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Research Article

Influence of Heat Treatment on the Morphologies of Copper Nanoparticles Based Films by a Spin Coating Method

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We have investigated the influence of heat treatment on the morphologies of copper nanoparticles based films on glass slides by a spin coating method. The experiments show that heat treatment can modify the sizes and morphologies of copper nanoparticles based films on glass slides. We suggest that through changing the parameters of heat treatment process may be helpful to vary the scattering and absorbing intensity of copper nanoparticles when used in energy harvesting/conversion and optical devices.

1. Introduction

Synthesis of metal nanoparticles with novel size-dependent physical and chemical and optical properties (e.g., quantum-confinement effects) plays a crucial role in many fields, such as optical label, catalysis, printed circuits, nanobrazing, and sensors during the past decade [1–5]. Among these various metal nanoparticles, noble metal nanoparticles such as Au, Ag, and Pt are getting special attention as they can be used in labels of immunoassays, lithographic fabrication, electronics, solar cell, nanobrazing, and surface enhanced spectroscope [6–10]. It is because they have large absorption and scattering coefficients. Furthermore, noble metal nanoparticles can be synthesized in different components, shapes (e.g., nanowire, nanodisk, nanorod, nanosphere, nanocube, and core-shell structure), and geometrical configurations, with which they can be self-assembled into different complex nanostructures required. Through these methods, the interaction between light and materials can be controlled and manipulated at a certain wavelength scale when they are used in energy harvesting/conversion and optical devices. Recently, a method is developed to enhance the efficiency and stabilize the emission spectrum in organic light-emitting diodes (OLEDs) using a light scattering layer fabricated with silver nanowires [11]. It is enhanced by 49.1% for the integrated external quantum efficiency. To reduce the usage of semiconductor materials, self-assembled gold nanorods are used to increase the photoconductivity in thin amorphous silicon semiconducting films. It is enhanced by a factor of 2 across the entire visible spectrum [12]. However, the high cost of noble metal nanoparticles has hindered their practical use.

In recent years, there are significant efforts to search cheap metal nanoparticles in order to displace noble metal nanoparticles such as Au, Ag, and Pt, although the studies still have little research. Recently, aluminum nanoparticle and copper nanoparticles have attracted interest as alternative candidates. In order to enhance the solar absorption, a method is suggested to fabricate aluminum nanoparticles based structure using a porous template assisted self-assembly process [13]. It is demonstrated that the effective solar absorption can be over 96%. However, the plasmon resonance wavelength of aluminum nanoparticles lies at the wavelength of around 150 nm. In order to be used in energy harvesting/conversion devices, it should be shifted with changing the shape and geometrical configurations of aluminum nanoparticles. Due to its high oxidation activity, it is difficult to synthesize various shapes such as nanosphere, nanowire, and nanorod using a simple and cheap method. Copper nanoparticles are promising for these applications because of their considerably low cost compared to Ag, Au, and Pt, high electrical and thermal conductivities, and excellent resistance to ion migration. Furthermore, the plasmon resonance wavelength of copper nanoparticles lies in the visible wavelength region, similar to that of gold and silver nanoparticles. The scattering efficiency can be varied by changing shapes and geometrical configurations. Compared with the difficulty of synthesizing aluminum nanoparticles, various shapes and geometrical configurations of copper nanoparticles and copper based alloy nanoparticles have been synthesized by physical, chemical, and biological methods [2]. The study of various geometrical configurations and shapes has been conducted thoroughly and substantial progress has been made [14]. However, only little research has been focused on enhancing luminescence of laser dye or rare-earth by plasmonic coupling and scattering of copper nanoparticles [15, 16]. In addition, there are many reports on preparing nanoparticles film using self-assembly technique (utilizing the chemical interaction between nanoparticles and the surface), lithography, and spin coating methods [17–19]. Among these methods, the spin coating method has getting attractions because self-assembly technique and lithography methods need a lot of procedures. Ag nanoparticle film is fabricated by the spin coating method and the sintering effect is investigated [20]. Unfortunately, there are few reports on preparing copper nanoparticles film using spin coating method.

In this paper, a simpler and cheaper method by the spin coating was used to fabricate copper nanoparticle based films on glass slides. Due to the importance of the shapes of copper nanoparticles when they are used in energy harvesting/conversion and optical devices, the influence of heat treatment on the sizes and morphologies of copper nanoparticles based film was investigated.

