



In situ growth of copper nanocrystals from carbonaceous microspheres with electrochemical glucose sensing properties



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ABSTRACT

In situ growth of copper nanocrystals from carbon/copper microspheres was observed in a well-controlled annealing or an electron beam irradiation process. Carbonaceous microspheres containing copper species with a smooth appearance were yielded by a hydrothermal synthesis using copper nitrate and ascorbic acid as reactants. When annealing the carbonaceous microspheres under inert atmosphere, copper nanoparticles were formed on carbon microspheres and the copper particle sizes can be increased to a range of 50–500 nm by altering the heating temperature. Similarly, in situ formation of copper nanocrystals from these carbonaceous microspheres was observed on the hydrothermal product carbonaceous microspheres with electron beam irradiation in a vacuum transmission electron microscopy chamber. The carbon/copper composite microspheres obtained through annealing were used to modify a glassy carbon electrode and tested as an electrochemical glucose sensor.

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1. Introduction

Nanocrystals are fundamental in modern science and technology showing controllable size, shape, and new properties [1]. The weakness in monocomponent nanomaterials of instability in kinetics, thermodynamics, or mechanics and inconvenience in operation and recovery, as well as pursuing the multifunctional properties leads to the development of hierarchical composite materials. Those composites with a micrometer or bulk sized substrate, such as glass, ceramic, polymer or carbon, would provide applications in fields like electronic, magnetic, optical, catalysis, and electrochemical energy storage [2–7]. The emergence or transformation of nanocrystals inside of or onto such substrate matrix is one of key issues for fabrication and application of these nanocomposites, providing special functionalities, requiring mechanical supports from substrate or damaging the substrate, offering opportunity to the in situ study of nanosized objects [2–16]. Herein, we choose to study a nanocomposite system of carbon microspheres supported copper nanocrystals, in which the emergence of these copper nanocrystals “in situ” from a homogeneous carbonaceous sphere matrix would be of great interest for solving the related issues, such as segregation of extruded nanocrystals [8], elemental distribution in phases [9,10],

growth dependence on external conditions [11–15], particle size growth mechanism and controlling [16].

As is well known, copper is malleable, ductile, excellent thermal and electrical conductor, and sometimes acting as cheap substitutes for noble metals in catalysis. The synthesis of copper nanocrystals has been reported in vast numbers with various strategies [17–19]. Also a number of reports give good results on metal/alloy nanoparticles (including copper) with carbon spherical composite nanostructures, using one step or multi-step routes [20–22]. In one strategy, carbonaceous spheres are obtained and metal nanoparticles are deposited by subsequent reduction of metal cations or decomposition of metal complexes [21–23]. In another route, the metal nanoparticles, assemblies of nanoparticles, or their precursors are formed in the first step and carbon spherical shells are coated later [24]. When one pot solution based route is used, the carbon source and metal source are usually mixed in aqueous solution, then hydrothermal treatment or other methods is taken to carry out a reaction to form a carbonaceous matrix containing metal species, and a post annealing may be required to form a clearly defined microstructure either with a carbon sphere decorated or containing with small metal particles [20,25–27].

The copper/carbon composites have attracted great interest, however, it is still unclear about the emergence and evolution of copper nanocrystals from carbon substrate [11,12,15,20,25]. In this paper, carbonaceous microspheres by hydrothermal process were taken as starting point, and well controlled annealing process and electron beam irradiation in high vacuum TEM chamber are carried out to study in situ growth and evolution of copper nanocrystals within the carbon microsphere matrix. Interestingly the particle size

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and crystal shape could be well controlled by the experimental parameters, and diffusion of copper species of micrometer scale is hinted. Finally, as a test for electrochemical activity and possible application of the obtained carbon/copper composite materials, glucose sensing electrode is made with the samples and measurements are carried out.

2. Experimental

2.1. Synthesis of materials and in situ growth of copper nanocrystals

The composite of carbon microspheres and copper nanoparticles is obtained through a two step synthesis route. In the first step, carbonaceous microspheres containing copper species are synthesized by a simple low temperature hydrothermal carbonization route. All the reagents were of analytical grade. In a typical synthesis, copper nitrate and ascorbic acid were dissolved in 40 mL deionized water to form clear solutions, respectively. The concentration was controlled in the range of 0.1 – 1 mol/L with appropriate reactant ratios. The two solutions were mixed and transferred to a 100 mL Teflon-lined stainless steel autoclave, sealed, and heated for hydrothermal treatment at 150–180 °C for 4–6 h. When the reaction was finished, the autoclave was allowed to be cooled to room temperature naturally. A powder product with black color was harvested and washed with deionized water several times. Then it was separated with centrifugation, washed with anhydrous ethanol, and dried at 60 °C overnight. A small amount of by-products was mostly removed during the washing process.

