Electrochemical fabrication of metal nanostructures by using a hydrophilic/hydrophobic sponge-like NiOOH/Ni(OH)$_2$ template

Ya-Huei Chang, Chang Liu, Shien-Ping Feng *
Department of Mechanical Engineering, The University of Hong Kong, Hong Kong

A R T I C L E   I N F O
Article history:
Received 27 November 2015
Received in revised form 18 January 2016
Accepted 24 January 2016
Available online 26 January 2016

Keywords:
NiOOH/Ni(OH)$_2$ pair
Template synthesis
Metal nanofabrication
Surface plasmon resonance

A B S T R A C T
A 3D nanosponge-like NiOOH/Ni(OH)$_2$ film, showing inherent switchable wettability and high compatibility with different electrolytes, is demonstrated to be a suitable template for synthesizing metal nanoparticles with different sizes (from nanoscale to submicroscale range) and diverse shapes (from spherical to branched nanostructures). The rich nanostructures, including peapod-like, spherical, and dendritic nanocomposites, exhibit different optical responses. Furthermore, the nanoparticles are easily isolated from the template in a non-destructive manner and well-dispersed in the acidic environment with good uniformity.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction
Because of the profound importance of metal nanoparticles in the fields of photonics, electronics, catalysts, biosensors, and chemosensors, their synthesis and construction, which involves the use of template-assisted techniques, has been extensively studied [1–3]. Two types of template – hard templates and soft templates – are generally used to synthesize metal nanoparticles, with particular emphasis on size or shape control. In hard-template techniques, rigid and porous materials with mesoscale features are routinely used as frameworks; examples of such materials are anodized aluminum oxide (AAO), track-etched membranes, silica, polystyrene latex spheres, and block copolymer films [4–8]. In-situ impregnation of monodisperse metal nanoparticles in preformed hard templates can be achieved by filling the pores or channels of the templates and then subjecting the templates to chemical or electrochemical reduction [5]. However, only a specific particle size and a spherical or cylindrical shape, corresponding to the diameter and geometry of the pores or channels, are obtained from a single hard template. In addition, methods used for separating the formed nanoparticles from the template are either complex or time-consuming. By contrast, soft-template techniques involve flexible media, such as micelles, vesicles, liquid crystals, microemulsions, and gas bubbles [9,10]. Unlike hard-template techniques, the precursors of metal nanoparticles actively participate in the self-assembly process or interact with functional groups of soft templates, thereby offering a route to organize and control nanoparticle growth. Furthermore, metal nanoparticles with a variety of sizes and shapes can be produced [11,12]. However, most of the flexible media are dynamic and influenced by the reaction conditions such as pH value, temperature, solvent type, ionic strength, and adsorbates. It is a daunting task to well manipulate the complex interaction between flexible media and their surroundings. Although amphiphilic molecules can be aggregated into micelles with a perfect shape, the deformation of the micelles is inevitable during carbonization or calcination, thereby reducing the uniformity of the synthesized metal nanoparticles [13]. More importantly, soft-template techniques are incapable of producing metal nanocomposites through in-situ impregnation of metal nanoparticles within the matrix. The incorporation of metal nanoparticles into matrix directly endows metal nanocomposites with the unique optical or physicochemical properties that overwhelm the individual metal nanoparticles [14].

A combination of hard- and soft-template techniques balances the advantages and disadvantages of the individual techniques and offers a synergistic route to synthesize metal nanoparticles with ordered and intricate structures [15]. For example, Luo et al. synthesized different Te@ cross-linked poly(vinyl alcohol) core-shell structures, such as nanorod bundles penetrating a ball, branched cables, and separated cables, by varying the PVA content based on a synergistic soft–hard template mechanism [16,17]. The main drawback of combinations of hard- and soft-template techniques is the complex process involved.

