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Facile coupling of content design and efficient modulation on the activity of CNT-supported PdAgCu nanoparticle electrocatalysts: Leaching lift-up and annealing fall-off

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ABSTRACT

In the present study, carbon nanotubes (CNTs) decorated with Pd, PdAg and PdAgCu nanocatalysts with various Cu content have been synthesized by a wet chemical route. These catalysts are characterized by X-ray diffraction (XRD), transmission electron spectroscopy (TEM), high-resolution transmission electron spectroscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV) and chronoamperometry (CA). After suffering an efficient electrochemical leaching activation, the post-activated $Pd_{25}Ag_{25}Cu_{50}$/CNTs catalyst demonstrates the best catalytic activities toward common small organic molecules oxidation reaction including methanol, ethanol and formic acid. Apart from the triggered high electrochemical active surface area (S_{EAS}) owing to surface reconstruction via Cu depletion, the widespread geometric donation (i.e., lattice mismatch, strain, defect and/or dislocations) and strengthened electronic interaction between Pd, Ag and residual buried Cu should play significant roles in the catalytic activity enhancement. It also evidences that the annealing toward as-synthesized catalyst results in a significant decrease of S_{EAS} value, thus engendering a degradation on the mass activities of electrocatalytic oxidation reaction toward small organic molecules.

1. Introduction

In view of the gradually imminent energy crisis (i.e., depletion of fossil fuel) and ecological environment problems (i.e., global warming and pollution), pursuit of alternative energy sources becomes increasingly important and urgent. Direct alcohol fuel cells (DAFCs) and direct formic acid fuel cells (DFAFCs) have positioned as the smartest choice as a renewable power source owing to their low work temperature and high efficiency [1–3]. However, their large-scale commercial application (i.e., in automotive field) is severely hindered by the unsatisfied durability of current electrocatalyst materials for electro-catalytic reaction [4,5]. In order to improve the performance of fuel cells, one of the most important strategies is to develop an anode catalyst with high-performance for electro-oxidation reaction toward the feeding fuels such as common small organic molecules. Palladium (Pd) has attracted much attention in recent years due to the reason that possessing the same number of outermost electrons and similar physicochemical properties but being more cost-effective relative to Pt. In order to promote the practical progression, much research has been devoted to improve the catalyst activity per unit mass of Pd so as to further reduce the loading of noble metal and the cost as well.

It is found that, multiple element Pd-based alloys exhibit improved catalytic activities than pure Pd, such as binary Pd-Pt [6,7], Pd-Au [8], Pd-Ru [9], Pd-Pb [10], Pd-Cu [11] and ternary PdAuCu [12], AuPdPt [13], PdSnPt [14], etc. In addition, the less noble metal Ag is also verified to be an effective additive to noble metal based nanocatalysts owing to the fact that the as-revealed promoting functionality via Ag-dope is more significant than the other common transition metals (i.e., Ni, Co, Fe, etc.) [15–18]. For example, Tong et al. [19] have reported a novel Ag-Pt nano-clusters with silver nano-particulate (NP) core and ultra-thin platinum

