



Full length article

Copper nanoparticle@graphene composite arrays and their enhanced catalytic performance



Lifeng Hang^{a,b}, Yang Zhao^c, Honghua Zhang^a, Guangqiang Liu^a, Weiping Cai^a,
Yue Li^{a,b,*}, Liangti Qu^c

^a Key Lab of Materials Physics, Anhui Key Lab of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, PR China

^b University of Science and Technology of China, Hefei 230026, PR China

^c Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry, Beijing Institute of Technology, Beijing 100081, PR China

ARTICLE INFO

Article history:

Received 1 November 2015
Received in revised form
29 November 2015
Accepted 8 December 2015
Available online xxx

Keywords:

Copper nanospheres
Graphene oxide
Core–shell structure
Catalyst

ABSTRACT

Noble metal nanoparticles have been widely investigated for catalysis, while the source of noble metal is limited. Copper nanoparticles are the ideal candidates for replacing noble metal nanoparticles in the specific catalysis field. However, Cu NPs from traditional methods are generally nonuniform in morphology and wide distribution in size. In this work, a simple method is developed to fabricate uniform copper nanosphere arrays on a large scale ($\sim\text{cm}^2$) using monolayer colloidal crystals as templates. A reduced graphene oxide (rGO) is further introduced on the surfaces of Cu nanospheres to form the Cu NPs@rGO core–shell structured arrays on the substrates by the redox reaction. The rGO shell can protect the Cu NPs from oxidation, which guarantees the good stability of Cu@rGO nanoparticle arrays. The obtained Cu@rGO core–shell arrays (periodic length: 350 nm, diameter: 110 nm) exhibit excellent catalytic performance towards the reduction of 4-nitrophenol to 4-aminophenol, which is 14 times larger than that of Au nanoparticles as previously reported. With decreasing the length of periodicity of Cu@rGO core–shell array, its catalytic activity increases. When the periodicity is fixed, with increase of Cu NP size, the value of activity factor k is decreasing. More importantly, such Cu@rGO core–shell arrays on the supporting substrates can be easily recycled for the catalytic reaction. These Cu@rGO arrays have also other potential applications in SERS, electrochemistry, biosensor, etc.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Recently, core–shell structures, i.e. a metallic nanoparticle as a core and an inorganic or organic coating as a shell, have attracted enormous interest in fundamental studies and technical applications due to their enhanced performances caused by the coupling between the core and shell structures in comparison to single-component counterparts [1–5]. In the investigations of core–shell structures, noble metal nanoparticles (NPs) have been widely used as the cores, owing to the unique optical [6–8], electronic [9,10], and catalytic properties [11,12], however, noble metal

sources are limited and they are very expensive.

Although noble metal NPs have received special attention mostly, copper NPs exhibit high potential in some applications for replacing the noble metal NPs due to their relatively low cost and high electrical conductivity. Since the last century, the use of copper as catalysts has been known, but this research field is less explored than noble metals, such as gold, palladium, and platinum [13–16]. In the periodic table of elements, copper element occupies a place among transition metals, unlike other members (Au, Ag), metallic copper generally shows less catalytic activity. However, copper with nanometre-sized dimensions demonstrates remarkable activity in catalytic properties [17,18]. Copper nanoparticles (Cu NPs) are ideal candidates for core materials with similar properties like noble metal nanoparticles, i.e. strong local surface plasmon resonance (LSPR), good performance in electrochemistry and catalysis [19,20].

Cu NPs are generally synthesized through the reduction of

* Corresponding author. Key Lab of Materials Physics, Anhui Key Lab of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, PR China.

E-mail address: yueli@issp.ac.cn (Y. Li).

copper (II) ions by using reducing agents and surface stabilizing agents in solution [21,22]. They can also be prepared by milling, and volatilizing component from volatilization of a copper solid [23,24]. However, the obtained Cu NPs from above approaches generally demonstrate nonuniformity in morphology and wide distribution in size. Until now, it still keeps a challenge to prepare monodispersed Cu NPs with well controlled uniform morphology.

Additionally, these Cu NPs are easily oxidized in air to form an oxidation layer on their surfaces, further limiting their practical applications. If the nano-shells are introduced onto the surfaces of Cu NPs, the surface oxidizing process of Cu NPs may be avoided and Cu NPs can be well protected, which is helpful for applications in catalysis, SERS etc.

Graphene is an ideal shell material for protecting Cu NPs and improving the oxidation resistance of Cu NPs. As we know, graphene, a two-dimensional honeycomb lattice of sp^2 -bonded carbon atoms, has been widely applied in sensors, nanoelectronic devices, hydrogen storage and catalysis due to high surface area and tunable electrical properties [25–28]. At the same time, a shell of graphene can play an important role in protecting the Cu NPs from oxidation. However, the creation of graphene coating on Cu NPs has not been well investigated. Wang et al. [29] tried to prepare the core–shell structures of Cu nanoparticles encapsulated by multi-layer graphene from the gaseous copper acetylacetonate at $(Cu(acac)_2)$ at 600 °C by metal-organic chemical vapour deposition (CVD). However, the preparing process is complex and those core/shell structures are not uniform. Therefore, there is a lack of effective route to synthesize monodispersed Cu NPs-graphene core–shell structures.