Recently, tailored hard-template techniques have become attractive because of their simplicity and flexibility. In these techniques, functional components are directly or indirectly introduced into the restricted space of the hard templates to enhance interfacial interactions, which direct the growth of final architectures with different lengths, site-specific placement or oriented alignments [18]. For example, Yang et al. obtained silica nanofibers (average diameter: 9.8 nm) and nanotubes (average diameter: 12.3 nm) by manipulating the pore-wall
wettability of an AAO template with or without the direct chemical modification of hydrophobic alkyl self-assembled monolayers (SAMs) [19]. Padbury et al. dispersed and embedded gold nanoparticles in a hybrid organic–inorganic matrix by cyclically and sequentially exposing Au-nanoparticle-coated PA-6 fibers to trimethylaluminum, water, and nitrogen vapors [20]. Nguyen et al. found that the lateral or vertical growth of organic semiconductors was decisively affected by the surface wettability of graphene-mounted substrates modified with ultraviolet (UV)/ozone or hydrophobic alkyl SAMs; graphene indirectly delivered the wetting behavior of the underlying substrate to crystal growth [21].

As demonstrated in the aforementioned examples, direct or indirect chemical modification of hard templates through tailored hard-template techniques is an effective and straightforward strategy to obtain metal nanoparticles with a wide range of sizes and shapes. However, the required chemical modification increases the complexity of the fabrication process and reduces the purity of the metal nanoparticles during template removal. Furthermore, little research has been conducted on simultaneously achieving size and shape control. The achievement of shape diversity has been limited on hierarchical porous structures, 1D nanostructures, and 2D arrays, imposed by the spatial confinement of metal nanoparticles in rigid frameworks. In this study, we addressed the problems faced in the use of a cost-effective 3D nanosponge-like nickel oxyhydroxide/hydroxide (NiOOH/Ni(OH)2) film with inherent switchable wettability as a hard template for producing metal nanoparticles with different sizes (from nanoscale to submicron scale) and shapes (from spherical to branched structures). As an earth-abundant semiconductor, NiOOH/Ni(OH)2 nanostructures are used in various practical applications because of their unique optical, electrochromic, and electrochemical properties [22–24]. Our previous study demonstrated the capability of the nanostructures to show rapid and reversible switching of wettability when triggered by external stimuli of UV/ozone and environmental chamber (EC) [25]. The combined effects of chemical conversion between NiOOH and Ni(OH)2 and short-range ordered-disordered transitions endowed NiOOH/Ni(OH)2 films with facile switchable wettability between superhydrophilic (contact angle: approximately 0°) and hydrophobic (contact angle: approximately 142°). In this study, in view of three major merits of the films, we extended the application of the films to metal nanoparticle fabrication, for use as a tailored hard template. First, the inherent switchable wettability and high compatibility with various electrolytes make the chemical modification of the template surface unnecessary. Second, unlike current hard-template techniques in which the electroplated metal nanoparticles are spatially confined to pores or channels, the mesopores and top surface of the scaffolds of the porous electrically conductive NiOOH/Ni(OH)2 film can serve as nucleation sites during electroplating. These two merits could enable the size to be tuned up to the submicron scale level, and rich metal nanoparticle nanostructures to be obtained. Third, metal nanocomposites embedded or suspended in/on NiOOH/Ni(OH)2 film show interesting optical properties, which are strongly related to the size, shape, and spatial distribution of the metal nanocomposites.

2. Experimental

2.1. Fabrication of NiOOH/Ni(OH)2 with switchable wettability

The fabrication process was identical to that used in our previous study [25]. A 3D nanosponge-like NiOOH/Ni(OH)2 film was electrodeposited on FTO glass by using three-step constant current densities along with a potentiostat/galvanostat (CHI 660E). A standard three-electrode configuration consisting of the FTO as the working electrode, a saturated Ag/AgCl as the reference electrode, and a platinum mesh as the counter electrode was employed in the electrochemical deposition. The electrolyte comprised 0.13 M sodium acetate, 0.13 M nickel sulfate, and 0.1 M sodium sulfate [26]. The deposition started with a low current density of 0.005 mA/cm² for 30 min; the current density was then increased to 0.05 mA/cm² for 30 min and finally set to 0.5 mA/cm² for the last 30 min at room temperature. The as-prepared films were subjected to the EC (HongHui, THH80L) at 85 °C and 70% relative humidity for 60 min and to a UV/ozone atmosphere (Kingo, TK-110) for 10 min to obtain hydrophobic and superhydrophilic templates, respectively.

