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Short communication

Seed-mediated growth of Ag nanocubes and their size-dependent activities toward oxygen reduction reaction

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ABSTRACT

A non-epitaxial growth method for the synthesis of Ag nanocubes by using Pt seed crystals was successfully developed. Tuning the amount of Pt seeds introduced into the reaction allowed for precise control over the size of the Ag nanocubes from 12 nm to 38 nm. Further experiments demonstrated the size-dependent properties of surface oxides and specific activities in terms of electrochemical surface areas for these Ag nanocubes to act as oxygen reduction catalysts in the KOH solution without and with methanol.

Introduction

The shape and structure of metal nanoparticles strongly impact their electronic, optical, and catalytic properties. Controllable synthesis of metal nanoparticles with different shapes and facet orientations has been studied extensively in order to tune particle properties toward various applications [1–4]. Ag nanoparticles, an extremely important nanomaterial in catalysis, can provide efficient electrocatalytic activity in oxygen reduction reactions (ORR) for fuel cell applications [5–7]. Previous studies comparing different Ag nanoparticle catalysts with a constant electrochemical surface area showed that 45 nm Ag nanocubes were more efficient at catalyzing ORRs compared to 18 nm polycrystalline Ag particles [8]. Ag nanocubes showed their potential as catalysts in ORRs. In this regard, herein, a method for the size-controlled synthesis of Ag nanocubes via non-epitaxial growth using Pt seeds is reported. By adjusting the amount of Pt seeds, the size of Ag nanocubes can be successfully decreased from 38 nm to 12 nm. Further, the size effect of these Ag nanocubes as methanol-tolerant catalysts in ORRs is discussed.

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Experimental

The size-controlled synthesis of Ag nanocubes

To prepare the Pt seed crystals, 50 μL of 0.05 M $H_2PtCl_{6(aq)}$ was added to 10 mL of 2.5×10^{-4} M sodium $citrate_{(aq)}$. While stirring continuously, 200 μL of 0.1 M hexadecyltrimethylammonium bromide (CTAB) aqueous solution was gradually added to the mixture. Finally, 25 μL of 0.02 M $NaBH_{4(aq)}$ was added to the reaction, forming brown Pt seeds. To form the Ag nanocubes, 100 μL of 0.05 M $AgNO_{3(aq)}$ was added to 20 mL of 0.1 M $CTAB_{(aq)}$. Next, 1 mL of 0.1 M ascorbic $acid_{(aq)}$ and 10 μL of the Pt seed solution were gradually added to the CTAB/Ag solution. Finally, 80 μL of 2 M $NaOH_{(aq)}$ was added, yielding 38 nm Ag nanocubes. Solutions containing 26 nm, 17 nm, and 12 nm Ag nanocubes were prepared by increasing the amount of the added seed solution to 50 μL, 100 μL, and 1 mL, respectively.

Characterization and analyses of Ag nanocubes

Transmission electron microscopy (TEM; JEOL JEM-2100) samples were prepared by placing the nanocubes on copper grids, covering them with a carbon film, and drying them in ambient air. TEM determined the size and shape of the different Ag nanocube samples. The structure, crystalline structure, and electron diffraction (ED) patterns of the nanocube containing a Pt seed was measured by high-angle annular dark-field scanning TEM (HAADF-STEM; JEOL JEM-2100F CS STEM) combined with spectroscopy (EDX). X-ray diffraction (XRD; Bruker D8; Cu anode; 1.54184 Å) determined the crystal structure of the prepared Ag nanocubes.

Ag nanocubes as methanol-tolerant catalysts for electrocatalytic oxygen reduction reactions

We evaluated the electrochemical properties of the Ag nanocubes to determine whether they would be suitable catalysts for ORRs. Cyclic voltammetry (CV) or linear scan voltammetry (LSV) was combined with rotating ring-disk electrode (RRDE) measurements. Prior to characterization and electrochemical measurements, 20 mL of the nanocube solution was centrifuged at 14,000 rpm for 10 min. The precipitate was resuspended in 20 mL H_2O and the solution was centrifuged again at 12,000 rpm for 10 min. The precipitate was redispersed in the volume of H_2O that would generate a 2.94 μg/μL solution, based on the mass of Ag particles originally added. A quartz crystal microbalance (SEIKO EG&G, QCA 922) confirmed the weight of the nanocube powder in the solution. A solution containing 11.76 μg Ag nanocubes and 15 μL of 0.05 wt% Nafion (DuPont)

