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Construct 3D networked Au-Cu nanowires for enhanced plasmon-driven catalytic ethylene glycol oxidation through visible light irradiation

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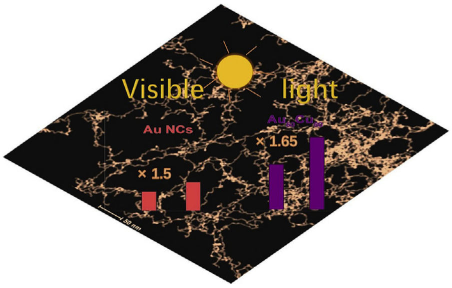
HIGHLIGHTS

- A wet-chemical method has been developed for the synthesis of networked Au-Cu NWs.
- The 3D networked Au-Cu nanowires are composed of abundant defects and kinks.
- The synergistic effect and 3D networked structure help enhance catalytic activity.
- The SPR also induce 1.65 times enhancement in catalytic activity towards EGOR.

GRAPHICAL ABSTRACT



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ABSTRACT

Photoelectrocatalytic liquid fuel oxidation holds great promise for clean energy, while their practical application greatly depends on the development of high-activity photocatalysts. We herein report the successful application of three-dimensional networked Au-Cu nanowires in the harvesting of visible light for ethylene glycol oxidation reaction. Owing to the coupling of three-dimensional networked nanowire structure and the synergistic effects, the optimized networked $Au_{50}Cu_{50}$ NWs have the best catalytic activity of 3348.3 mA mg^{-1} for the electro-oxidation of ethylene glycol. Notably, the surface plasmon resonance also induces $Au_{50}Cu_{50}$ NWs under visible light irradiation to display 1.65 times enhancement in catalytic activity than that under ambient conditions. This finding provides meaningful guidelines for engineering highly efficient photocatalysts composed of plasmonic metal nanostructures for various chemical reactions driven by sunlight.

1. Introduction

The utilization of solar energy to boost catalytic chemical conversion has been generally recognized as one of the most promising methods to substantially alleviate the modern energy crisis and environmental pollution [1–3]. Although the photocatalysts are almost exclusively semiconductors, it has been proved that plasmonic catalysis proceeded on plasmonic metals (mainly Au and Ag) has also received extensive notices due to their unique optical properties [4–6]. Plasmonic metals are featured by their unique interaction resonant photons excited by surface plasmon resonance (SPR). And SPR can be depicted as the resonant photon-induced collective oscillation of valence electrons, generated when the frequency of surface electron matches the newly established photons [7,8]. Moreover, the SPR can generate intense electric fields at the surface of the nanoparticles, which consequently lead to broad applications, such as photocatalysis,

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phototherapy, and organic molecules degradation [9–12]. Therefore, the generation and regulation of SPR are significant for widening the applications of plasmonic metals.

It has been well demonstrated that precisely controlling the shape and size of the plasmonic metallic nanocrystals allows for tuning their properties to meet the requirements of different reactions, for which the SPR intensity is largely dependent on the size and shape of nanocrystals [13–16]. For instance, the localized surface plasmon resonance (LSPR) wavelengths of Au can be efficiently tuned from the visible to near-infrared region by controlling the size and morphology of Au nanorods [7]. Accordingly, by manipulating the compositions, sizes, and morphologies of the plasmonic metals, it seems possible to engineer the nanocatalysts with enhanced photocatalytic performances [17–19].

Among various nanostructures, One-dimensional (1D) nanostructures assembled with noble metal nanoparticles would be potential plasmonic nanostructures due to its remarkable advantages such as inherent anisotropy, high conductivity, high flexibility, and high surface area [20–22]. 1D nanostructures have been highlighted as promising class of photocatalysts for various chemical reactions, such as degradation of pollutant, reduction of CO_2, and hydrogen evolution reaction [23–25]. During these photocatalytic reaction, the SPR effect and 1D plasmonic nanowire nanostructure play crucial roles in promoting photocatalytic activities. However, the applications of the liquid fuel photoelectrocatalytic oxidation induced by the SPR effects remain unexplored. To this end, the design and synthesis of 1D plasmonic photocatalysts that combined the superiorities from SPR effect and 1D nanowires (NWs) structure are indeed crucial for the substantial enhancement of photoelectrocatalytic performances of liquid fuel oxidation.

With this goal in mind, we herein proposed a new strategy for making a new class of 3D networked Au-Cu NWs. Impressively, totally different from previously prepared NWs, the newly generated Au-Cu NWs with 3D feature that contain many atomic steps and defects, providing additional surface active sites for photocatalysis. In virtue of the unique 3D networked NWs structure as well as the synergistic and electronic effects, the as-obtained 3D Au-Cu NWs display outstanding electrocatalytic activity of 3348.3 $mA\,mg^{-1}$ towards ethylene glycol oxidation reaction (EGOR), which is much higher than that of the pristine Au nanocrystals (Au NCs). More significantly, we take advantages of the plasmonic Au with strong SPR to enhance the catalytic activity towards EGOR under visible light illumination by the 3D networked Au-Cu NWs, and the resultant $Au_{50}Cu_{50}$ NWs with the optimized atomic ratio achieve 1.65-fold enhancements in catalytic activity, showing a significant promise for serving as ideal photoelectrocatalysts towards liquid fuel oxidation.

