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Electrochemical activated PtAuCu alloy nanoparticle catalysts for formic acid, methanol and ethanol electro-oxidation

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ABSTRACT

Through synthesizing a series of carbon supported ternary PtAuCu nanoparticle catalysts with the varied Cu content followed by subsequently electro-chemical activation treatment, highly active Pt-Au-rich nanoparticle catalysts have successfully been acquired in the present paper. The as-synthesized and activated catalysts were characterized using X-ray diffraction (XRD), transmission electron spectroscopy (TEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV) and chronoamperometry (CA). The results show that the electrochemical activation process has a strongly interrelationship with the compositional ratio between Pt/Au and Cu. The higher the Cu content is in the precursor, the lower the residual buried-underneath Cu atoms retain after the activation. Among the catalysts, the activated $Pt_{10}Au_{10}Cu_{80}/C$ exhibits the best catalytic performance for the electro-oxidation of commonly-targeted small organic molecule fuels including formic acid, methanol and ethanol in acid circumstance. The catalytic activity enhancement mechanism based upon the electrochemical activation process as well as induced possible synergistic effect from elemental interactions was also discussed.

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1. Introduction

Electro-oxidation of small organic molecules especially formic acid, methanol and ethanol has been investigated extensively because of their great potential in the development of sustainable and clean energy technologies such as direct formic acid fuel cells (DFAFCs) and direct methanol/ethanol fuel cells (DMFCs/DEFCs) [1,2]. It is well known that Pt has been thought as the best catalyst in fuel cells. Unfortunately, pure Pt would easily suffer from CO deactivation during operating process. Moreover, high cost and limited available resources of Pt in the earth are the major obstacle to massive application of fuel cells. To further decrease the cost of fuel cells, many efforts are focused on the preparation of economical and effective nanocatalysts. Among them, the multi-elemental decorating/alloying route has emerged to be a cost-effective and high efficiency way to improve the catalytic activity of Pt catalyst [3,4]. From then on, different Pt-based multi-elemental nanocatalysts have been extensively investigated, such as PtRu [5], PtNi [6], PtCo [7], PtSn [8], Cu/Ni/Co@Pt [9–11], etc. The presence of foreign additives, not only greatly reduces the usage of the precious Pt metal, but also provides oxygen-containing reactive sites to facilitate the removal of adsorbed poisonous CO species at low potentials. Among them, the bimetallic nano-catalysts of Pt decorated/alloyed with Au have attracted more interest since the introducing of Au dopant can acquire excellently catalytic activity for the formic acid [12], methanol [13] and CO oxidation [14]. Especially for the formic acid oxidation (FAO), the bimetallic alloyed or decorated catalysts with separated Pt atoms embedded in Au surrounding exhibit a markedly superior catalytic activity [15]. Previous researches have shown that the FAO on Pt follows a dual-path mechanism: a dehydrogenation path (direct pathway) and a dehydration path (indirect pathway) [16]. However, on the appropriate alloyed or decorated Pt/Au surface, the FAO reaction should mainly undergo a dehydrogenation pathway by suppressing the formation of the CO poisoning intermediate (so-called ensemble effect [17]), eventually contributing to the catalytic activity promotion relative to the pure Pt. To further improve the usage efficiency of noble metals in the field of catalysis, people always introduce one or more prone leaching components into the catalyst precursor, such as Cu, Co, Fe, etc. After leaching of these sacrificial elements under an appropriate chemical or electrochemical condition, additional active sites will