2. Experimental Details

2.1. Preparation of Copper Nanoparticles. Copper nanoparticles were synthesized by a mature polyol method in ambient atmosphere. Details of preparation process were described elsewhere [21]. The sodium hypophosphite monohydrate ($NaH_2PO_2{\cdot}H_2O$), copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), ethylene glycol, and polyvinylpyrrolidone (PVP, K29-32) were purchased from Aladdin Chemical Reagent Co. Ltd., P. R. China. The average molecular weight of the PVP polymer used was 58000. All the chemical regents were used as received. PVP was used to get an organic shell on the surface of copper nanoparticles for avoiding being oxidized. The following procedure was used to prepare copper nanoparticles. First, 4 g $NaH_2PO_2{\cdot}H_2O$ and 2.5 g PVP were dissolved into 40 mL ethylene glycol at 90°C. Then, 10 mL of 1 M ethylene glycol solution of $Cu(NO_3)_2{\cdot}3H_2O$ at 90°C was injected into the above prepared solution of $NaH_2PO_2{\cdot}H_2O$ and PVP polymer under vigorously stirring. The mixture solution was stirred for about 10 minutes and cooled down to room temperature. Finally, the prepared copper nanoparticles were separated by centrifugation, washed with absolute alcohol, and repeated for three times. After the above steps, it was well-dispersed in absolute alcohol again and the suspension can be stable for several weeks.

2.2. Preparation of Copper Nanoparticle Based Films. To get the copper nanoparticle based films on glass slides, the required concentration of copper nanoparticles in absolute alcohol (0.4 g/4 g) was prepared under ultrasonic treatment for about 30 minutes. After setting well washed glass slides on the disk of the spin-coater machine, the solution of copper nanoparticles was dropped and spin-coated with 1000 rev. min^{-1} for 12 seconds in air. Finally, the glass slides were kept in a tube furnace and annealed in a 5% H_2-N_2 mix gas atmosphere for one hour at 100°C, 150°C, 200°C, 300°C, and 400°C, respectively.

2.3. Characterization of As-Prepared Copper Nanoparticles and Annealed Copper Nanoparticles Based Films. Thermogravimetric measurement (TG) was carried out by SMP/PF7548/MET/600W thermogravimetric/differential thermal analyzer from the Swiss Mettler company. The heating rate is 10°C/minute of the heating rate with argon as a testing atmosphere. The size and morphology of copper nanoparticles was investigated by scanning electron microscopy (SEM) using a Hitachi SU8010 field-emission scanning electron microscope. X-ray diffraction (XRD) patterns were obtained on a D2 Phaser Benchtop XRD system (Bruker AXS, Germany).

3. Results and Discussion

To investigate the relation between the scattering and absorbing intensity with the size of copper nanoparticles, the extinction, scattering, and absorbing spectra of copper nanoparticles are simulated by Mie theory given by BHMIE code [22]. The Drude-Lorentz model for copper is obtained from by Ung and Sheng [23] The Drude-Lorentz parameters for copper are obtained from Rakić et al. [24]. The diameters of spherical nanoparticle considered are 120 nm, 160 nm, 320 nm, and 640 nm, respectively. Figure 1 shows the extinction, scattering and absorbing spectra of copper nanoparticles with different diameters. It has been found that the tunability of extinction, scattering, and absorbing efficiency can be controlled effectively by change in diameters of copper nanoparticles. The methods of varying the diameters of copper nanoparticles here are heat treatment.

Figure 2 shows the XRD patterns of the as-prepared copper nanoparticles based films on glass slides. The results are in agreement with the values for a face-centered cubic crystal structure of copper phase (JCPDS number 04-0836). The peaks at $2\theta = 43.17°$, 50.33°, and 74.16° correspond to (111), (200) and (220) Bragg reflections, respectively. No observed diffraction peaks are detected from any other impurities. There results identify that, under the protection

