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One-step synthesis of copper nanoparticles embedded in carbon composites

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ABSTRACT

Copper nanoparticles embedded in carbon composites were prepared via spray pyrolysis by adjusting the polyvinylpyrrolidone (PVP) to copper nitrate mass ratio. When the equal amount of two precursors was mixed and spray pyrolyzed, copper nanoparticles with sizes in the range 30–50 nm were incorporated into the carbon composites arising from PVP. X-ray photoelectron spectroscopy demonstrated that the copper nanoparticles exhibit oxidation resistance. In addition, the effects of carbon on the surface plasmon bands were investigated. This synthetic process is simple and environmentally friendly and reduces the problems associated with their oxidation through one-step passivation.

1. Introduction

There is considerable interest in the synthesis of copper nanoparticles because they could be used in many industrial applications such as catalysts and optical and magnetic materials, as well as in sensors and microelectronics [1–5]. In particular, copper nanoparticles have diverse optical properties and exhibit various surface plasmon bands (SPBs) according to their size, morphology, concentration and surrounding medium. Accordingly, copper nanoparticles have potential as replacements for gold and silver in SPB-related applications such as biodetection, electronics and optical devices [6–8].

However, unlike noble metal nanoparticles, fine copper particles are prone to oxidation in the atmosphere, which can degrade their desired properties and limit their potential applications [9–12]. As a result, the capping of copper particles with various materials such as carbon and silver, as well as with conducting polymers and semiconductors, has been extensively attempted [6–8,11–18]. Carbon has several advantages over the wide range of capping materials [11–13,19–22]. Firstly, a carbon capping can enable the attachment of many functional groups to metal nanoparticles, which is useful in biochemical, electrical and optical applications, and also enables ternary coating. Secondly, the conductivity of carbon is higher than those of the insulators used as coating materials in fuel cells or biosensors. Lastly, carbon can retard or exclude the oxidation of core metal nanoparticles not only under mild conditions but also under extreme conditions such as in the presence of alkalis or acids.

Copper nanoparticles coated with various materials have been prepared with a variety of methods, including polyol method, thermal reduction, sol–gel processing, and spray pyrolysis [6–8,11–18]. In certain cases, spray pyrolysis is an efficient method for the uniform and aggregation-free coating of particles [16]. However, it is difficult to synthesize nanoparticles with conventional spray pyrolysis because the size of precursor droplets is limited to a few micrometers [23]. Although a few groups have previously reported the preparation of copper nanoparticles with spray pyrolysis, they used special apparatus such as a diffusion dryer, a droplet impactor plate or an electrostatic classification system [24,25].

This paper reports for the first time a spray pyrolysis technique for the synthesis of copper nanoparticles concurrently passivated with carbon composites without the use of special apparatus. The variations in morphology and composition with the PVP to copper salt ratio were examined by using field emission transmission electron microscopy (FE-TEM) and energy-dispersive X-ray spectroscopy (EDS). In addition, the stabilities of the prepared particles against oxidation were compared by using X-ray photoelectron spectroscopy (XPS). Finally, the surface plasmon bands of pure Cu and the Cu/carbon composites were determined by using UV–vis–NIR spectrophotometry.

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2. Experimental methods

The Cu/carbon composites were prepared by using a spray pyrolysis apparatus consisting of an ultrasonic atomizer (1.7 MHz), a quartz tube (height, 1000 mm; inner diameter, 50 mm), and a collection filter. The precursor solution was prepared by dissolving copper nitrate trihydrate ($Cu(NO_3)_2·3H_2O$, Junsei, 99%) and polyvinylpyrrolidone (PVP, Sigma–Aldrich, $M_w = 40{,}000\ g\ mol^{-1}$) in a mixture of distilled water and ethanol and adjusting the copper salt concentration to 0.05 mol L^{-1}. The PVP to copper salt mass ratio was varied from 0 to 1.5 to investigate the effects of PVP on the morphologies of the Cu/carbon composites. Ethanol was used as a co-solvent to create strong reducing atmosphere in the pyrolysis chamber. The precursor droplets generated in the nebulizer were transported into the pyrolysis chamber, which was maintained at 600 °C, by nitrogen gas with a flow rate of 5 L min^{-1}. The prepared pure copper powders and Cu/carbon composites were characterized by using an X-ray diffractometer (Rigaku, D/MAX-2500 (18 kW)) to determine their crystal structures. To examine the morphologies and sizes of the prepared powders, high resolution TEM images were acquired with FE-TEM (FEI Company, Tecnai G2 F30, 300 kV). EDS mapping was carried out in the TEM to observe the component elements and determine the elemental distributions. The oxidation states of the constituent elements on the surfaces of the pure Cu sample and the Cu/carbon composites were investigated by using XPS (Thermo VG Scientific, Sigma Probe). The absorbance spectra were obtained with UV–vis–NIR spectrophotometry (Shimadzu, UV-3101PC) to investigate the optical properties of the prepared powders.