2.2. In-situ impregnation of metal nanoparticles and isolation

The superhydrophilic template was immersed in commercial gold (Samtec) and nickel (Caswell) electrolytes at a potential of −1 V for 60 s, as well as silver (Metalor) electrolyte at a potential of −2 V for 5 s to produce peapod-like nanocomposites. Similarly, the suspended metal nanoparticles on the hydrophobic template were obtained using commercial gold (Samtec) and silver (Metalor) electrolytes at a potential of −2 V for 5 s. To fabricate dendritic Au nanocomposites, 0.1 vol% (3-aminopropyl)trimethoxysilane (APTS) was introduced in an Au electrolyte consisting of 3.4 mM gold(III) chloride trihydrate (HAuCl4·3H2O) and 0.1 M perchloric acid. Electrodeposition was performed at −0.08 V for 5 min. Isolation of individual Au particles was achieved by dissolving the template in 0.05 M H2SO4 for 2 h in an ultrasonic bath and then centrifuging the solution at 12 krpm for 10 min.

2.3. Characterization

The morphology and atomic structure of individual metal nanoparticles and their nanocomposites were examined using FE-SEM (Hitachi S-4800) and HR-TEM (Tecnai, G220S-Twin). The optical responses of Au nanocomposites were monitored using UV–visible spectroscopy (HP 8453).

3. Results and discussion

In this study, 3D nanosponge-like NiOOH/Ni(OH)2 films were fabricated on a polycrystalline fluorne-doped tin oxide (FTO) substrate through anodic deposition. The pore size, which can be determined from the applied current densities, could be tuned from 30 to 150 nm [27]. A NiOOH/Ni(OH)2 film with an average pore size of 150 nm was chosen as the hard template. Fig. 1 illustrates the process of in-situ impregnation of metal nanoparticles in/on NiOOH/Ni(OH)2 templates with inherent switchable wettability. Prior to the in-situ impregnation of metal nanoparticles (i.e., Au, Ni, and Ag), as-prepared 3D nanosponge-like NiOOH/Ni(OH)2 films were exposed to a UV/ozone atmosphere to obtain superhydrophilic templates, and to the EC (85 °C, 70% relative humidity) to produce hydrophobic templates, respectively. In the superhydrophilic templates, the active components of metal electrolytes were incorporated into the interior of mesopores to form embedded metal nanocomposites; by contrast, in the hydrophobic templates, the active components were supported on the surface of scaffolds to form suspended metal nanocomposites during electrodeposition. Finally, individual metal nanoparticles were easily collected in an acidic environment in which the NiOOH/Ni(OH)2 template was dissolved.

The field-emission scanning electron microscopy (FE-SEM) images in Fig. 2 show the effects of the surface wettability of the template on the size and structure of the metal nanoparticles. Polydisperse Au nanoparticles (size distribution: 8–50 nm) were embedded in a superhydrophilic template (Fig. 2(a)), whereas uniform Au submicroparticles (average size: 0.8 μm) were supported on a hydrophobic template (Fig. 2(c)); this observation indicated that the surface wettability of templates played a critical role in Au nucleation and growth. The mesopores of the superhydrophilic template served as a mesocontainer where a Au electrolyte could be imbibed; the imbibed electrolyte infiltrated the pore wall because of enhanced 3D capillary force [28,29]. The surface tension confinement triggered a reduction
reaction within the pores for a voltage of $-1$ V. The size distribution and shape edges of the Au nanoparticles followed the mesopore contour, resulting in a peapod-like Au nanocomposite. Fig. 2(b) shows energy-dispersive spectra of an NiOOH/Ni(OH)$_2$ template and a Au nanocomposite, and they confirm the high purity of the Au nanoparticles. Embedded Ni nanocomposites could also be obtained through the same process (Fig. 3(a–c)). In addition, embedded Ag nanocomposites were obtained even at a high overpotential of $-2$ V, indicating that surface-tension-confinement-triggered reduction existed in the superhydrophilic template even at a relatively high overpotential (Fig. 3(d)). By contrast, the hydrophobic template exhibited nonpolar properties and was prone to trap air at the active sites of the pore wall, resulting in a reduction in the surface energy and the formation of air pockets. When the electrolyte was in contact with the hydrophobic template, it was suspended on top of the surface asperities and the air pockets. This observation agrees with the wetting behavior.