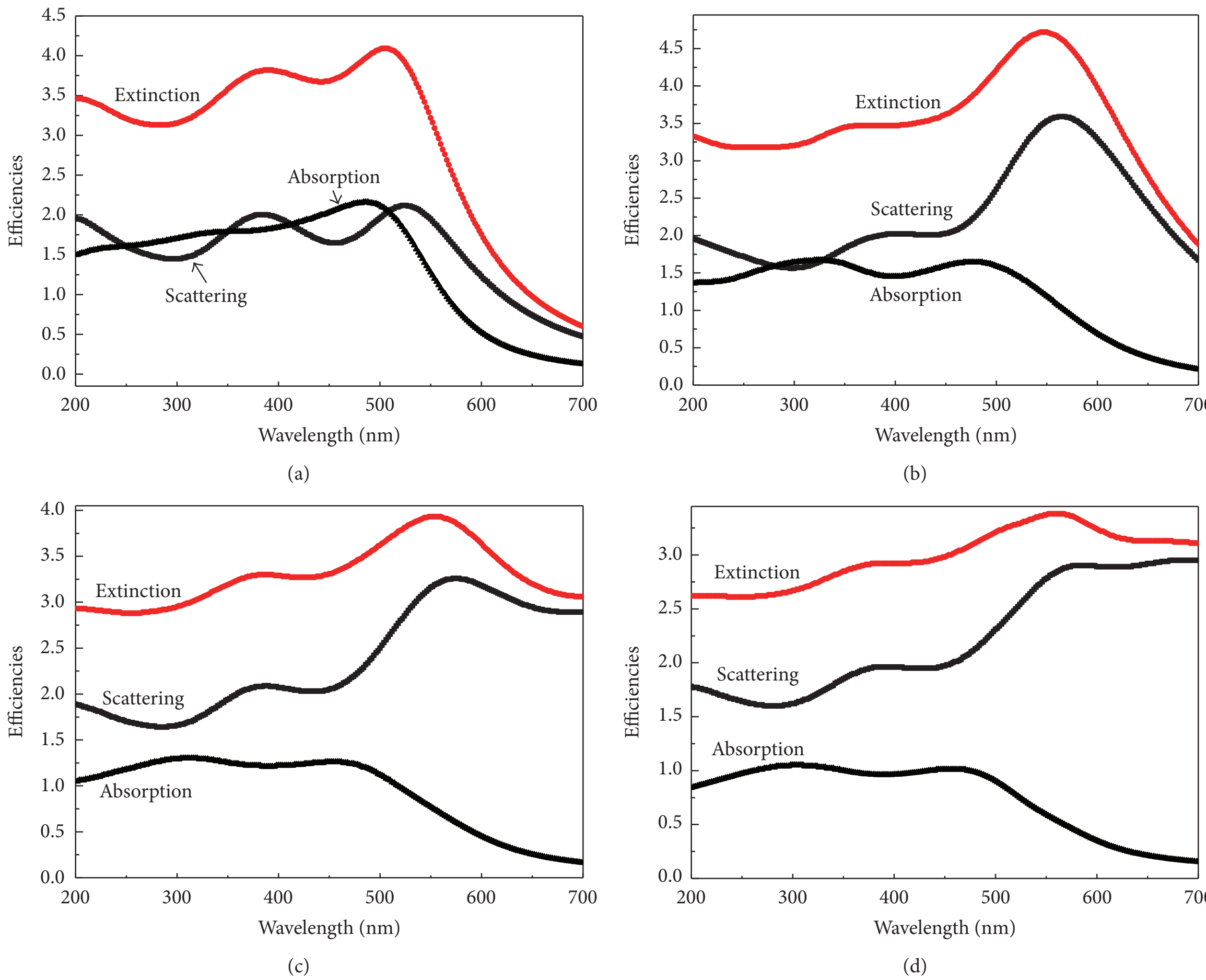

Figure 1: Calculated extinction, scattering, and absorption spectra of copper nanoparticles with different diameters. (a) 120 nm, (b) 160 nm, (c) 320 nm, and (d) 640 nm.

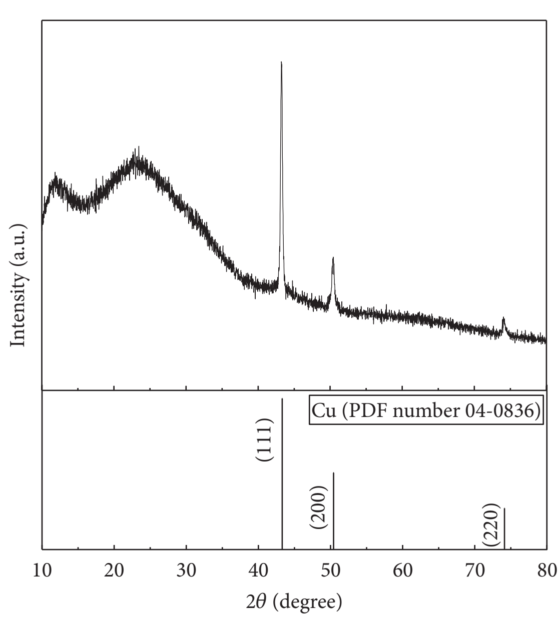

Figure 2: XRD diffraction patterns of the as-prepared copper nanoparticles based films on glass slides without anneal.

by PVP polymer, the as-prepared copper nanoparticles are hardly oxidized into Cu_2O, CuO, or $Cu(OH)_2$. The sharp and strong diffraction peaks confirm that the as-prepared copper nanoparticles are highly crystalline.