3. Results and discussion

The XRD patterns of the pure Cu sample and the Cu/carbon composites are shown in Fig. 1. The locations of all the peaks were the same and, regardless of the presence of PVP, corresponded to the *f c c* copper phase ($2\theta = 43.3^\circ, 50.4^\circ, 74.1^\circ$, PDF #00-004-0836); the addition of PVP affected only the intensities of the peaks. The crystallite sizes, calculated by using the Scherrer equation, decreased from approximately 187 nm to an average of 25 nm with the addition of PVP to the precursor solution. Fig. 1(a) shows that copper nitrate was completely reduced to metallic copper in the reaction temperature (600 °C) and volume percent of ethanol (60 vol.%), as found by other groups synthesizing copper particles via co-solvent-assisted spray pyrolysis, although the specifications of the reactor and residence time in the reactor used in this study were different [24,25].

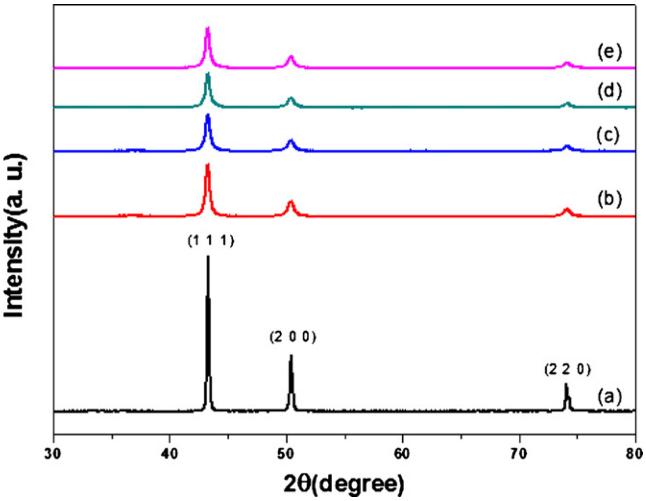

Fig. 1. XRD patterns of the powders prepared with various PVP to copper nitrate mass ratios: (a) 0, (b) 0.25, (c) 0.5, (d) 1, and (e) 1.5.

The TEM images in Fig. 2 show that the morphology and size of the particles varied significantly with the PVP to copper salt ratio. Dense copper particles with a size of approximately 300 nm were formed when there was no PVP in the initial precursor (Fig. 2(a)). Overall, as shown in Fig. 2(b)–(e), the sizes of composites were increased by the addition of PVP, which is consistent with other studies that have used a polymeric precursor in spray pyrolysis [23], whereas the crystallite sizes of copper were decreased, which is consistent with the results obtained from XRD data. The decrease in the crystallite sizes of copper particles can be explained by the presence of translucent areas between irregular and polygonal copper nanoparticles which are made up of carbonaceous materials.

The mechanism of formation for pure Cu particles and Cu/carbon composites is suggested in Fig. 3. A dense copper particle was synthesized from one droplet only containing copper nitrate. This is performed in multiple steps which include drying, decomposition, reduction and densification, and can be observed as a conventional mechanism of synthesis of metal particles using spray pyrolysis process [26]. In contrast to aerosol droplets generated from precursor solution without PVP, those derived from precursor solution with PVP underwent a significant change in the viscosity, since the solvent evaporated first, leaving the concentration of PVP in the microdroplets to increase. Although gases produced from evaporation of solvent and decomposition of solute were released, the morphology of Cu/carbon composites changed from spherical to crumpled morphology, while maintaining a relatively large size owing to the high viscosity of droplets. When solvent evaporated in aerosol droplet, the polymer also dried and then formed the coiled structure [27]. This enveloped the decomposition product or nuclei of copper nanoparticles in droplets. The short residence time of aerosol droplets in the hot tubular reactor also enables PVP not to be completely decomposed [27,28], even though temperature of the electrical furnace is higher than that of the decomposition of PVP. Accordingly, PVP or carbon containing residues could stabilize and disperse copper nanoparticles in the Cu/carbon composites.

On the other hand, when the precursor solution comprised of only PVP was nebulized, any carbon containing residues were not obtained. This also proves that the temperature of electrical furnace and flow rate of carrier gas were insufficient for PVP to carbonize and indicates that Cu^{2+} ions played a role for catalyzing carbon support [28–30]. To sum up, nuclei of copper particles were formed and grown into copper nanoparticles in carbon matrix, which was generated by mutual interaction. Finally, whereas copper nanoparticles with smaller crystallite size were generated in the carbon composites, the size of composites was larger, when compared with the case of absence of PVP in the precursor solution.

When the PVP to copper salt ratio was 1, copper nanoparticles with a mean size of 30–50 nm were embedded in carbon composites consisting of the decomposition products of PVP (Fig. 2(d)). TEM images at high magnification of a Cu/carbon composite prepared at 600 °C are presented in Fig. 4(a). Fig. 4(b) consists of the EDS maps of C, O and Cu which show that core parts (marked yellow) were copper nanoparticles, whereas external parts (marked red) of core were composed of carbon. However, oxygen was also detected especially around copper nanoparticles. In general, oxygen in the PVP molecules was chemically or physically absorbed onto the surfaces of the copper nanoparticles [31,32]. Particularly, according to the report of Moon's group [31,32], when copper nanoparticles were capped with PVP of high molecular weight (40,000 g mol^{-1}), most likely oxygen atoms on the surface of copper nanoparticles are derived from PVP, compared to copper nanoparticles capped with PVP of low