

Received: 7 July 2013; Accepted: 12 Sepember 2013

ABSTRACT

The nanoparticles of gold doped with various percentage of copper (Cu 10%, 25%, 75%) were synthesized by wet-chemical method at room temperature. Copper (II) sulfate and gold (III) chloride trihydride was taken as the metal precursor and ascorbic acid as a reducing agent and anhydride maleic as surfactant. The reaction is performed with high-speed stirring at room temperature under nitrogen atmosphere. X-ray diffraction (XRD), Scanning electron microscopy (SEM) and DRS UV-Vis spectroscopy have been used for the characterization of the samples. Moreover the X-ray diffraction results indicated that the synthesized Cu doped Au nanoparticles had a pure single phase face-centered cubic structure and the average particle sizes were between 5.43 - 12.6 nm. SEM images shows a spherical shape and dopant Cu influenced the particles size of the powder.

Keyword: Anhydride maleic; Wet-chemical; Optical properties; Cu nanoparticle doped; Surfactant.

1. INTRODUCTION

In an analogous fashion to traditional bulk metallurgy, some properties of bimetallic nanoparticles can be modified by changing their compositions. However, the phenomena which one expects here are not simply related to what happens when the two corresponding metallic elements are mixed to form a bulk alloy. That is, the metallurgy for a certain bimetallic system at the bulk scale and at the nano-scale may be somewhat different from each other. In the bulk, Au can be mixed with Pt to form a continuous solid solution at high temperature (although these two species are immiscible at low temperatures) whereas bimetallic Au-Pt nanoparticles of around 20 nm in size exhibit a layer segregation between Au and Pt when annealed at 600°C [1]. The interaction between the two metals plays an important role in the properties of bimetallic nanoparticles. These characteristics are

---

(*) Corresponding Author - e-mail: prmashayekhi@gmail.com quite sensitive to the medium in which the particles are studied. This is because the elemental arrangements of bimetallic nanoparticles depend strongly on which method is used to produce them [2], and the system of the two metals is generally not in thermodynamic equilibrium. Moreover, surface passivating ligands, which are normally employed to prevent particle aggregation, may also affect the relation between the metallic components [2]. One of the most interesting kinds of element arrangement for bimetallic nanoparticles is the doping. The doping of transition metal ion such as Mn, Cu, Co etc. opens up possibilities of forming new class of material and new properties of the material are expected [3]. Doping the impurities into nanomaterials is an effect approach for tuning the electronic, optical, mechanical and magnetic properties of matrix nanomaterials [4-8]. The growth rate of nanocrystals is strongly depending upon doping concentration, capping agent concentration and synthesis temperature. In order to understand better these properties of doped nanoparticles, the choice of sample preparation method is therefore of greatest importance. The preparation method should be the one that can compel the doped ions into substitutional site and have atomic scale homogeneous mixing with host atoms without the formation of secondary phases, nanoclusters etc. For the same, extensive research efforts have been carried out worldwide to synthesize nano-sized particles using various methods [9] such as thermal decomposition, chemical vapor deposition, sol gel, spray pyrolysis, micro emulsions and wet-chemical. Among these synthesis methods, wet-chemical method compared with other traditional methods provides a simple growth process for large scale production, and which of course is an efficient and inexpensive way. The distinctive feature of this process is that an atomic scale homogeneous distribution of doped ions the host matrix can be achieved.

2. EXPERIMENTAL

2.1. Material

Gold (III) chloride trihydrate ($HAuCl_4.3H_2O$, 99.9%) was obtained from sigma- Aldrich. Copper (II) sulfate pentahydrate salt ($CuSO_4.5H_2O$, 98%), ascorbic acid ($C_6H_6O_6$, 99.7%), sodium hydroxide NaOH (>98%), anhydride maleic ($C_4H_2O_3$) were obtained from Merck. All the chemical materials were used without further purification. Deionized water was purified for use during the synthesis.

2.2. Method

All glassware were cleaned with an aqua regia solution (3:1, HCl: HNO_3), and then rinsed. In this work, at first time, we prepared four solutions namely 0.05 M $HAuCl_4.3H_2O$ (Solution A), 0.0087 M $CuSO_4.5H_2O$ (Solution B), 0.026 M $CuSO_4.5H_2O$ (Solution C), 0.078 M $CuSO_4.5H_2O$ (Solution D). These were used inpreparing Cu doped Au precursor solutions with different ratios as shown in Table1. Combination of solution A and B is labeled as concentration 1, solution A and C is labeled as concentration 2, and solution A and D is labeled as concentration 3. 0.001 M anhydride

