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Article

Origin of symmetry breaking in the seed-mediated growth of bi-metal nano-heterostructures

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ABSTRACT

Seed-mediated growth is the most general way to controllably synthesize bimetal nano-heterostructures. Despite successful instances through trial and error were reported, the way for second metal depositing on the seed, namely whether the symmetry of resulted nano-heterostructure follows the original crystal symmetry of seed metal, remains an unpredictable issue to date. In this work, we propose that the thermodynamic factor, i.e., the difference of equilibrium electrochemical potentials (corresponding to their Fermi levels) of two metals in the growth solution, plays a key role for the symmetry breaking of bimetal nano-heterostructures during the seed-mediated growth. As a proof-of-principle experiment, by reversing the relative position of Fermi levels of the Pd nanocube seeds and the second metal Au with changing the concentration of reductant (L-ascorbic acid) in the growth solution, the structure of as-prepared products successfully evolved from centrosymmetric Pd@Au core-shell trisoctahedra to asymmetric Pd-Au hetero-dimers. The idea was further demonstrated by the growth of Ag on the Pd seeds. The present work intends to reveal the origin of symmetry breaking in the seed-mediated growth of nano-heterostructures from the viewpoint of thermodynamics, and these new insights will in turn help to achieve rational construction of bimetal nano-heterostructures with specific functions.

1. Introduction

Symmetry breaking has long been considered a key factor in the origin of the universe as well as the life activities [1–4]. For the understanding in narrow sense, symmetry breaking means the losing of symmetric elements from a highly symmetric system. In the field of nanomaterials, control of the symmetry (e.g., centrosymmetry or non-centrosymmetry) of nano-heterostructures is of significance and attracts extensive attentions, because it offers an efficient and distinctive mean to achieve complex structures and realize novel properties that are usually inconceivable for homogeneous particles or symmetric nano-heterostructure particles [5–10]. However, it is very difficult to artificially manipulate the symmetry of as-resulted nano-architectures because the final morphology usually follows the intrinsic symmetry of crystal structure [11].

In the past decade, bimetal nano-heterostructures have emerged as an important class of multifunctional nanomaterials [11–16]. Benefiting from the strong coupling between two metals, bimetal nano-heterostructures often exhibit superior performance to their monometallic counterparts in a deal of applications, e.g., catalysis, sensing, disease diagnosis and therapy, and so on [17–23]. Though diversified strategies have been developed to construct various bimetal nano-heterostructures, it remains a great challenge to produce asymmetric bimetal nano-heterostructures, as crystal structures of metals are usually of high symmetry. For example, most of noble metals are of face-centered-cubic (fcc) structure, which own O_h point group; their shapes are usually cube, octahedral or cuboctahedral with the O_h symmetry [24–32]; and their corresponding physical/chemical properties are also related to the inherent symmetry of these noble metal crystals [33]. As such, the growth of second metal (such as Au) on a free-standing metal seed (such as Pd nanocube) usually follows the high symmetry. For this reason, in the seed-mediated growth of bimetal nano-heterostructures, the final products (i.e., a core-shell structure) preferentially maintain the symmetry of seed materials [34–39]. Although bimetal nano-heterostructures with lower sym-

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metry than their inherent crystal symmetry were synthesized by interface-confined galvanic replacement reaction [26,40], introducing eccentric capping agents [41,42], or highly subtle manipulation over apparent growth kinetic parameters [43–46], the intrinsic factors to break the symmetry were not fully understood due to the inherent complexity of crystal growth at nanoscale. To date, researchers have tried to illustrate their own understanding on the formation mechanism of asymmetric nano-heterostructures in the seed-mediated growth from different aspects, such as the release of lattice-mismatch induced strain between two metals [47,48] and surface diffusion kinetics of second metal atoms on the seeds [43–45]. These insights provide us useful guidance for the designed fabrication of asymmetric bimetal nano-heterostructures, but they are still not enough to understand the symmetry breaking during the formation of bimetal nanoparticles.

In this work, we intend to reveal the intrinsic factors of symmetry breaking of bimetal nano-heterostructures during their initial growth from the viewpoint of thermodynamics. We propose that the difference of equilibrium electro-chemical potentials of two metals in the growth solution (corresponding to their Fermi levels) is the driving force that thermodynamically determines the symmetry breaking in the seed-mediated growth of bimetal nano-heterostructures or not, i.e., forming either asymmetric or centrosymmetric bimetal nano-heterostructures. This idea is well demonstrated by experimentally determining the relative position of electrochemical potentials of the corresponding two metals. Therefore, our finding provides a general criterion for predicting the growth type of second metal on the seeds. This work not only contributes to understanding of the origin of reducing symmetric elements in the seed-mediated growth of bimetal nano-heterostructures, but also helps to design complex metal nano-heterostructures with desired functions.