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be evolved with the enlargement of surface roughness as well as the enrichment of precious elements on the surface [18]. For example, Strasser and co-workers [19,20] have developed a series of as-dealloyed Pt-based nanoparticle catalysts with excellent activities for oxygen reduction reaction (ORR). They found that, after suffering a suitable electrochemical cycling treatment in acid solution, the non-noble element (M: Cu, Co or Ni) can be selectively leached away from the surface of the bimetallic Pt-M nanoparticles. Simultaneously, these nanoparticles gradually evolve into typical core (Pt-M)-shell (Pt) or nanoporous structures, depending on the size of the initial alloy particles [21,22]. In the Pt-Cu binary system, this surface non-noble element leaching phenomenon is particularly significant for acquiring good catalytic performance. To the best of our knowledge, there exist few reports on the Cu-leaching/activation of trimetallic Cu-Pt-Au system till now. Herein, we designed a series of carbon black supported PtAuCu nanoparticle catalysts with a varied copper content and investigated the effect of Cu content on the electrochemical leaching behavior as well as the electrocatalytic activities toward formic acid, ethanol and methanol oxidation in acid media. The result shows that, the electrochemical activated PtAuCu catalyst exhibits much better catalytic activity and stability toward formic electro-oxidation as compared with the bimetallic Pt-Au counterpart. Moreover, the superior electrocatalytic performance is also achieved for the methanol and ethanol oxidation.

2. Experimental

2.1. Synthesis of catalysts

The activation of carbon black support (Cabot Vulcan XC-72R) was performed in a concentrated HNO_3 (20 %) at 60 °C for 1 h and then washed repeatedly with ultra-purified water and evaporated to dryness. All of the chemicals used were of analytical grade. The carbon supported $Pt_xAu_xCu_{100-2x}$($x = 10/20/30/40/50$) catalysts were prepared as follows: K_2PtCl_6, $HAuCl_4{\cdot}4H_2O$ and $CuSO_4{\cdot}5H_2O$ were selected as metal sources. The required stoichiometric amounts of metal source salts were dissolved in ethylene glycol. Then, an appropriate amount of as-treated active carbon black (ca. 30 wt.% metal/70 wt.% carbon) was added in the mixture and ultrasonically stirred for 4 h. After that, a fresh mixing solution of $NaBH_4$ and ethanol with a pH value of ca. 13 was added, drop by drop, to the well-dispersed mixtures under vigorous stirring to facilitate the formation of metal nanoparticles on active carbon support. Finally, the as-prepared suspensions were washed repeatedly with ultra-purified water to neutral and evaporated to dryness in nitrogen atmosphere.

2.2. Physical characterization of catalysts

The crystalline structure of catalysts was detected by X-ray diffractometer (XRD, Bruker-D8-Advance) with the Cu Kα radiation ($\lambda = 0.15406$ nm) generated at 40 kV and 40 mA. The microstructure and morphology were examined by transmission electron microscopy (TEM, JEM-2100, JEOL). The chemical composition of catalysts was analyzed using energy dispersive X-ray analyzer (EDX, Bruker-QX-200). X-ray photoelectron spectroscopy (XPS) experiments were performed with a ThermoFisher Scientific ESCALAB 250 spectrometer using a monochromatised Al Kα radiation at 15 kV and 10 mA. The binding energies (BE) were corrected by referencing the C1s peak at 284.87 eV.

2.3. Electrochemical measurements

All electrochemical measurements were performed in a standard three-electrode cell using a CS-350 Potentiostat. A saturated calomel electrode (SCE) and platinum foil was used as the reference and counter electrode, respectively. The working electrode was prepared as follows: 5 mg carbon supported catalyst was ultrasonically mixed with 400 μL isopropanol and 100 μL Nafion solution (0.5 wt. %) to form a well-dispersed catalyst ink. Then, 4 μl of the catalyst ink was pipetted and uniformly spread on the surface of carefully polished glassy carbon electrode (GCE, Ø4 mm). After the ink dried, another 4 μl Nafion solution (0.5 wt. %) was covered on the surface to protect the pre-loaded catalyst film. The successive cyclic voltammetry (CV) scans were carried out in a 0.5 M H_2SO_4 solution between −0.25 and 1.5 V at a scan rate of 50 mV s^{-1} until a steady CV curve was obtained. After the pre-activation treatment, the electrocatalytic activities of the as-treated catalysts towards formic acid, methanol and ethanol electro-oxidation were measured in solutions of 0.5 M H_2SO_4 + 0.5 M HCOOH, 0.5 M H_2SO_4 + 0.5 M methanol (MeOH) and 0.5 M H_2SO_4 + 0.5 M ethanol (EtOH), respectively. If no specific emphasis, the electrochemical experiments were performed at ambient temperature (~25 ± 1 °C).