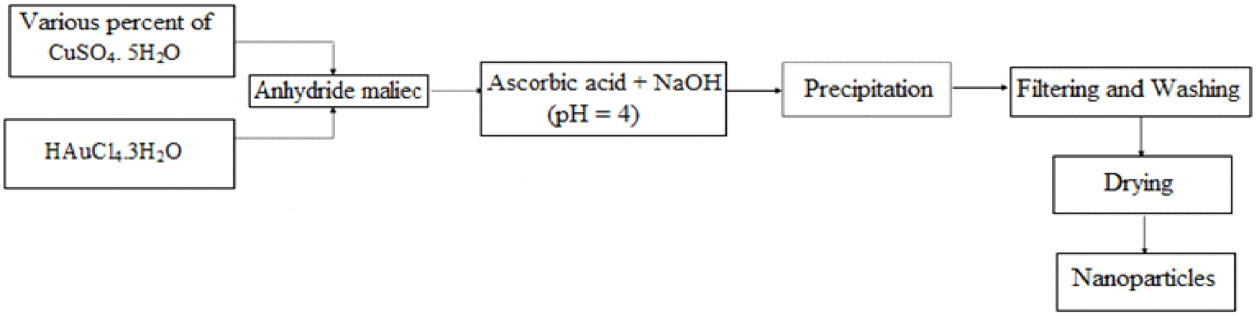


Figure 1: *Schematic of samples preparation using Wet-chemical.*

maleic polymer solution was used throughout the synthesis. Then, with constant stirring and under N_2 atmosphere mixture ascorbic acid (0.2 M) and sodium hydroxide (0.2 M) added to the synthesis solution. Color change occurred in the aqueous phase to black. When the solution color did not change, the reaction was ceased. After separation from the mixed solution, the precipitation washed 3-4 times by de-ion water and the 2-3 times by ethanol.

The powder of Cu doped with Au nanoparticles was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) and DRS UV-Vis spectroscopy. X-ray powder diffraction (XRD) analysis was performed on a D5000-siemens with Cu Kα radiation (λ = 1.541Å) using a 30 KV operation voltage and 40 mA current. Scanning electron microscopy (SEM) images were obtained using a LEO 1430 VP microscopy. DRs UV-Vis spectra of the synthesized materials were recorded in the scan range 200-1000 nm, using a UV-Visible spectrophotometer (S-4100, scinc Korea).

3. RESULTS AND DISCUSSION

3.1. SEM Characterization

The SEM image of 10-50% Cu doped Au nanoparticles is shown in Figure 2. In addition, more uniform and homogeneous distribution of nanoparticles was obtained by doping Cu into the Au nanoparticles. All the nanoparticles exhibited spherical morphology. Moreover the increasing percent copper leads to the decreasing grain size.

3.2. XRD Diffraction analysis

The XRD patterns of the prepared samples were recorded by an X-ray diffractometer are shown in Figure 3. It is noteworthy that no secondary diffraction peaks were detected in the XRD patterns. All the diffraction peaks can be well indexed to face-centered cubic (FCC) Au according to the JCPDS card (NO.1-1172). Four pronounced Au diffraction peaks (111), (200), (220) and (311) appear at 2θ = 37.36°, 44.70°, 63.94° and 76.94° respectively. The four most intense peaks of the XRD pattern of sample show a slight shifting of the center of the diffraction peaks toward a lower angle. The shifting of the XRD lined suggests that Cu has been successfully substituted in to Au host structure at the Au site.

