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Morphology-dependent structures and catalytic performances of Au nanostructures on Cu_2O nanocrystals synthesized by galvanic replacement reaction[☆]

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ABSTRACT

Au nanostructures were prepared on uniform Cu_2O octahedra and rhombic dodecahedra via the galvanic replacement reaction between $HAuCl_4$ and Cu_2O. The compositions and structures were studied by Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), High-Resolution Transmission Electron Microscope (HRTEM), X-Ray Diffraction (XRD), X-Ray Absorption Spectroscopy (XAS), X-ray Photoelectron Spectroscopy (XPS) and in-situ DRIFTS spectroscopy of CO adsorption. Different from the formation of Au–Cu alloys on Cu_2O cubes by the galvanic replacement reaction (ChemNanoMat 2 (2016) 861-865), metallic Au particles and positively-charged Au clusters form on Cu_2O octahedra and rhombic dodecahedra at very small Au loadings and only metallic Au particles form at large Au loadings. Metallic Au particles on Cu_2O octahedra and rhombic dodecahedra are more active in catalyzing the liquid phase aerobic oxidation reaction of benzyl alcohol than positively-charged Au clusters. These results demonstrate an obvious morphology effect of Cu_2O nanocrystals on the liquid–solid interfacial reactions and prove oxide morphology as an effective strategy to tune the surface reactivity and catalytic performance.

1. Introduction

Metal alloys generally exhibit advantageous properties compared to their monometallic counterparts [1] and thus great effects have been devoted in the synthesis of catalytic metal alloys. Conventional methods mostly involve complex procedures or harsh preparation conditions [2–6], and galvanic replacement reactions employing metal nanoparticles have recently emerged as a relative mild method to fabricate metal alloy nanoparticles [7–9]. Different from the metallic bond, the ionic bond will get much weakened in water with a large dielectric constant and thus galvanic replacement reactions employing metal oxide particles should occur more facilely than those employing metal particles. On the basis of such considerations, we successfully developed a very mild method to fabricate Au–Cu alloys on Cu_2O cubes via the galvanic replacement reaction between $HAuCl_4$ and Cu_2O at ambient temperature in which the formed Au–Cu alloy nanoparticles exhibited high catalytic activity in liquid phase aerobic oxidation reaction of benzyl alcohol [10].

Rich morphologies of uniform Cu_2O nanocrystals, including uniform cubes [11,12], octahedra [13,14] and rhombic dodecahedra [15], were successfully synthesized. Employing various Cu_2O nanocrystals as models, we have demonstrated strong crystal plane effect of Cu_2O nanocrystals on their surface reactivity [16–20] and catalytic performance [21–23], and then generalized a concept of crystal plane-controlled surface reactivity and catalytic performance of oxide catalysts [24,25]. The galvanic replacement reaction between $HAuCl_4$ and Cu_2O involves surface reactions on Cu_2O surface and the morphology of Cu_2O particles and exposed crystal planes should be expected to affect the galvanic replacement reaction and the resulting nanostructures. In this paper we studied the galvanic replacement reactions between $HAuCl_4$ and uniform Cu_2O octahedra and rhombic dodecahedra, whose results were compared with the previous results of the galvanic replacement reaction between $HAuCl_4$ and uniform Cu_2O cubes [10]. The morphology/crystal plane of Cu_2O nanocrystals were observed to strongly affect the galvanic replacement reaction and subsequently the structures and catalytic performances of resulting Au nanostructures.

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2. Experimental

2.1. Sample preparation

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification.

2.1.1. Surfactant-free Cu_2O nanocrystals

Cu_2O octahedra were synthesized with the procedure reported by Zhang et al. [14]. Typically, NaOH aqueous solution (2.0 mol/L; 10 mL) was added dropwise into $CuCl_2$ aqueous solution (0.01 mol/L; 100 mL) containing 4.44 g PVP ($M_w = 30{,}000$) at 55 °C. After stirring for 0.5 h, ascorbic acid solution (0.6 mol/L; 10 mL) was added dropwise into the solution. The resulting solution was stirred at 55 °C for 3 h. The resulting precipitate was collected by centrifugation and decantation and was then washed with distilled water and absolute ethanol and finally dried under vacuum at room temperature for 12 h (denoted as o-Cu_2O-PVP). The synthesis of Cu_2O rhombic dodecahedra followed the procedure reported by Liang et al. [15]. Typically, $CuSO_4$ (1 mmol) was dissolved in water (40 mL) to form a clear solution, into which OA (4 mL) and absolute ethanol (20 mL) were added successively with vigorous stirring. When the mixture was heated to 100 °C, an aqueous solution of NaOH (10 mL; 8 mmol) was added. After 5 min, an aqueous solution (30 mL) containing D-(+)-glucose (3.42 g) was added under constant stirring. The mixture reacted for another 60 min and a brick-red color gradually appeared. The resulting precipitate was collected by centrifugation and decanting, then washed with distilled water and absolute ethanol, and finally dried in vacuum at room temperature for 12 h (denoted as D-Cu_2O–OA). A controlled oxidation process carried out under an atmosphere consisting of 4% O_2 and 8% C_3H_6 balanced with N_2 was developed to remove the capping ligands on o-Cu_2O-PVP and D-Cu_2O–OA according to our previous literatures [22,23,26]. Typically, Cu_2O nanocrystals (200 mg) were placed in a U-shaped quartz microreactor and purged in the stream of $C_3H_6 + O_2 + N_2$ gas mixture (C_3H_6:O_2:N_2 = 2:1:22, flow rate: 50 mL/min) at room temperature for 30 min, and then heated to the desirable temperature (o-Cu_2O-PVP: 200 °C; D-Cu_2O–OA: 215 °C) at a rate of 5 °C/min and kept for 30 min, then the stream was switched to pure Ar (flow rate: 30 mL/min) in which the sample was cooled down to room temperature. The acquired octahedral and dodecahedral Cu_2O nanocrystals were denoted as o-Cu_2O and D-Cu_2O, respectively.