3. Results and discussion

3.1. Characterization of $Pt_xAu_xCu_{100-2x}$ /C catalysts

Fig. 1 shows the X-ray diffraction (XRD) patterns of as-prepared $Pt_{10}Au_{10}Cu_{80}$/C, $Pt_{20}Au_{20}Cu_{60}$/C, $Pt_{30}Au_{30}Cu_{40}$/C, $Pt_{40}Au_{40}Cu_{20}$/C and $Pt_{50}Au_{50}$/C samples. For the $Pt_{50}Au_{50}$/C, there exist two face-centered-cubic (fcc) sets of diffraction peaks of Au (PDF, no. 04-0784) and Pt (PDF, no. 04-0802), which should be due to their thermodynamic immiscibility over a wide composition and temperature range [23]. With increasing of Cu content, the diffraction peaks may presumably be assigned to Au_3Cu-type (PDF, no. 34-1302) ($(Au,Pt)_3Cu$) crystallite for the $Pt_{40}Au_{40}Cu_{20}$/C and $Pt_{30}Au_{30}Cu_{40}$/C samples. In the case of samples with much higher Cu content, such as $Pt_{20}Au_{20}Cu_{60}$/C and $Pt_{10}Au_{10}Cu_{80}$/C, except for the Au_3Cu-type ($(Au,Pt)_3Cu$) crystallites, the excess Cu could exist in the form of Cu_2O crystallite (PDF, no. 65-3288). In addition, all diffraction peaks shift to higher angles compared to the standard reference profile of Au_3Cu, especially for the high-index reflections. According to Bragg's law, $\lambda = 2d\sin\theta$, if the value of d decreases, the values of the angles θ and 2θ of the fundamental reflections increase at a given radiation wavelength λ. This demonstrates that the introduction of Pt with a smaller atomic radius causes the lattice contraction of Au_3Cu cell. Meanwhile, it

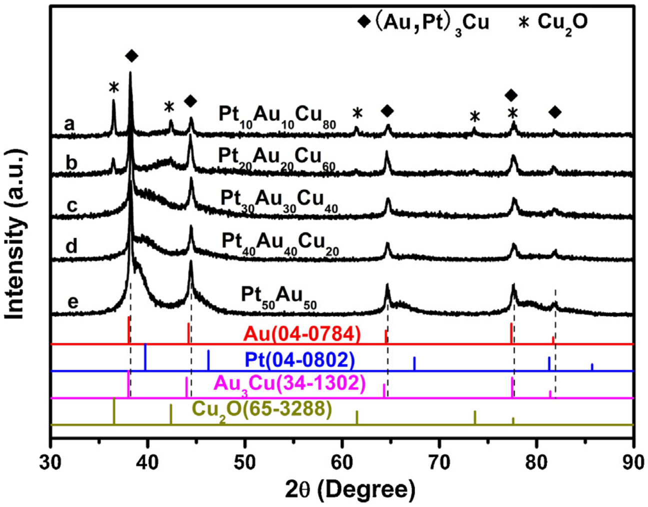

Fig. 1. XRD patterns of the as-prepared (a) $Pt_{10}Au_{10}Cu_{80}$/C, (b) $Pt_{20}Au_{20}Cu_{60}$/C, (c) $Pt_{30}Au_{30}Cu_{40}$/C, (d) $Pt_{40}Au_{40}Cu_{20}$/C and (e) $Pt_{50}Au_{50}$/C catalysts.

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