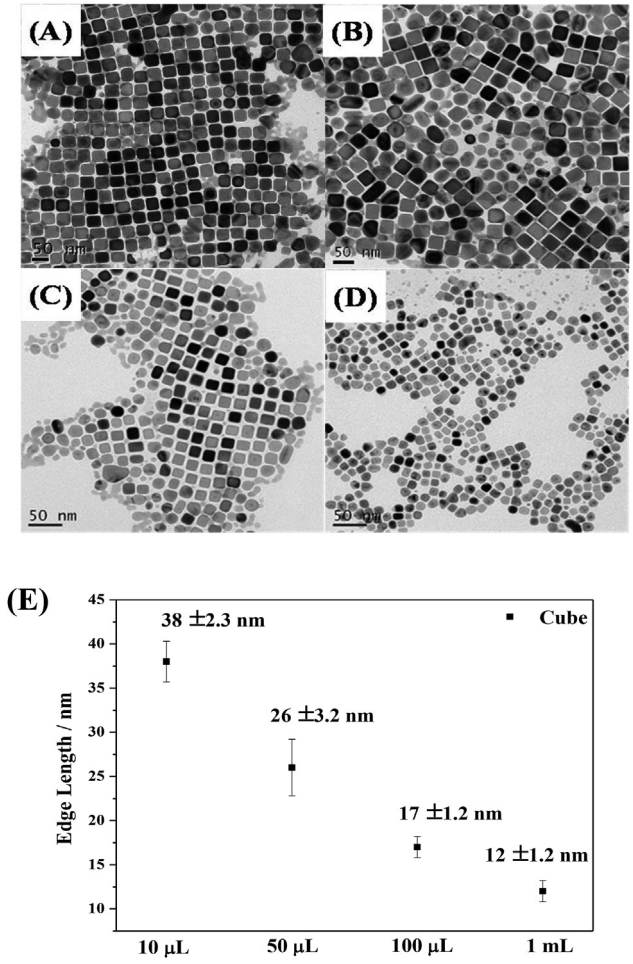

Fig. 1 – TEM images (A–D) and statistics for the edge lengths (E) of Ag nanocubes prepared using 10 μL (A), 50 μL (B), 100 μL (C), and 1 mL (D) of Pt seeds.

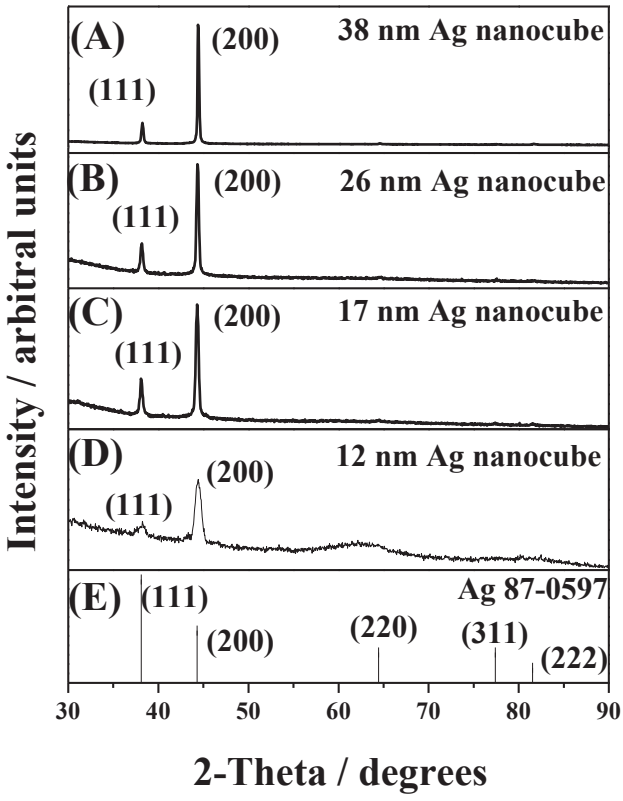

Fig. 2 – XRD patterns of different-sized Ag nanocubes: (A) 38 nm, (B) 26 nm, (C) 17 nm, and (D) 12 nm compared to pure Ag (E).