In situ Synthesis of Cu Nanoparticles on MWCNTS using Microwave Irradiation

Sanchita Dey, Vijaya K Rangari* and Shaik Jeelani
Materials Science and Engineering, Center for Advanced Materials Tuskegee University

ABSTRACT

Carbon nanotubes are one of the most extensively studied nanostructured materials. In particular, carbon nanotubes are unique and ideal templates onto which to immobilze nanoparticles allowing the construction of designed nanoarchitectures that are extremely attractive as supports for heterogeneous catalysts, for use in fuel cells and multifunctional composite structural applications. This paper describes a simple and efficient way of deposition of Cu nanoparticle on multiwalled carbon nanotube (MWCNTS) using microwave irradiation technique. Cu/MWCNTS composites were prepared by microwave heating of ethylene glycol (EG) solutions of Cu acetate precursor salt. 250 gm copper(II)acetate dissolved in 100 ml of ethylene glycol in a round bottom flask by using magnetic stirrer. Cetylmethyl Ammonium Bromide (CTAB) used as a surfacent. Then 50mg MWCNTS were dispersed. The flask was placed in the center of a microwave oven (SHARP 1000V/R21HT) for 10-20 min under microwave power of 60 W. The products obtained were centrifuged and washed thoroughly with ethanol and vacuum dried at room temp for overnight. For comparison similar experiments were carried out with and without CTAB and MWCNTS. In this method, metal acetate acts as source of metal and ethylene glycol acts as a solvent as well as reducing agent. The as-prepared nanocomposites were structurally and morphologically characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM). These results clearly show that the MWCNTS are covered by crystalline Cu nanoparticles. The copper nanoparticles are uniform in size and shape.

Keywords: MWCNTS, microwave synthesis, copper nanoparticles, and coating

1. INTRODUCTION

Multi-walled carbon nanotube (MWCNT) is an ideal raw material for various applications due to its outstanding mechanical characteristics such as high tensile strength and high elastic modulus, high thermal conductivity and electric conductivity [1]. Recently, there has been great interest in the metal coating of MWCNTs [2] for creating new metal-matrix-based carbon tube composites. The metallization process is a kind of surface modification of MWCNTS. This kind of modification not only can increase the surface active sites to improve bonding between nanotube and resin or ceramic [3], but also can preserve the superior performance and excellent intrinsic properties of MWCNTS in the composites. Furthermore, this metal coating of MWCNTs has been shown to have significant potential for the fabrication of new powder MWCNTS-metal composites [4] thus extending the application fields of MWCNTS. In the past, some successful attempts have been made to synthesize nanoparticles of copper and copper oxides, using various method including sonochemical, microwave irradiation photochemical, hydrothermal, solvothermal, electrochemical, sol-gel methods, solid-state reactions, chemical reduction and decomposition route and so on [5].

Microwaves are a portion of the electromagnetic spectrum with frequencies in the range of 300 MHz to 300 GHz. The corresponding wavelengths of these frequencies are 1 m to 1 mm. The most commonly used frequency is 2.45 GHz. The degree of interaction of microwaves with a dielectric medium is related to the material's dielectric constant and dielectric loss. [6] When microwaves penetrate and propagate through a dielectric solution or suspension, the internal electric fields generated within the affected volume induce translation motions of free or bound charges such as electrons or ions and rotate charged complexes such as dipoles. [6]

The resistance of these induced motions due to inertial, elastic, and frictional force, which are frequency dependent, causes losses and attenuates the electric field. The main advantages of microwave-assisted reactions over conventional methods in synthesis are: (a) the kinetics of the reaction are increased by one to two orders of magnitude, (b) novel phases are formed, (c) the initial heating is rapid, which can lead to energy savings, and (d) selective formation of one phase over another often occurs. [7] One possible hypothesis for these microwave-induced effects is the generation of localized high temperatures at the reaction sites to enhance reaction rates in an analogous manner to that of ultrasonic waves, where both high temperatures and pressures have been reported during reactions. The enhanced kinetics of crystallization can lead to energy savings of up to 90%. [8]

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 restricting agglomeration. Recently, this method has also been extended to the preparation of metal oxides and metal chalcogenides. [9]

In this paper, we present a microwave-induced polyol route to synthesize and characterization of cu coated carbon nanotube.