Two dimensional (2D) ordered micro/nanostructured arrays have already attracted considerable interest due to their promising applications in a variety of fields [30–34]. In several decades, monolayer colloidal crystal template strategy has been extensively applied to fabricate periodic micro/nanostructured arrays [35–40]. In this work, we present a facile, green and environment friendly approach to synthesize spherical monodispersed Cu NP arrays on a substrate by using the colloidal monolayer as a template. The colloidal monolayer on a large scale ($\sim cm^2$) was fabricated on the substrate by an interfacial self-assembly, and a copper thin layer was then deposited on colloidal monolayer. After annealing at proper temperature under the reduced gas, the organic colloidal spheres were removed and the spherical Cu nanospheres were formed *in-situ* under previous colloidal spheres. By this route, Cu hexagonal non-close-packed (hncp) nanosphere arrays were finally created on a substrate and the periodic length of such hncp Cu NP arrays could be tuned by colloidal templates with different sizes of colloidal microspheres. A reduced graphene oxide (rGO) was further introduced on the surfaces of Cu nanospheres by strong reduction of Cu nanosphere to graphene oxide (GO) in solution. So Cu NPs@rGO core–shell structured arrays (periodic length: 350 nm, diameter: 110 nm) were successfully fabricated on the substrates and they exhibited a very high stability in the air and enhanced catalytic performance in reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), which is 14 times larger than that of Au nanoparticles as previously reported ($0.35 s^{-1} mg^{-1}$) [12]. The as-prepared Cu NPs@rGO core–shell structured arrays could be recycled for many times used as catalysts and the catalytic performance still remained good. Cu NPs@rGO core–shell structures exhibit high potential as a heterogeneous catalyst and are expected to replace noble metal, such as gold, palladium, and platinum. Importantly, after forming the Cu NPs@rGO core–shell structured arrays on the substrates, the nanoparticle agglomeration could be avoided, they could be easily recycled and their catalytic activity still keeps high level. Such Cu NPs@rGO core–shell structured arrays have other potential applications in SERS, electrochemistry, biosensor, etc.

2. Experiment section

2.1. Chemicals

Monodispersed polystyrene (PS) microsphere suspensions (2.5 wt% in water, surfactant-free) with different sizes (350, 500 and 750 nm in diameter) were purchased from Alfa Aesar Corporation. The target of copper (purity, 99.99%; 60×4 mm) was bought from ZhongNuo Advanced Material (Beijing) Technology Corporation. The Si wafers were used as substrates for self-assembling of PS spheres. Mixed gas (N_2 (98%), H_2 (2%)) was bought from Nanjing Special Gas Factory Corporation. Graphite powder, acetone, ethanol, H_2O_2 , $NH_3 \cdot H_2O$, $NaBH_4$ and 4-nitrophenol (4-NP) were of analytical grade and were bought from Sinopharm Chemical Reagent Co. Ltd. Deionized water used in all experiments (18.2 M Ω cm) was obtained from ultrafiltration system.

2.2. Fabrication of periodic Cu nanosphere arrays

Monolayer colloidal crystals were fabricated by interfacial self-assembling process, as we previously reported [41,42]. The Si wafers were washed with ethanol, acetone and deionized water in the ultrasonic bath in sequence, then cleaned in $H_2O/H_2O_2/NH_3 \cdot H_2O$ (3:1:1 in volume) and deionized water in turn, followed by drying in the oven at 90 °C for 20 min. After above cleaning steps, the substrates were sufficiently hydrophilic. Subsequently, PS microsphere suspensions were mixed evenly with the same volume of ethanol by the ultrasonic bath for 15 min. Finally, a large-area colloidal monolayer was fabricated on the cleaned substrate by interfacial self-assembling process, as shown in Fig. 1(a).

Colloidal monolayer templates with different periodic length (350, 500 and 750 nm) on the Si wafers were placed on the platform of sputtering device for copper deposition. During sputtering process, the sputtering current of 20 mA was applied and the deposition process was performed with different time from 3 to 20 min according to colloidal templates with the periodicities from 350 nm to 750 nm. The colloidal monolayer templates after copper deposition were annealed at 900 °C for 2 h under the mixed gas (N_2 (98%), H_2 (2%)), as shown in Fig. 1(b) and (c).

2.3. Synthesis of Cu@rGO nanoparticle arrays

Graphene oxide (GO) was prepared from graphite powder by acid-oxidation according to a modified Hummers method [43–45]. Briefly, 1 g of graphite was added into 25 mL of H_2SO_4 (98%) in a 250 mL beaker. After that, $NaNO_3$ (0.5 g) was introduced into the mixture, followed by stirring for 30 min at ice bath. Then $KMnO_4$ (6 g) was added into the mixture slowly. The temperature was kept to 35–40 °C for another 30 min, 46 mL water was slowly added into above mixture with vigorous stirring for 25 min. Afterwards the residual MnO_2 was reduced by adding 10 mL H_2O_2 into the mixture, and the unexploited graphite was removed from the resulting mixture by centrifugation. Finally, the synthesized GO was washed by HCl (5%) solution and deionized water for several times, and GO solution was prepared with a concentration of 0.5 mg/mL for further use.

One millilitre of as-prepared GO aqueous solution (0.5 mg/mL) was added into the 19 mL deionized water and then sonicated for 5 min. Afterwards, the ordered Cu nanosphere arrays on the substrates were placed into above GO aqueous solution to keep them for 1 h in the 90 °C water bath. The samples were washed with deionized water to remove the unreacted GO, and dried at 60 °C in the vacuum, Cu@rGO core–shell nanoparticle arrays were finally obtained on the substrates, as shown in Fig. 1(f).

Download English Version:

<https://daneshyari.com/en/article/7878951>

Download Persian Version:

<https://daneshyari.com/article/7878951>

[Daneshyari.com](https://daneshyari.com)