Well controlled annealing or electron beam irradiation process is a vital step to form copper nanocrystals. The experimental procedure was conducted as follows: a certain amount of the black powder was loaded in an alumina boat, put into a tube furnace, which was then vacuumed. The sample was heated with a slow heating rate of 2.5 °C/min under a protective argon flow heated to a preset peak temperatures of 200–1200 °C and maintained for 1 h, respectively. Further carbonization as well as the formation of copper nanoparticles took place in this step. Later the sample was cooled to room temperature in the tube furnace naturally, which may take several hours. The black-colored powder was harvested and characterized. In situ electron beam irradiation experiments were carried out in a JEM-2010 transmission electron microscopy operating at accelerating voltage of 200 kV.

2.2. Characterization of materials

The obtained composites were characterized by several techniques. Powder X-ray diffraction (XRD) was carried out on a D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology of as-prepared products was observed by scanning electron microscopy (SEM) on a FEI Quanta 200 scanning electron microscopy and a FEI Quanta 600 field-emission scanning electron microscopy equipped with Oxford Inca X-Max energy-dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) observation were carried out on a JEOL-2010 and a JEOL-2010F microscopy both with an accelerating voltage of 200 kV, respectively. The electron beam radiation effects were observed during the same TEM operations. The samples prepared into ultra-thin sections with a minimal thickness of 60 nm were used for TEM, HRTEM, and SEM observations.

2.3. Fabrication and test of electrochemical glucose sensor using the composite materials

The electrochemical glucose electrodes were fabricated on a glassy carbon electrode. Typically, approximate 1 mg annealed

sample was dispersed in 0.5–1 mL deionized water under supersonic vibration. The suspension was re-dispersed and dropped onto the electrode for each drop and a drop was allowed to dry at room temperature before a second drop is applied. When Nafion is applied to fabricate the electrode, 10 μL of 0.2% Nafion ethanol solution was dropped onto the electrode and dried after the sample was deposited and dried.

The glucose sensor testing was performed in a process similar to the reference [28]. The electrochemical measurements were carried out at room temperature in a sealed conventional three electrode system with a CHI 1140A potentiostat. The sealed cell consists of a saturated calomel electrode (SCE) reference electrode, a platinum wire counter electrode, and the testing glassy carbon electrode deposited with sample. Before the tests were performed, the sealed glass cell was bubbled with high purity argon flow for at least 10 min in order to remove air and the cell was maintained under argon bubbling during the test. The cyclic voltammetry and amperometric current–time experiments were carried out under continuous magnetic stirring.

3. Results and discussion

3.1. Characterization of typical sample after annealing

The as-obtained products before and after annealing at 600 °C were characterized with XRD measurements (shown in Fig. 1a). Both XRD patterns show sharp reflection peaks, readily indexed to face-centered cubic metal copper ($a = 3.615 \text{ \AA}$, space group: Fm-3 m, JCPDS No. 85-1326). Widened XRD peaks located at $2\theta = 15\text{--}30^\circ$ in both patterns are ascribed to reflection by glassy carbonaceous spheres. No other characteristic peaks are observed. Low peak intensity for copper in hydrothermal sample is ascribed to small amount of copper particles formed in the hydrothermal process. After heat treatment, the rather sharp diffraction peaks of copper suggest a large amount of copper particles as well as high degree of their crystallinity.

The morphology of the products was investigated by SEM and TEM. Fig. 1b presents a general overview as low magnification SEM image. It shows that the carbon spheres after heat treatment are well separated microspheres of 1–5 μm in diameter. The light contrast spots uniformly distributed on these spheres are ascribed to copper nanoparticles of 50–120 nm in size. Typical TEM images of several microspheres before and after heat treatment are shown in Fig. 1c and d, before heat treatment, no contrast could be observed, after heat treatment, the copper nanoparticles with dark contrast are uniformly distributed on the surface of carbon microsphere which shows the light contrast, in accordance to the SEM results.

For a detailed view of an individual copper nanoparticle, the HRTEM image is shown in Fig. 1e and f. The electron beam is parallel to the [1 1 0] zone axis of a copper nanoparticles attached to a smooth carbon sphere. The thin light contrast shell out of the copper nanoparticle is ascribed to copper oxide wrapped on the particle. The HRTEM image along the same zone axis shows the lattice fringes of 0.21 nm indexed to d spacing of (1 1 1) in face center cubic metal copper. A twin boundary and Moiré fringes evidently appear, showing the multicrystalline nature of the copper nanoparticle. Twinning defects as well as stacking faults are common planar defects of face centered cubic metals. The copper nanocrystals approximate spherical and protrude from the carbonaceous matrix.

The elemental mapping results by EDS analysis in cooperation with high resolution SEM image of a single carbon sphere annealed at 600 °C are shown in Fig. 2. The Fig. 2a shows the carbon sphere, and Fig. 2b–e shows zoom-in image of the framed area and corresponding elemental mapping images of copper, carbon, and

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