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Facile synthesis of porous silver monoliths with excellent catalytic activity

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ABSTRACT

In this study, novel porous silver (Ag) monoliths have been successfully prepared via a facile process by combining an aging treatment with a thermal-induced reduction reaction. The obtained Ag samples display distinct morphologies via simply adjusting reaction conditions such as aging temperature and precursor's concentrations. More interestingly, the as-made porous Ag samples exhibit superior catalytic activity and durability in the catalysis over reduction of P-nitrophenol (4-NP). Remarkably, the synergistic effects of stabilizing and oxidative etching agents should be responsible for the fabrication of hierarchical metallic monoliths, which highlight significant advantages over the existing techniques given that the present method is facile, inexpensive, environmentally benign, and amenable to scale-up process.

1. Introduction

Colloidal nanoparticles of noble metals (particularly gold and silver) have proven as good candidates for applications in catalysis [1], surface-enhanced Raman scattering (SERS) [2], biosensors [3], imaging [4], and plasmonics [5]. Notably, most of these attractive applications are strongly dependent on their specific morphologies, sizes, and structures [6,7]. Hence, a variety of solution-based strategies such as polyol-thermolysis process, light-mediated reaction, ligand-assisted chemical synthesis, seeding process, electrochemical synthesis, template-directed procedures, and sonochemical routes, have been devoted to silver nanostructures with controllable morphologies over the past decades [8–10].

It should be noted that porous silver (Ag) monolith represents a very sought-after type of structured materials possessing a number of fascinating properties that can impact on various research fields [11,12]. In this regard, highly hierarchical Ag monoliths were prepared via direct aging reaction followed by a facile thermally-induced reduction process (Fig. S1). The as-made porous Ag monoliths exhibit superior activity and durability in the catalysis over reduction of P-nitrophenol (4-NP).

2. Experimental section

In a typical synthesis, 20 mL aqueous solution containing 30 mg $AgNO_3$ was mixed with 0.5 mL polyvinyl alcohol (PVA) (5 g L^{-1}) aqueous solution under magnetic stirring in water bath at 60 °C for 5 min. Followed by addition of desirable amounts trisodium citrate (0.25 M) and 100 μL H_2O_2 (30 wt%), the color of the resultant solution was changed gradually to white. After 5 min, 500 uL ascorbic acid (100 mM) was added into the homogeneous solution above which was continuously stirred for another 30 min. Subsequently, the resultant solution became pink-purple color, and thus was aged for 3 h in water bath at room temperature or 60 °C conditions. The silver precursor product was centrifuged and washed three times with absolute ethanol and water, respectively. The obtained sample was dried in oven at 60 °C for 8 h. Consequently, the sample was sintered in furnace at 650 °C for 4 h at a heating rate of 4 °C min^{-1} under nitrogen flow to obtain hierarchical silver monoliths.

Samples are characterized via Powder X-ray diffraction (XRD, Bruker AXS-D8), Scanning electron microscope (FEI Quanta-400 FEG (FE-SEM), transmission electron microscope (TEM, Philips Tecnai G2 F20) and Brunaur–Emmett–Teller (BET) surface analyzer (Tri Star-3020, Micromeritics, USA). Catalytic Activity Measurement of Ag toward the reduction of 4-NP was conducted in the presence of $NaBH_4$ at room temperature. The catalytic results were recorded with a UV–visible spectrophotometer.