2. EXPERIMENTAL

Cu/MWCNTS composites were prepared by microwave heating of ethylene glycol (EG, Aldrich) solutions of Cu acetate (Aldrich) precursor salts. 250 gm copper(II)acetate dissolved in 100 ml of ethylene glycol in a round bottom flask by using magnetic stirrer. Cetylmethyl ammonium bromide (CTAB, 500 mg) or polyvinyl alcohol (PVA, 5 mg) used as a stabilizing agent in a different reactions. All solutions were prepared using reagent grade chemicals. Then 50 mg MWCNTS were dispersed in the solution. The flask was placed in the center of a microwave oven (SHARP 1000V/R21HT) and irradiated for 10 min under microwave power of 60 W. After the reaction completed, the solution was cooled to room temperature, and the products obtained were separated from the liquid by centrifugation and followed by repeated washing with absolute ethanol several times and vacuum dried at room temperature overnight.

Similarly the Cu nanoparticles were also synthesized using the same method as described earlier. Dissolving Cu acetate (250 mg) and stabilizing agent (CTAB or PVA) in Ethylene glycol and then irradiated 20 min with microwave. Then particles the obtained were separated from the liquid by centrifugation and then repeated washing with absolute ethanol and vacuum dried at room temperature overnight

The XRD measurements were carried out using a Rigaku, D/Max 2200 instrument. Transmission electron microscopy (TEM) examinations of the samples were carried out with a JEOL-2010 microscope. The powdered samples were dispersed in ethanol and subjected to ultrasonic treatment and dropped on to a conventional carbon coated molybdenum grid.

3. RESULT AND DISCUSSION

The x-ray diffraction patterns reveal that the synthesized copper particles have high crystalinity and high purity. Figure 1 depicts the powder XRD patterns of the powder XRD patterns of: (a) Cu/MWCNT without CTAB, (b) Cu/MWCNT with CTAB (c) Copper nanoparticles with CTAB. Figures 1(a) and 1(b) indicate that the Cu/MWCNT composite particles are crystalline and all the peaks match with the standard MWCNT and copper JCPDS file number 4-0836. In figure 2 represents the TEM pictures of (a) the as prepared Cu nanoparticle with CTAB, and (b) the as prepared Cu coated MWCNT. The as prepared Cu particles show a polydispersion and the particles sizes measured are about size of 200-400 nm. Figure 2(b) also shows that the Cu particles coated on carbon nanotube shows much smaller size (~ 50nm) nanoparticles compared to the copper nanoparticles prepared without MWCNT. The shapes of these nanoparticles are similar to the nanoparticles prepared without MWCNT. It has been found that if the irradiated for longer time the Cu particles are prone to merge in to large particles to reduce surface energy.

Figure 3 represents the TEM pictures of (a) the as prepared Cu nanoparticle with PVA and (b) the as prepared Cu coated MWCNT with PVA. The as prepared Cu particles show a monodispersion and the particles sizes measured are about size of 20 nm. Figure 2(b) also shows that the Cu particles coated on carbon nanotube also of similar dimension and almost round shape. It has been found that if the irradiated for longer time the Cu particles are prone to merge in to large particles to reduce surface energy as in the case of Cu/MWCNT with CTAB. The interaction and percentage of coating on MWCNTS are under investigation.

The initial dispersion of carbon nanotube in the polyol solution is also an important factor to produce uniform coating of copper nanoparticles on MWCNT. The better the dispersion of MWCNT in initial solution is the better the coating. The reaction scheme for producing fine and dispersed Cu particles using polyol process involves the following reactions: reduction of soluble copper (II) acetate by ethylene glycol, nucleation of metallic Cu and growth of individual nuclei in the presence of a protective agent. The nucleation of Cu particles involves intermediate solid phase formed between the starting material and the final metal powder is formed; during the second stage of the reaction the re-dissolution of the intermediate solid phase takes place. 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. The reaction can be summarized as follows:

$$2CH_2OH\text{-}CH_2OH \xrightarrow{-H_2O} 2\ CH_3CHO$$

$$\xrightarrow{\text{Intermediate stage}} CH_3\text{-}CO\text{-}CO\text{-}CH_3 + H_2O + 2Cu \qquad (1)$$

Since Carbon nanotubes absorb maximum microwave [10] (graphite powder of 1mm can reach 1072 ^{o}C in 1.76 min) it require less time to coat MWCNT with similar size Cu particles.