2. Experimental section

2.1. Preparation of 3D networked Au-Cu NWs

In the synthesis of 3D networked Au-Cu NWs, 100 mg polyvinylpyrrolidone (PVP) was firstly dissolved into 10 mL deionized water in a flask. After that, 0.45 mL $HAuCl_4$ (24.3 mM) and 1.0 mL $CuCl_2$ (10.0 mM) solutions were added to above homogeneous solution in sequence. The reaction was carried out by the sequential injection of 2 mL $NaBH_4$ solution (20 mM) under rapid stirring. After continuous reaction for 3 h, the products were centrifuged twice at 10000 rpm for 10 min, and the precipitate was re-dispersed into 10 mL deionized water for further use. For comparison purpose, the $Au_{33}Cu_{67}$ and $Au_{67}Cu_{33}$ NWs were also produced following the same procedure, just with the amounts of involved $CuCl_2$ solution varied.

2.2. Physicochemical characterizations

The morphology and structure of the samples are analyzed by transmission electron microscopy (TEM) conducted on TECNAI-G20 and HITACHI HT7700 transmission electron microscope. The high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and high-resolution transmission electron microscopy (HRTEM) tests were conducted on a FEI Tecnai F20 transmission electron microscope operated at an accelerating voltage of 200 kV. An X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source (λ = 1.540598 Å) was used to obtain the power X-ray diffraction (PXRD) patterns of the samples. The compositions and elemental valences were characterized by X-ray photoelectron spectroscopy (XPS), which were performed on a VG Scientific ESCALab 220XL electron spectrometer using 300 W Al Kα radiation. The concentrations of the catalysts before and after electrochemical measurements were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, 710-ES, Varian).

2.3. Electrochemical measurements

A standard three-electrode cell was employed to perform all the electrochemical measurements. In the preparation of catalysts-coated electrode, firstly, the catalysts should be re-dispersed in a mixture solvent containing nafion (5%; v-v = 1:0.005) and isopropanol to form a homogeneous catalyst ink by sonicating for 30 min. Next, 5 μL of the dispersion was transferred onto the GC electrode and dried naturally. The electrochemical tests were operated in the CHI760e electrochemical workstation (CHI760e Instruments) at room temperature. For ease of comparison, the mass activities of all the electrocatalysts were normalized with respect to the mass of Au loaded on the surface of GCE. Besides, the continuous cyclic voltammetry (CV) sweeps of 500 cycles have also been conducted for evaluating their long-term stability. Notably, all the visible light photo-electrochemical measurements were carried out by irradiating working electrodes using a xenon lamp (150 W), which equipped with UV cut–off filter (> 400 nm).

3. Results and discussion

The 3D networked Au-Cu NWs were synthesized by directly co-reducing $HAuCl_4$ and $CuCl_2$ with the protection of PVP. The morphologies, shapes, and structures of the as-prepared products were characterized by a series of tests. The TEM images (Fig. 1a–c) clearly showed that the ultrathin Au-Cu NWs displayed the typical 3D networked morphology with many kinks. And the diameter was calculated to be ca. 4.1 nm (Fig. S1). The atomic ratio of Au/Cu was 50.3/49.7, as determined by EDX (Fig. 1d), being consistent with ICP-AES (Au/Cu = 50/50). The HAADF-STEM images (Fig. 1e–g) also showed the unique 3D networked NWs structure with many low coordination atoms and defects on the surface, which was considered as the electrocatalytic active sites. PXRD was carried out to investigate their structure properties, as seen, the diffraction peaks of Au-Cu NWs located between pristine Au and Cu (Fig. 1h) are in good agreement with the face-center-cubic (fcc) Au (JCPDS no. 04–0784) [26,27], indicating the presence of Au-Cu alloy phase in the 3D networked Au-Cu NWs [28]. For further confirming their crystal structures, the HRTEM test has also been performed, a clear view in Fig. S2 indicated that the as-prepared ultrathin Au-Cu NWs contained many defects and atomic steps, which could provide additional active sites for enhancing electrocatalysis. Moreover, the *d*-spacing of adjacent fringes was calculated to be *ca.* 0.212 nm, which is slightly smaller than that of {111} lattice spacing of Au, indicating the occurrence of lattice contraction, which further confirmed the formation of Au-Cu alloy. For comparison, the pristine Au nanocrystals (Au NCs) with larger diameter have also been prepared through the same method (Fig. S3).

By simply changing the concentration of $CuCl_2$ solution, 3D networked Au-Cu NWs with tunable compositions can also be made. Fig. 2 showed the representative TEM and HAADF-STEM images of $Au_{67}Cu_{33}$ (Fig. 2a and b) and $Au_{33}Cu_{67}$ NWs (Fig. 2d and e). As observed, both $Au_{67}Cu_{33}$ and $Au_{33}Cu_{67}$ NWs possessed the typical 3D networked