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SYNTHESIS OF Au AND Au/Cu ALLOY NANOPARTICLES ON MULTIWALLED CARBON NANOTUBES BY USING MICROWAVE IRRADIATION[1]

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Abstract
Gold nanoparticles and gold-copper alloy nanoparticles were synthesized by reduction of chloroauric acid ($HAuCl_4.xH_2O$) and co-reduction of chloroauric acid ($HAuCl_4.xH_2O$) and Copper(II) acetate [$(CH_3COO)_2Cu.H_2O$] by ethylene glycol through microwave irradiation technique. In this reaction ethylene glycol used as a solvent and also reducing agent. The cetyltrimethyl ammonium bromide (CTAB) used as surfactant. Au nanoparticles and Au-Cu naanoparticles on the surface of multiwalled carbon nanotube also producd by using same procedure. The XRD analysis confirmed the formation of Au and Au-Cu alloy nanoparticles on multiwalled carbon nanotubes(CNTs). The morphology and size of the particles were examined by the transmission electron microscopy. The EDS analysis on individual particles confirmed that the presence of two metals in a particle in case of alloy nanoparticle. The results presented here show that a variety of well defined metal and metal alloy nanoparicles can be produced by using the microwave polyol process with in a short period of time.
Key words: CNTs; Metal alloys; Gold-Copper; Hybrid nanoparticles.

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1 INTRODUCTION

Nanometer sized metal and metal alloy nanoparticles have attracted considerable attention in recent years.[1] For small metallic particles, the quantum size effect is manifested in terms of particle-size dependence on electronic susceptibility and magnetic relaxation.[2] Research on the synthesis of metal nanoparticles and their application in physical,[3] chemical,[4] biological,[5] medical,[6] magnetism[7] and photoelectronics[8] is increasing tremondousely. The high surface area and exceptional surface activity displayed by these particles, make them ideal catalyst for many reactions.[9] Metal nanoparticles also used in advanced materials such as quantum dots and in miniaturization of electronic devices. The intrinsic properties of metal nanoparticles depend on its size, shape, composition, crystallinity and structure (solid versus hollow). In principle, any one of these paprameters can be controles to fine-tune the properties of these nanoparticles.[10] Ming Shen et al. reported the microwave irradiation synthesis and characterization of various alkylamine-capped gold nanoparticles.[11] Yugang Sun et al describe a solution-phase route to the large-scale synthesis of silver nanocubes. Uniform gold nanoboxes with truncated cubic shape were also produced by reacting the silver cubes with in a aqueous $HAuCl_4$ solution.[10] Min Zhau et al reported the synthesis of gold–silver alloy nanoparticles with various mole ratios in aqueous solution by an electrochemical co-reduction of chloroauric acid ($HAuCl_4$) and silver nitrate ($AgNO_3$) in presence of polyvinyl-pyrrolidone (PVP) as a protecting agent.[12] Angshuman Pal et al. synthesized highly stable gold-silver alloy nanoparticles with varying mole fractions in aqueous sodium dodecyl sulfate solution by simultaneous reduction of chloroauric acid ($HAuCl_4$) and silver nitrate ($AgNO_3$) using sodium citrate.[13]

Recently microwave radiation is widely used in many fields. In case of materials processing, microwave irradiation directly couples electromagnetic energy (frequencies ranging from 300 MHz-300 GHz) with the material through molecular interactions and enables energy dissipation through the release of heat.[14] Microwave heating offers some advantages compared to conventional heating processes such as the use of a remote source, the relative speed of the process, and the volume and materials selectivity.[15]

The polyol method is a low-temperature process that is environmentally friendly because the reactions are carried out under closed-system conditions. It was first introduced to produce metal submicron-sized powders. In this method, a suitable solid metal salt is suspended in a liquid polyol. The suspension is stirred and heated to a certain temperature, the reduction of the starting compound yields fine metal powders. The polyol itself acts not only as a solvent in the process but also as a stabilizer, limiting particle growth and prohibiting agglomeration. Recently, this method has also been extended to the preparation of metal oxides and metal chalcogenides.[16] Tarascon and co-workers have demonstrated that in these reactions the temperature is a dominant factor in affecting the reactivity. Three factors are influenced by the temperature: (1) the reduction potential of ethylene glycol, (2) the rupture and creation of chemical bonds, and (3) diffusion.[17] All these factors make microwave-heating techniques favorable for the fabrication of metal and metal oxides by using ethylene glycol as a solvent. The ethylene glycol is an excellent susceptor for the microwave radiation because of its high permanent dipole. The metallic particles produced as intermediates in the polyol reaction

are also good for this purpose. In this study, Au nanoparticles and Au-Cu alloy nanoparticls in the presecence of and abscence of CNTs have been synthesized by using microwave irradiation technique.