TG analysis in an Ar atmosphere was used to study thermal decomposition behaviors of the as-prepared PVP coated copper nanoparticles, shown in Figure 3. An Ar atmosphere was used for TG measurement in order to prevent the oxidation of copper nanoparticles. The results indicate that the weight loss of ~2.5%, which could be attributed to small amount of absolute alcohol, ethylene glycol, and PVP polymer absorbed on the surface of as-prepared copper nanoparticles. The weight increases again at temperature over 600°C, which is ascribed to the oxidation of Cu nanoparticles.

To investigate the oxidation protection performance of copper nanoparticles based films on glass slides, XRD patterns are measured at different heat treatment temperatures. According to TG analysis shown in Figure 3, the copper nanoparticles based films were annealed in a 5% H_2-N_2 atmosphere for one hour at 100°C, 150°C, 200°C, 300°C, and 400°C, respectively. Considering the glass transition

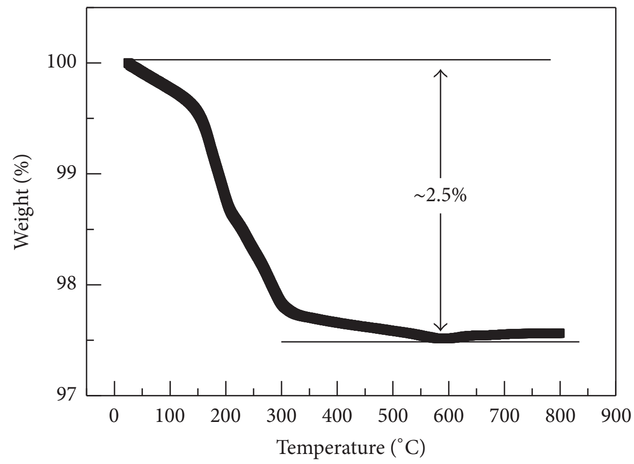

Figure 3: Thermal analysis of the as-prepared copper nanoparticles with argon as a testing atmosphere.

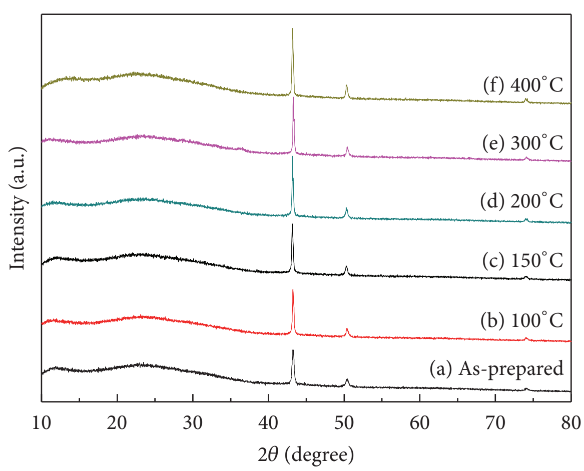

Figure 4: XRD diffraction patterns of the copper nanoparticles based films on glass slides annealed at different heat treatment temperatures by a spin coating method: (a) as-prepared, (b) 100°C, (c) 150°C, (d) 200°C, (e) 300°C, and (f) 400°C.

temperature of glass slides used as substrates, the highest heat treatment temperature used is 400°C. As shown in Figure 4, the intensity of the XRD peaks increases with heat treatment temperature from room temperature to 400°C. These results show that the crystallizations of copper nanoparticles in the films become better. There are no observed characteristic peaks attributed to oxide impurities such as Cu_2O, CuO, or $Cu(OH)_2$ till 400°C.

Due to the importance of the shapes and geometrical configurations of copper nanoparticles when used in energy harvesting/conversion and optical devices, it is significant to control the size and morphologies of copper nanoparticles. One of the simple methods to control them is changing the parameters of heat treatment process. Under heat treatment the residual solvent and organics are removed, leading to coalescence between adjacent copper nanoparticles. Figure 5 shows SEM images of the copper nanoparticles based films on glass slides. These results show that the copper nanoparticles pack to a multilayered structure. When heat treated at temperature under 200°C, the morphologies of copper nanoparticles are still isolated nanoparticles, which are independent of heat treatment and the distributions of the size of copper nanoparticles are not uniform, shown in Figures 5(a)–5(c). The sintering process has not happened at these temperatures. However, when the heat treatment temperature increases to 200°C, the copper nanoparticles start to melt as shown in Figure 5(d). As the heat treatment temperature increases to 300°C, the size of copper nanoparticles increases obviously, as shown in Figure 5(e). When the heat treatment temperature increases to 400°C, the size of copper nanoparticles continues to increase and some copper nanoparticles are interconnected, indicating that apparent sintering necks appeared. Furthermore, significant coarsening can be observed, shown in Figure 5(f).