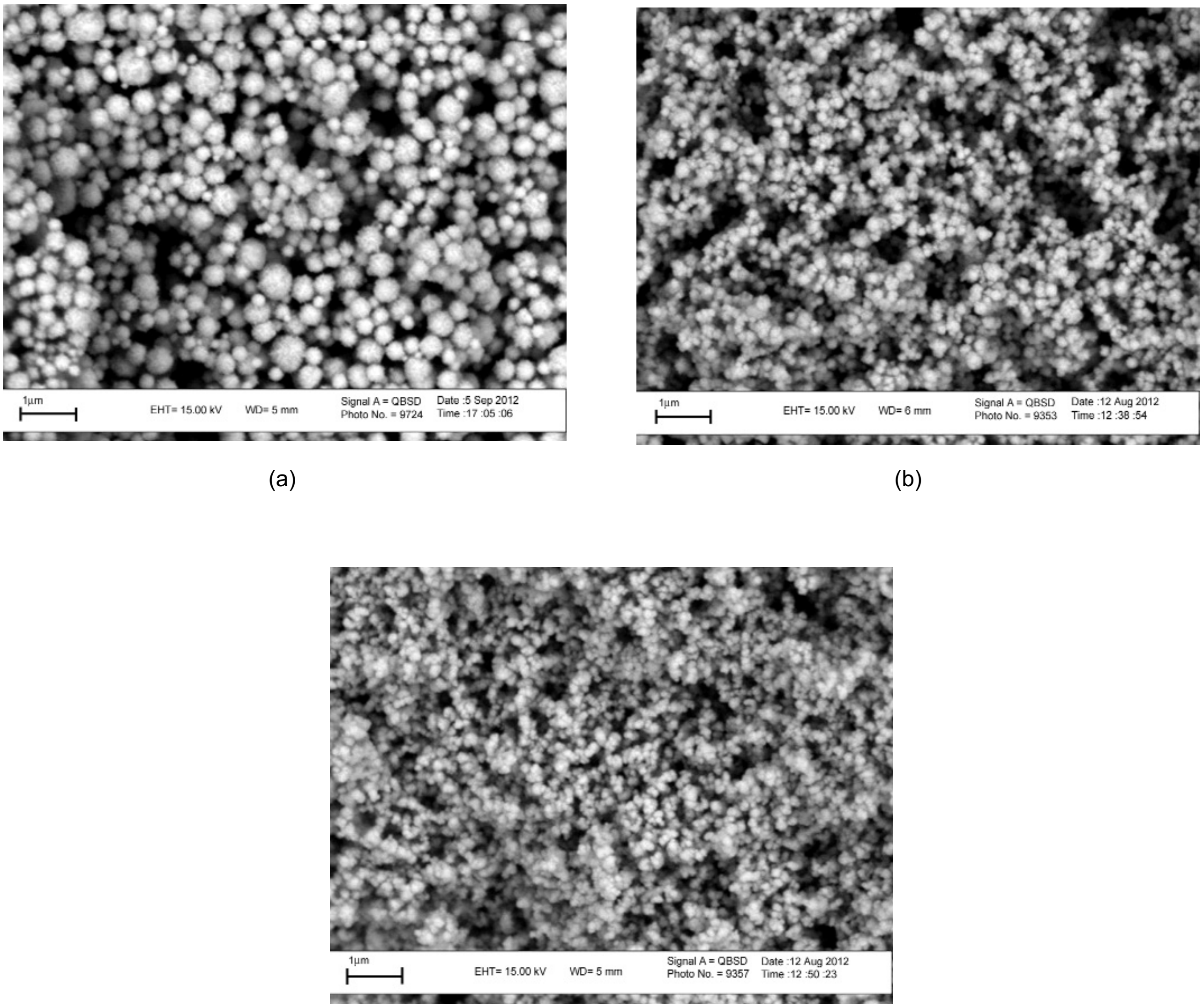
The crystalline size has been estimated from the broadening of the first diffraction peak using Debye-Scherrer formula:

$$D = 0.9\lambda / \beta\cos\theta \qquad (1)$$

Where D is crystallite size, θ is Bragg angle, λ is wave length and β is Full-width at half maximum of peak. The grain size of the samples was calculated from Eq. (1) using (111) reflection in XRD pattern. The average particle size of Cu: Au nanoparticles have been obtained between 5.43 - 12.6 nm.

***Table 1:** Detailed experimental parameters and dopant amounts for preparation of copper doped with Au nanoparticles.*

Morphology	Concentration of $CuSO_4.5H_2O$ (Mol L^{-1})	Concentration of $HAuCl.3H_2O$ (Mol L^{-1})	Doping percentage of Cu %	Concentration of ascorbic acid (Mol L^{-1})	Surfactant (the type and the Concentration)	Sediment color
Spherical	0.0087	0.05	10%	0.2	Anhydride maleic (0.001)	Black
Spherical	0.026	0.05	25%	0.2	Anhydride maleic (0.001)	Black
Spherical	0.078	0.05	50%	0.2	Anhydride maleic (0.001)	Black



(a)

(b)

(c)

Figure 2: *SEM image of the Cu doped Au nanoparticles: (a) 10%, (b) 25% and (c) 50%.*

Table 2: *Size of Cu doped Au nanoparticles with various doping percent copper at temperature.*

%Doping of Cu	Average size of particles for samples
10%	12.6
25%	9.82
50%	5.43

3.3. DRS UV-Vis spectra

The DRS UV-Vis of Cu doped Au nanoparticles prepared at various dopant percentages are shown in Figure 4. It exhibits an intense peak centered at 375 nm and another peak with low intensity at 475 nm as shown in Figure 4. Optical absorption measurements indicate blue shift in the absorption band edge with increase dopant percentages. It is clearly shown in Figure (4) the absorption edges reveal a large shifting (30 nm) with increase dopant percentage (Cu).