2 MATERIALS AND METHODS

Materials

Chloroauric acid ($HAuCl_4.xH_2O$) and Cu(II)acetate ($(CH_3COO)_2Cu.H_2O$) were used as precursors for Au, Cu and Au/Cu nanoparticles. Reagent grade ethylene glycol (mol wt 200) used as a solvent and as a reducing agent and cetyltrimethyl ammonium bromide (CTAB) was used as a surfactant. These chemicals were purchased from Sigma-Aldrich. CNTs (outside diameter 10-20 nm, Inside diameter 5-10 nm, length 10-30 μm) were purchased from Nanostructure & Amorphous Materials, Inc.

Synthesis of Au nanoparticles on CNTs

In this process, a 100 mg of CNTs are dispersed in 100ml of ethylen glycol containing 250 mg of CTAB in a roud bottom flask using a magnetic stirrer for 30min. Then a 250 mg of chloroauric acid is added to the reaction mixture of CNTs, CTAB, ethylenglycon and contined magnetic stirring for another 10min. This reaction mixture is irradiated with microwave (SHARP 1000V/R21HT) for 4 minutes. The final reaction solution was cooled to room temperature, and the reaction product was separated from the solution by centrifugation at 10,000 rpm for 10min. The final product was wahed weveral times double distilled water and finlly with ethanol and vacuum dried at room temperature overnight. Similarly the Au nanoparticles were also synthesized using the same method as described earlier without CNTs.

Synthesis of Au-Cu nanoparticles on CNTs

In a typical reaction a 100 mg of CNTs are dispersed in 100ml of ethylene glycol containing 250 mg of CTAB in a round bottom flask using a magnetic stirrer for 30min. Then a 107.8 mg copper(II)acetate and 183.49 mg chloroauric acid is added to the reaction mixture of CNTs, CTAB, ethylene glycol and continued magnetic stirring for another 10min. This reaction mixture was irradiated with microwave (SHARP 1000V/R21HT) for 4 minutes. The final reaction solution was cooled to room temperature, and the reaction product was separated from the solution by centrifugation at 10,000 rpm for 10min. The final product was wahed weveral times double distilled water and finlly with ethanol and vacuum dried at room temperature overnight. Similarly the Au nanoparticles were also synthesized using the same method as described earlier without CNTs. The evaporation of reaction mixture was controlled through out the reaction time by circulating the 5^{o}C thermostated liquid throught the condensor attached to the round bottom blask. Similarly the Au-Cu nanoparticles were also synthesized using the same method except in the absecence of the CNTs.

Characterization

As-synthesized particles were characterized by powder X-Ray diffraction (XRD). The XRD patterns were recorded on a Rigaku, D/Max 2200 X-ray diffractometer operated at 40 kV and 30 mA with CuK_{α} radiation. The size and morphology of synthesized particles were determined using a transmission electron microscope (JEOL-2010 Transmission Electron Microscope). The TEM samples were prepared by dispersion of the powdered sample in ehtnol and placing a drop of colloidal solutiion on to the copper or molybdenum grid.

3 RESULTS AND DISCUSSION

Characterzation of Au Nanoparticle on CNTs

Figure 1 (a) shows the XRD pattern of Au particle on CNTs. Figure 1(a) represents the XRD pattern of Au nanoparticle and 1(b) Au nanoparticles on CNTs. The XRD data shows a single phase face-centered cubic (f.c.c) diffraction pattern and well matched with JCPDS file 04-0784.

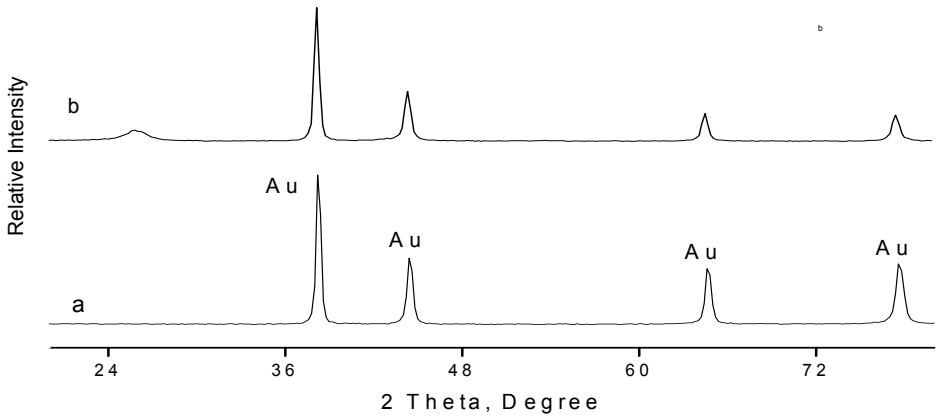

Figure 1. XRD patterns of (a) Au nanoparticle (b) Au on CNTs.