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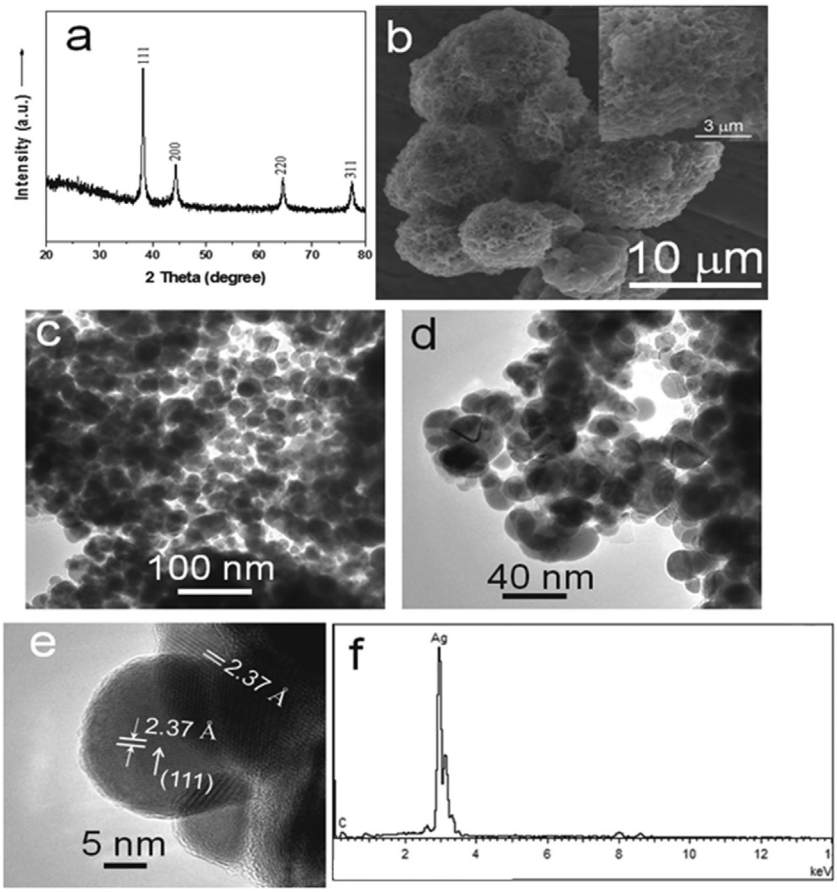

Fig. 1. Morphological, composition, and structural analysis of the prepared spherical Ag monolith: (a) XRD pattern; (b) SEM images with different magnifications; (c and d) TEM images; (e) HRTEM image; and (f) EDS spectrum.

3. Results and discussion

Two different silver monoliths were prepared via facile thermal-treatment processes, whose morphologies are summarized in Figs. 1 and 2. The as-prepared sample can be indexed to the face-centered cubic (*fcc*) phase of silver according to standard JCPDS card No. 04-0783, as determined by its XRD pattern (Fig. 1a). In the pattern, no impurity peaks are detected, indicating the presence of pure silver in our samples.

When the aging treatment was conducted at room temperature for 3 h, 2 mL trisodium citrate (0.25 M) was added, then, it was clearly observed that the prepared silver sphere was actually composed of numerous smaller nanoparticles with a mean size of 25 nm (Fig. 1c). In this unique superstructure, well-defined porous structure were formed via specific stacking and further fusion among these nanoparticles, as shown in Fig. 1c and d. Additionally, HRTEM characterization (Fig. 1e) reveals that the spacing of lattice fringes was measured to be 2.37 Å, corresponding to (111) planes. Energy-dispersive spectrum (EDS) was taken to identify the presence of silver element (Fig. 1f), further confirming the purity of Ag sample.

In particularly, when the aging treatment was conducted in 60 °C water-bath for 3 h, 5 mL trisodium citrate (0.25 M) was added, and then a novel hierarchical monolith structure was observed as shown in Fig. 2. The specific morphology makes highly analogous to coral reef in nature (i.e., inset in Fig. 2b). The specific silver monolith displays well-defined hierarchically porous features. HRTEM characterization was further employed to determine the crystallinity and growth orientation. The spacing between lattice fringes was measured to be 2.35 Å, which can be assigned to (111) planes (Fig. 2e). Electron diffraction (ED) pattern (Fig. 3f) exhibits obvious multiple diffraction circles, implying its polycrystalline feature. Additionally, the porous features of the Ag monoliths can be seen Fig. S2.

The as-prepared Ag monoliths display well-defined porous featuring, and thus are expected to have superior catalytic performance. Herein, the reduction of 4-NP by sodium borohydride has been chosen as a model reaction for investigating the catalytic performances of the as-prepared Ag samples. The light yellow aqueous 4-NP solution shows absorption at ~317 nm. After addition of sodium borohydride, the absorption maximum shifts to 400 nm (Fig. S3), indicating the formation of nitorphenolate [13]. No change in absorbance was observed even after maintaining the system for 12 h, indicating that the reduction reaction does not