Fig. 1. Schematic illustration of in-situ impregnation of Au particles into/onto templates with switchable wettability.

Fig. 2. (a) FE-SEM image and (b) its corresponding EDX spectrum of peapod-like Au nanocomposite embedded into superhydrophilic NiOOH/Ni(OH)$_2$ template under $-1$ V for 60 s. The inset in (b) shows NiOOH/Ni(OH)$_2$ template on FTO without embedded Au nanoparticles. FE-SEM images of hydrophobic template with suspended (c) spherical Au sub-microparticles under $-2$ V for 5 s and (d) Au dendrites under $-0.08$ V for 300 s.
according to the Cassie–Baxter theory [30]. Initially, Au islands start forming on active nucleation sites of the top scaffolds as Au ions come into close proximity with the top of the surface asperities of the template. Subsequently, Au atoms preferentially land on existing Au islands, leading to spherical growth morphology; this morphology is suggestive of 3D nucleation and island growth (i.e., the Volmer–Weber mechanism) [31]. This method was also used to obtain spherical Ag submicroparticles suspended on a hydrophobic template (Fig. 4). As seen, the individual Ag submicroparticle composed of abundant small Ag nanoparticles on its surface, which is beneficial to the application in electrocatalysis.

Dendritic metal nanoparticles with sharp corners, sharp edges, and nanoscale junctions offered enhanced selectivity and catalytic ability. To this end, Xie et al. produced Pd dendritic nanostructures within the pores of a hard template by using ultrasonic waves; however, the limited space available for growth and diffusion resulted in a low aspect ratio [32]. In the current study, the addition of 0.1% (3-aminopropyl)trimethoxysilane (APTS) to an Au electrolyte enabled the facile preparation of high-aspect-ratio Au dendrites with relatively sharp tips on a hydrophobic template. Fig. 2(d) displays hyperbranched Au dendrites with threefold symmetry obtained in the presence of APTS at a potential of $-0.08$ V for 5 min. The length of the main stem exceeded 7 μm, and the branched trunks had a length of 4 μm and a width of 200 nm. APTS molecules were presumed to be adsorbed onto or desorbed from specific crystallographic facets during electrodeposition, resulting in anisotropic growth along a specific crystallographic direction.

To capitalize on the intrinsic characteristics of metal nanoparticles, it is essential to fabricate them in a nonperturbing manner, namely without any residue of tailored ligands or weak interaction with substrates. In our method, chemical modification is not required, and 500-nm-high intersecting mesopores prevent the metal nanoparticles from being directly electrodeposited on the underlying FTO substrate. Consequently, all types of individual Au nanoparticles could be easily obtained by completely removing the NiOOH/Ni(OH)$_2$ template by using a 0.05 M H$_2$SO$_4$ solution (Fig. 5). High-resolution transmission electron microscopy (HR-TEM) images in Fig. 6(a) and (b) show polycrystalline Au nanoparticles collected from embedded peapod-like Au nanocomposites after template removal. Polydisperse Au nanoparticles...
were further sorted using centrifugation. Larger nanoparticles (average size: 50 nm) were at the bottom, whereas smaller nanoparticles (average size: 10 nm) were distributed on top of the centrifugal tube in a well-dispersed manner [33]. Fig. 6(c) shows an FE-SEM image of individual Au submicroparticles dropped on a Si wafer after template removal. Notably, the shape edges of Au nanoparticles are more irregular than those of Au submicroparticles because they are determined by pore structures.