Figure 2 shows the TEM micrographs of (a) Au particle (b) Au particle on CNTs. (c) Au-Cu alloy nanoparticle (d) Au-Cu alloy nanoparticle on CNTs (e) EDS analysis on Au-Cu alloy shown in Figure (d). The Au particles shown in Figure 2(a) are highly polydispersed and polymorphous: most of the particls are spherical in shape. These particles are about ~100 nm in diameter. The Au coated on CNTs are shown in Figure 2(b) and these particles are also about 100 nm in diameter. The percentage of coating of CNTs are ~3-5wt% and most of the CNTs sufraces are still not covered with Au. The further studies on higher coating of Au on CNTs are under investigation. Figure 2(c) shows the as-prepared Au-Cu alloys and these particle are spherical in shape and ~5-10 nm in diamter. When these Au-Cu alloys were coated on CNTs the particles sizes are increased to 20nm. The reason for this increase in sizes of these Au-Cu alloy

particles may be the high absorbance of microwave irradiation of CNTs in the reaction. Figure 2(e) shows the energy dispersive specroscopy (EDS) of Au-Cu/CNTs and all the peaks are assigned to the Au, Cu and Carbon.

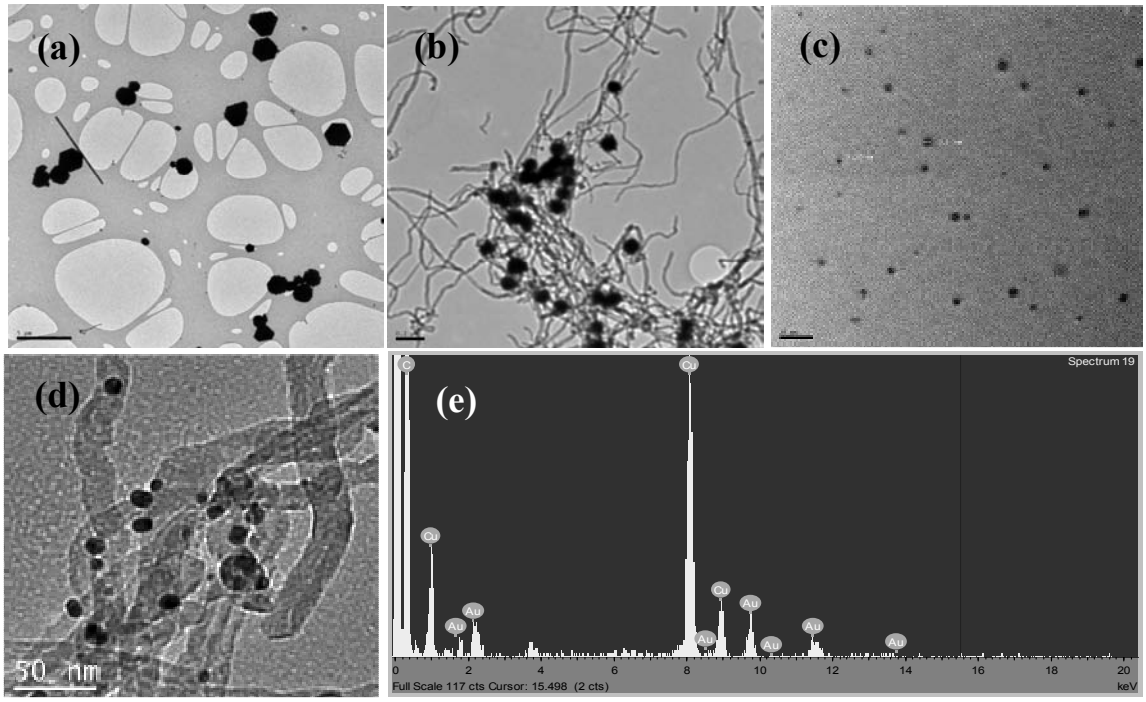

Figure 2. Transmission electron micrograph of (a) Au particle (b) Au particle on CNTs. (c) Au-Cu alloy nanoparticle (d) Au-Cu alloy nanoparticle on CNTs (e) EDS analysis on Au-Cu alloy shown in figure (d).