2.1.2. Au/Cu_2O nanocomposites

Au/Cu_2O nanocomposites were synthesized with our reported procedure [10]. Typically, 50 mg o-Cu_2O or D-Cu_2O nanocrystals were placed in a 250 mL conical flask containing 40 mL absolute ethanol and 4.2 mL water. The mixture was adequately dispersed under ultrasonication for 10 min and then magnetically stirred at room temperature. Then 5.8 mL $HAuCl_4$ aqueous solution of calculated concentrations was added dropwise to the above mixture. After an additional reaction for 30 min, the solid product was collected by rinse centrifugation cycles with water and absolute ethanol and then dried in vacuum for 12 h at room temperature. The acquired Au/Cu_2O nanocomposites were denoted as Au/o-Cu_2O-*x* and Au/d-Cu_2O-*x* (*x* is the calculated Au:Cu_2O weight ratios).

2.2. Structural characterization

Composite compositions were analyzed on an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). Power X-ray diffraction (XRD) patterns were acquired on a Philips X'Pert PROS diffractometer using a nickel-filtered Cu Kα (wavelength: 0.15418 nm) radiation source with the operation voltage and operation current being 40 kV and 50 mA, respectively. X-ray photoelectron spectroscopy (XPS) were performed on an ESCALAB 250 high performance electron spectrometer using monochromatized Al Kα ($h\nu = 1486.7$ eV) as the excitation source. The likely charging of samples was corrected by setting the binding energy of the adventitious carbon (C 1 s) to 284.8 eV. Scanning electron microscope (SEM) images were obtained on a JEOL JSM-6700 field emission scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEM-2100F high resolution transmission electron microscope. In-situ DRIFTS measurements were performed on a Nicolet 6700 FT-IR spectrometer equipped with an in situ low-temperature DRIFTS reaction cell (Harrick Scientific Products, Inc.) in which the sample temperature could be controlled between 120 K and 773 K. 20 mg catalyst was loaded on the sample stage of the reaction cell and then the reaction cell was evacuated and the sample was cooled to 173 K whose DRIFTS spectrum was taken as the background spectrum. Then CO (1% CO/Ar) was introduced into the reaction cell by a leak valve to 300 Pa and the DRIFTS spectrum was recorded after CO adsorption reached the steady state at a resolution of 4 cm^{-1} with over 256 scans using a MCT/A detector. X-ray absorption spectra (XAS) were collected in the fluorescence mode at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF), China.

2.3. Catalytic performance evaluation

Catalytic performances of Au/Cu_2O nanocomposites in liquid phase aerobic oxidation of benzyl alcohol (BA) were evaluated in a stainless steel autoclave with a nominal volume of 50 mL. Typically, 0.5 mL BA, 20 mL deionized water and 50 mg as-synthesized Au/Cu_2O nanocomposites were mixed with 5 mL Na_2CO_3–$NaHCO_3$ buffer solution (pH = 9). Prior to the catalytic reaction, the autoclave was purged with pure O_2 for five times. The O_2 pressure was kept at 3 atm during the reaction and the reaction proceeded at 100 °C with a stirring rate of 1200 rpm. The reaction was terminated after 2 h and then the system was cooled down to room temperature. The reaction products were extracted with ethylacetate and then analyzed by a FID-equipped GC. Cu_2O octahedra and rhombic dodecahedra were found to slightly react with BA to produce benzaldehyde (BD) but the reaction ceased within 2 h, thus this amount of BA reacting with Cu_2O octahedra and rhombic dodecahedra was deducted to calculate the BA conversion catalyzed by Au/o-Cu_2O and Au/d-Cu_2O nanocomposites.

3. Results and discussion

Our previous results showed that supported $AuCu_3$ and AuCu alloy particles were selectively formed respectively in Au/c-Cu_2O-*x* ($x \le 0.1\%$) and Au/c-Cu_2O-*x* ($0.75\% \le x \le 1\%$) during the galvanic replacement reaction between $HAuCl_4$ and uniform Cu_2O cubes [10]. Thus in the present study, we prepared Au/(o or d)-Cu_2O-*x* nanocomposites with $x \le 1\%$. The actual Au loadings of various as-synthesized Au/(o or d)-Cu_2O-*x* nanocomposites were measured by ICP-AES. The results (Table 1) are close to the corresponding calculated values, indicating the complete reduction of $HAuCl_4$ by o-Cu_2O and D-Cu_2O nanocrystals via the galvanic replacement reaction ($6H^+(aq) + 2AuCl_4{}^-(aq) + 3Cu_2O(s) = 6Cu^{2+}(aq) + 8Cl^-(aq) + 2Au(s) + 3H_2O(l)$). These results, together with our previous results on Cu_2O cubes [10], demonstrate that the galvanic replacement reaction between various Cu_2O nanocrystals and $HAuCl_4$ can adequately proceed in an ethanol–water mixture solution at ambient temperature.

As-Synthesized Au/o-Cu_2O and Au/d-Cu_2O nanocomposites were used as catalysts for the liquid phase aerobic oxidation of

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