4. Conclusions

We have reported on the influence of heat treatment on the sizes and morphologies of copper nanoparticles based films by a simple spin coating method. The heat treatment of copper nanoparticles based films on glass slide may be a promising method for modulating the sizes and morphologies of copper nanoparticles. When increasing the heat treatment temperature, the size keeps no obvious change while increasing at a critical heat treatment temperature. Significant coarsening of copper nanoparticles occurs when it continues increasing heat treatment temperature. Through this method it may be helpful to vary the scattering and absorbing intensity of copper nanoparticles within the entire visible spectrum.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

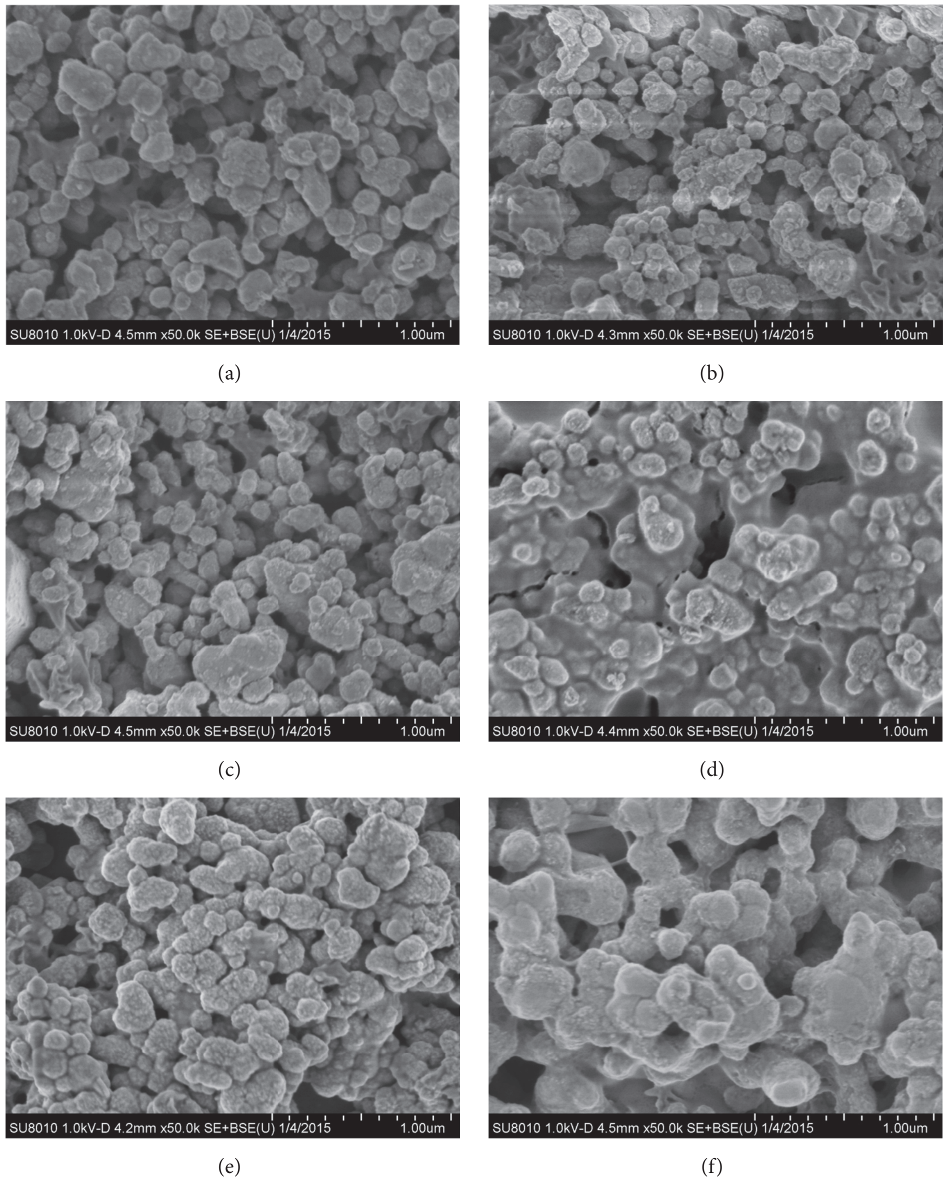

Figure 5: SEM images of the copper nanoparticles based films on glass slides at different heat treatment temperatures by a spin coating method: (a) as-prepared, (b) 100°C, (c) 150°C, (d) 200°C, (e) 300°C, and (f) 400°C.

Acknowledgments

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