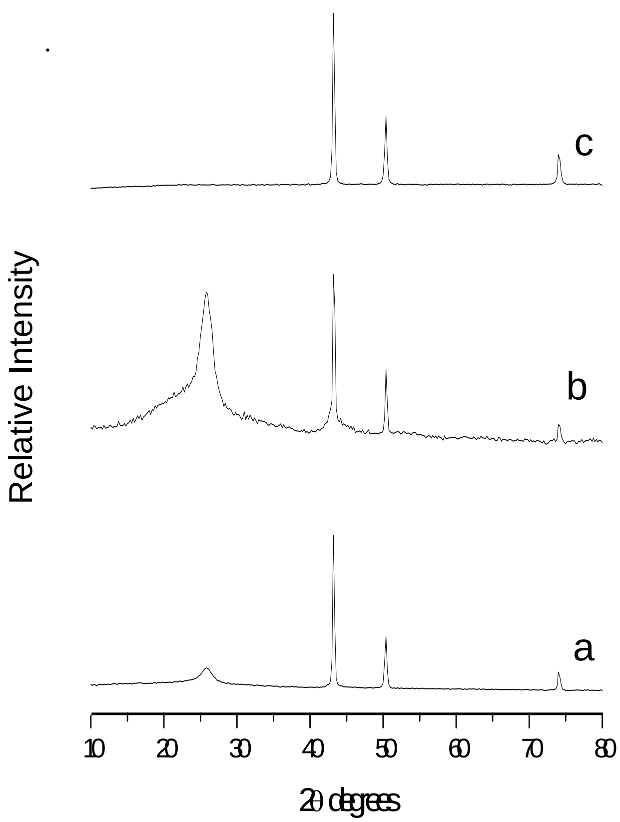

Figure 1. The powder XRD patterns of: (a) Cu/MWCNT without CTAB, (b) Cu/MWCNT with CTAB (c) Copper nanoparticles with CTAB

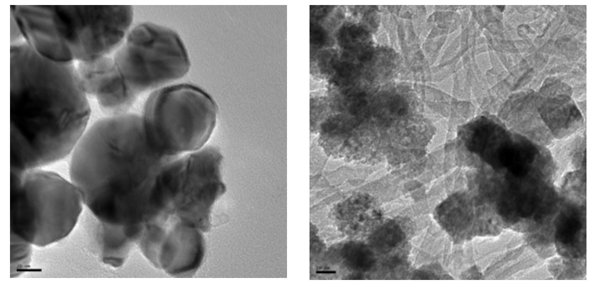

Figure 2. The Transmission electron micrograph of (a) As prepared Cu nanoparticle with CTAB (b) As-prepared Cu coated MWCNT with CTAB

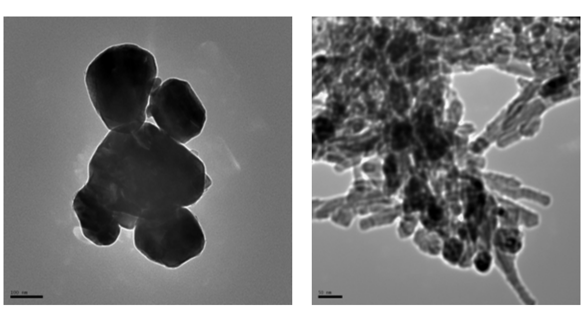

Figure 3. The Transmission electron micrograph of (a) As prepared Cu nanoparticle with PVA (b) As-prepared Cu coated MWCNT with PVA.

4. CONCLUSIONS

Microwave irradiation technique is successfully used to synthesize the copper coated MWCNTs in a one-pot reaction with and without surfactant. Since the graphite carbon absorbs the (in 1.76min 1072^{o}C) maximum microwave radiation had led to the quick and uniform copper nanoparticles coating on MWCNTs. The advantage of this method is particles sizes and extent of coating can be controlled by varying the concentration of precursor and surfactant. Besides this the method is also can be used to synthesize or coating of other transition metals from their metals acetates. The method can be scalable for bulk production, which is the key element in the usage of multifunctional nanostructural materials for structural composite applications.

5. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of this research by NSF-PREM, RISE, and CREST grants.

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*Dr.Vijaya Kumar Rangari
Email: rangariv@tuskegee.edu
Fax: 334 727 2286