HR-TEM images of sprouts of individual Au dendrites are shown in Fig. 7. The corresponding selected-area electron diffraction (SAED) revealed that the single-crystalline Au dendrites were obtained, in which the main stems and branched trunks grew in the [111] direction. The spots were assigned to the (111) and (111) planes along the [011] zone axis. The angles between the central stems and the secondary branches were approximately 70.5°, which accords with the theoretical value. [34] The d-spacing was approximately 2.35 Å, corresponding to the (111) planes of the face-centered cubic Au, and it indicated that anisotropic growth along the [111] direction was preferred in the presence of APTS molecules because of two possible mechanisms. First, APTS molecules might preferably be adsorbed on the (100) and (110) facets, and therefore, the attachment of Au atoms on these facets is hindered. Otherwise, APTS molecules are preadsorbed on three low-index planes and subsequently selectively desorbed from the (111) facet during electrochemical reduction, thereby facilitating growth along the [111] direction [35]. The interaction between APTS molecules (i.e., amino and hydroxyl groups) and Au crystallographic facets, and the effect of the template on the diffusion of Au atoms will be the further investigated in future studies.

The optical absorption spectra of the nanosponge-like NiOOH/Ni(OH)2 template and various Au nanocomposites were studied using UV–visible spectroscopy, as shown in Fig. 8. The bare template is nearly transparent, and the incorporation of Au particles in/on the templates leads to a broad absorption in the visible region. Compared with peapod-like Au nanocomposites, the suspended Au submicroparticles on the template show a noticeable red shift (from 580 nm to 614 nm), band broadening, and an increase in the band intensity of the surface plasmonic absorption peak. These observations are attributed to the complex effects of the particle size, interparticle spacing of Au nanoparticles, and the surrounding dielectric medium [36–38]. A large particle size, small separation, and high refractive index lead to the red shift of the surface plasmon resonance (SPR). Suspended Au nanocomposites exhibit a larger Au particle size, larger separation, and lower refractive index (surrounding media: air and template) than embedded Au nanocomposites (surrounding medium: template), which results in the offset of the red shift of the SPR. Miao et al. reported that pure Au submicroparticles with a close arrangement exhibit a significant red shift near 700 nm, which is longer than our suspended Au nanocomposite, implying that the effects of interparticle spacing and surrounding dielectric medium should be considered [39]. Dendritic Au nanocomposites exhibit a pronounced absorption broadening from approximately 500 nm to the near-infrared region which is ascribed to longitudinal localized SPR. The absorption spectrum is broader and its intensity is

Fig. 5. Photographs of (a) as-deposited peapod-like Au nanocomposite on FTO and (b) individual Au nanoparticles dispersed in a diluted H2SO4 solution with Tyndall effect.

Fig. 6. HR-TEM images of Au nanoparticles after removal of superhydrophilic NiOOH/Ni(OH)2 template and collected from (a) the top and (b) the bottom of centrifugal tube. The inset shows the corresponding SAED pattern of (b). (c) FE-SEM image of Au sub-microparticles after removal of hydrophobic NiOOH/Ni(OH)2 template and dropped on Si wafer. All templates were dissolved with diluted H2SO4.
higher compared with the absorption spectra of the other two Au nano-composites, indicating that an unusual overlap between the transverse band and the longitudinal band, and intense local electromagnetic field enhancement occur because of the high aspect ratio and sharp tips of the dendritic Au nanocomposites and the coupling between major stems and branched trunks [40].

4. Conclusions

In conclusion, we demonstrated that because of its switchable wettability and high compatibility with different electrolytes, a 3D nanosponge-like NiOOH/Ni(OH)$_2$ film is a hard template that fulfills the requirements for synthesizing metal nanoparticles with different sizes and diverse shapes. The extreme wetting contrast of the film enables metal nanoparticles to be encapsulated into mesopores or suspended on the template surface, leading to a wide range of sizes, from the nanoscale to the submicroscale. Both isotropic and anisotropic growth of metal nanoparticles is viable in the NiOOH/Ni(OH)$_2$ template; therefore, peapod-like, spherical and dendritic nanocomposites exhibiting different optical responses can be obtained. More importantly, individual metal nanoparticles can be easily isolated from the NiOOH/Ni(OH)$_2$ template in a nondestructive manner. Such a unique hard template offers a rational design for metal nanoparticles with desired sizes and shapes.

Acknowledgments

This study was supported by the General Research Fund of the Research Grants Council of Hong Kong Special Administrative Region, China (Award Number: HKU 712213E).

References