Mechanism of formation of Au and Au-Cu on CNTs

Microwave radiation is a portion of electromagnetic spectrum. The energy of the quantum of microwave is too mall to break down chemical bonds or to influence the chemical equilibrium,[18] but polar molecules can produce orientation polarization and steering movement in the high frequency electromagnetic field. The interaction and heat movement among molecules hinder the steering movement of molecules and produce molecules' inner friction for molecule-selves, which results in the generation of heat that is called inner heating.[18] The reduction reaction can quickly be carried out under microwave irradiation according to the following equation.[19]

$$2CH_2OH\text{-}CH_2OH \longrightarrow 2\ CH_3CHO + H_2O$$

$$2\ CH_3CHO + Au^{2+} + H_2O \longrightarrow CH_3\text{-}COO^- + 3H^+ + Au$$

The formation of Au nanoclusters obtained by this method can be mainly because of heating effect.[20] The producing colloidal particles do not adhere to the wall of glass reactor by using the microwave irradiation method. Therefore, Au nanopartices with narrow size distribution can be easily obtained by quick heating in a microwave oven.

Co-reduction of Au and Cu nanoparticles occurred by ethylene glycol in microwave radiation according to same mechanism stated above. Accordingly ethylene glycol reduced the chloroauric acid and Cu (II) acetate to metallic Au and Cu by using following reaction and at nano level the two metallic elements combined to produce alloy nanoparticles. The reaction scheme for producing fine and dispersed metal particles using polyol process involves the following reactions: reduction of soluble metal (II) acetate by ethylene glycol, nucleation of metallic Cu/Au and growth of individual nuclei in the presence of a protective agent. The initial dispersion of carbon nanotube in the polyol solution is also an important factor. The better the dispersion of CNTs in initial solution is the better the coating. Since CNTs absorb maximum microwave (graphite powder of 1 mm can reach 1072^{o}C in 1.76 minute) it require less time to coat CNTs with similar size metal nanoparticles CNTs influence heterogeneous nucleation results in a fine metal dispersion depresses the homogeneous nucleation causes growth of large aggregates. The reduction reaction of ethylene glycol is due to diacetyl, which is formed by a duplicative oxidation of acetaldehyde previously produced by dehydration of ethylene glycol.

$$2CH_2OH\text{-}CH_2OH \longrightarrow 2\ CH_3CHO + H_2O$$
$$2\ CH_3CHO + Cu^{2+} + H_2O \longrightarrow CH_3\text{-}COO^{-} + 3H^{+} + Cu$$
$$2\ CH_3CHO + Au^{2+} + H_2O \longrightarrow CH_3\text{-}COO^{-} + 3H^{+} + Au$$
$$2\ CH_3CHO + Au^{2+} + Cu^{2+} + H_2O \longrightarrow CH_3\text{-}COO^{-} + 3H^{+} + Au\text{-}Cu$$

The particles prepared by above method are spherical in shape and 5-10 nm range diameter. In order to examine the composition of the particles formed, EDS analysis of Au-Cu alloy nanoparticles was performed. EDS analysis of these particles reveals an average composition of 50:55 (Au:Cu), which is within of the nominal 1:1 stoichiometry and also within the thermodynamic stability window for Au-Cu alloy based on phase diagram.[21] The spherical Au-Cu nanoparticles were produced by simultaneous reduction of $AuCl_4^-$ and Cu^{+2} ions in CTAB containing ethylene glycol solution. CTAB was added to stabilize the alloy nanoparticles by preventing them from aggregating. CTAB seemed to be a good stabilizer for the alloy nanoparticles since particles size and particles size distribution were small and narrow. The CTAB molecules are adsorbed on the surface of nanoparticles generated by reduction reaction, hence preventing their agglomeration.

4 CONCLUSIONS

Microwave polyol process is an efficient route to synthesis metal and metal alloy nanoparticles. Control of size and shape is possible by varying the concentration of precursor salt, type and concentration of surfactant. Obviously time is also important controlling parameters. Although the fundamental basis of shape selectivity for Au particles has yet to be fully understood, it is believed that the selective adsorption of CTAB on various plane of Au nanoparticles influence the product morphology. These Au and Au-Cu alloy nanoparticles can be use in various appication including catalysis, sensing and fillers in polymers.

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