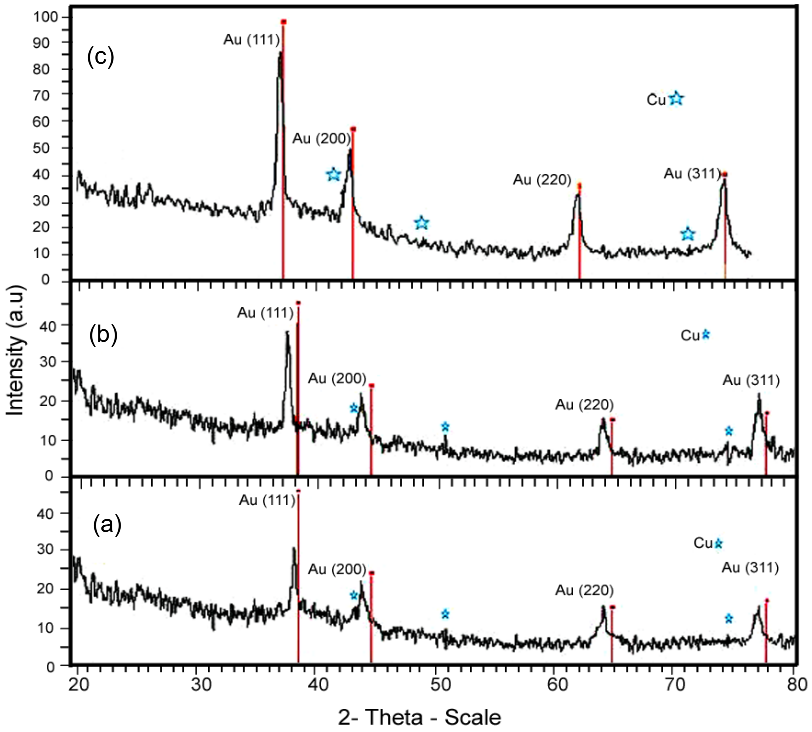


Figure 3: *X-ray diffraction patterns of (a) 10% Cu, (b) 25% Cu and (c) 50% Cu.*

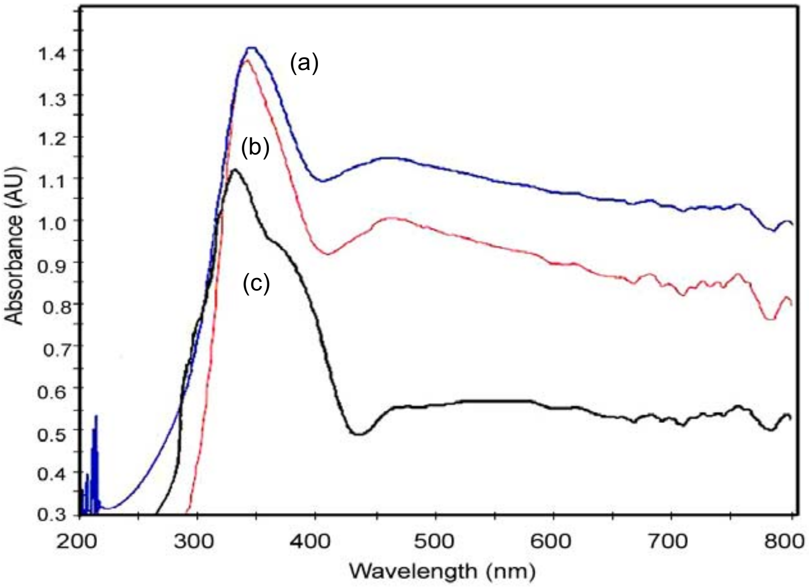


Figure 4: *Optical absorption spectrum of Cu doped Au nanoparticles (a) 10%, (b) 25% and (c) 50%.*

4. CONCLUSIONS

Cu doped Au nanoparticles were synthesized using wet-chemical method. We used anhydride maleic as surfactant agent. The formations of the nanoparticles were confirmed by XRD peaks and result shows that the samples have cubic phase. The effect of doping percent of samples has been studied. In addition, the Cu doping can control size of resulting nanoparticles.

REFERENCE

1. Braidy N., Purdy G.R., and Botton G.A., *Acta Materialia*, **56** (2008), 5972.
2. Ferrando R., Jellinek J., and Johnston R.L., *Chem. Rev*., **108** (2008), 845.
3. Dong L.S., FU X.F., Wang M.W., Liu C.H., *J. Lumin.*, **87-89** (2000), 538.
4. Cheng C., Xu G., Zhang H., Wang H., Cao J., Ji H., *Mater. Chem. Phys.*, **97** (2006), 448.
5. Quan Z., Wang Z., Yang P., Lin J., *J. Fang, Inorg. Chem.*, **46** (2007), 1354.
6. Park K., Yu H.J., Chung W.K., Kim B.J., Kim S.H., *J. Mater. Sci.*, **44** (2009), 4315.
7. Chandra B.P., Baghel R.N., Chandra V.K., *Chalcogenide Lett*., **7** (2010), 1.
8. Murugadoss G., Rajamannan B., Madhusudhanan U., *Chalcogenide Lett.*, **6** (2009), 197.
9. Wang J., Gao L., *Inor. Chem. Com.*, **6** (2003), 877.