2. Experimental

2.1. Materials

Chloroauric acid hydrate ($HAuCl_4{\cdot}4H_2O$, analytical grade), silver nitrate ($AgNO_3$, analytical grade), L-ascorbic acid (AA, analytical grade), polyvinylpyrrolidone (PVP, K-30, Guaranteed reagent), cetyltrimethylammonium bromide (CTAB) and sodium hydroxide (NaOH, analytical grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. Cetyltrimethylammonium chloride (CTAC, 99%) was purchased from J&K Co. Ltd. Palladium (II) chloride ($PdCl_2$, analytical grade) was purchased from Shanghai Fine Chemical Materials Institute. All reagents were used as received without further purification. All aqueous solutions were prepared with ultrapure water with a resistivity of 18.2 MΩ cm.

2.2. Overgrowth of Au on Pd nanocubes

The growth model of Au on Pd nanocubes was evolved from on all corners to on one corner by introducing different concentrations of reducing agent AA in the reaction solution, as described next. The Pd seeds were dispersed in the CTAC solution (0.1 mol/L). A Pd nanocube seed solution (1 mL) was added in a solution consisting of a CTAC solution (1 mL, 0.1 mol/L) and ultrapure water (1 mL). Then a NaOH solution (0.1 mL, 20 mmol/L), a $HAuCl_4$ solution (2 mL, 1 mmol/L) and a freshly prepared 0.1 mol/L AA solution (0.1, 0.04, or 0.02 mL) were added into the above solution in order. After that, the solution was kept at 30 °C for 12 h. The product was collected by centrifugation (10,000 r/min, 10 min), washed twice with distilled water and then dispersed in distilled water. The detailed experimental parameters and corresponding growth modes of Au on Pd nanocube seeds are listed in Table S1 (online).

2.3. Measurement of the relative equilibrium potential position of Au and Pd metals in given solutions containing $HAuCl_4$ and AA

The relative equilibrium potential position of Au and Pd was determined by measuring the difference of the open-circuit potentials (i.e., V_{oc}) between the two metal (Au and Pd) electrodes in a given solution consisting of $HAuCl_4$ and different concentrations of AA solution with a Keithley 2182A nanovoltmeter. The measurements were carried out in a three-electrode cell at 30 °C. Before measurement, the electrolytic cell was immersed in a mixed solution of concentrated sulfuric acid and concentrated nitric acid with a volume ratio of 1:1, and then washed thoroughly with ultrapure water. The tested metal electrodes were polished with 0.3 and 0.05 μm Al_2O_3 powder and washed with alcohol and ultrapure water for three times, respectively. To acquire the ΔV_{oc} between Au and Pd metal in the given solution, typically, H_2O (2 mL), a $HAuCl_4$ solution (4 mL, 1 mmol/L), a NaOH solution (0.2 mL, 20 mmol/L) and a CTAC solution (4 mL, 0.1 mol/L) were added into the electrolytic cell. After a solution of 100 mmol/L AA (0.2 mL, 0.08 mL or 0.04 mL) was added, Au and Pd electrodes were inserted immediately in the electrolytic cell and connected with the positive electrode and the negative electrode of nanovoltmeter, respectively. The ΔV_{oc} values were recorded immediately. The detailed experimental parameters were listed in Table S2 (online).

2.4. Overgrowth of Ag on Pd nanocubes

Considering Cl^- ions from CTAC could react with Ag^+ ions to produce AgCl, we replaced the surfactant CTAC with PVP in the growth of Pd-Ag heterostructures: the Pd seeds were dispersed in water. A Pd nanocube seed solution (1 mL) was added in a solution consisting of a PVP solution (2 mL, 80 mg/mL) and ultrapure water (0.5 mL), and then a AA solution (1 mL, 26.1 mmol/L) and a $AgNO_3$ solution (0.02 mL, 0.55 mL, 1.2 mmol/L) were added into the above solution in order. After that, the resulting solution was kept at 30 °C for 12 h. The product was collected by centrifugation (10,000 r/min, 10 min), washed twice with distilled water and then dispersed in distilled water. The detailed experimental parameters and corresponding growth mode of Ag on Pd nanocube seeds are listed in Table S3 (online).

2.5. Measurement of the relative equilibrium potential position of Ag and Pd metals in given solutions containing $AgNO_3$ and AA

The measurements were carried out in a three-electrode cell at 30 °C. To acquire the ΔV_{oc} between Ag and Pd metal in the given solution, H_2O (4.5 mL), a PVP solution (6 mL, 80 mg/mL) and a AA solution (3 mL, 26.1 mmol/L) were added into the electrolytic cell. After that, a $AgNO_3$ solution (0.06 mL, 1.65 mL, 1.2 mmol/L) was added, then the Ag and Pd electrodes were inserted in the electrolytic cell and connected with the positive electrode and the negative electrode of nanovoltmeter, respectively. The ΔV_{oc} values were recorded immediately. The detailed experimental parameters were listed in Table S4 (online).

2.6. Characterization of products

Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) analysis were taken using a Hitachi S-4800 field emission scanning electron microscope operated at 15 kV. Low magnification transmission electron microscopy (TEM) images were taken using a JEOL-2100F transmission electron microscope operated at 200 kV. The high-angle annular

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