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nano-rod (NR) shell, which exhibited high activity and stability for methanol electro-oxidation reaction. Wang et al. [20] have put forward a novel bimetallic nanoporous Pd-Ag catalyst and ascribed their superior activities to the synergy of bi-functional and electronic effect. Cai et al. [21] also synthesized a kind of PdAg/C catalysts with different metal ratios, and found that the Pd_1Ag_1/C showed much higher catalytic activity than the other Pd-Ag binary counterparts as well as mono-Pd catalyst. And the in-depth reason should be ascribed to the fact that, the difference in the x:y value of Pd_xAg_y nanoparticles (NPs) will lead to distinct distribution of Pd monomer, Pd2 dimer, Pd3 trimer as well as larger ensembles on the particle surfaces, thus resulting in different abilities to adsorb reactants. Moreover, it is generally acknowledged that Cu as an assistant component also plays an important role for promoting catalytic activity of noble metals such as PtCu [22,23]. Similar to the noble Pt, the combination of Cu with congeneric Pd can also generate intriguing catalytic performance [24,25]. Meanwhile, the different standard potential gap between Cu (Cu^{2+}/Cu = +0.337 V) and noble metal (Pt^{2+}/Pt = +1.2 V, Pd^{2+}/Pd = +0.987 V) facilitates the selective leaching or de-alloying of Cu in electrolyte under galvanic mode. During this typical activation (de-alloying) or reconstruction process, newly self-assembled noble metal rich shell will gradually evolved, which undoubtedly provides more accessible active sites per unit mass of precious metal so as to lower the total cost of electrocatalyst effectively. Generally, annealing of multi-component materials can not only make the chemical composition more uniform but also remove the residual stress. And it also triggers thermal-induced re-crystallization for either metastable material or metastable region. Apart from the situations mentioned above, the thermal-induced mergence and aggregation will indeed lead to either precipitation or remarkable growth of the constituent crystals especially for the nano-scale materials. For example, Strasser and co-workers [26] have studied the effect of annealing temperature and reaction time to the activity of $Pt_{25}Cu_{75}$ bimetallic nano-particulate electrocatalyst and found that crystallite sizes increase as the annealing temperatures rise. Inspired by the above analysis, how to develop an efficient methodology comprising elemental content design as well as composition/topography post-reconstruction is still one of the most promising paths to promote catalytic performance as well as to diminish the cost of precious metal related electrocatalyst.

Herein, we utilized multi-walled carbon nanotubes (CNTs) as supporting material to construct CNT-supported PdAgCu NPs catalyst via a simple wet-chemical route. Influence of the Cu content ratio and electrochemical leaching on the morphology, composition distribution as well as electrocatalytic performance was explored in detail. Meanwhile, annealing effect on the activation, morphology and catalytic activity of the PdAgCu NPs was also depicted. The leaching lift-up and annealing fall-off relationship on catalytic performance of CNT-supported PdAgCu catalyst was clarified for the first time. Till now, there are still rare reports focusing on post-modulation of physicochemical microstructure and electrocatalytic activities toward trimetallic Pd-Ag-based nanocatalysts. With the common small organic molecules as targeted fuels, the post-activated $Pd_{25}Ag_{25}Cu_{50}$/CNTs present the best electrocatalytic activities toward their electro-oxidation reaction, making it as an attractive anode electrocatalyst in the renewable energy-related field.

2. Experimental

2.1. Preparation of catalysts

Multi-walled CNTs (Φ 50 nm, Shenzhen Nanotech Port Co. Ltd.) was functionalized in a concentrated HNO_3 at 80 °C for 1 h. Then, the activated support was washed repeatedly with ultrapure water and evaporated to dryness. CNT-supported Pd, PdAg (with atomic ratio of 50:50), PdAgCu-A (45:45:10), PdAgCu-B (35:35:30) and PdAgCu-C (25:25:50) were synthesized using $PdCl_2$, $AgNO_3$ and $CuSO_4 \cdot 5H_2O$ as metal sources, $NaBH_4$ as reducing agent and functionalized-CNTs as support. All chemical reagents were of analytical grade and used as received without further purification. Herein, total metal of 0.1 mmol (Pd + Ag + Cu) was taken as datum point for all of the as-synthesized catalysts. Taking the preparation procedure of PdAgCu(25:25:50)/CNTs catalyst as an example: First, the required stoichiometric amount of metal source including 0.025 mmol $PdCl_2$ (0.00751 g), 0.025 mmol $AgNO_3$ (0.00426 g) and 0.05 mmol $CuSO_4 \cdot 5H_2O$ (0.0126 g) were completely dissolved in ethylene glycol under continuous magnetic stirring to maintain the atomic target ratio of Pd: Ag: Cu (25:25:50). Then, 0.0257 g functionalized-CNTs were dispersed in the above ethylene glycol solution containing metal salts to meet the appropriate ratio of metal/support (ca. 25 wt % metal/75 wt % support). In order to achieve the in-depth reduction, excessive $NaBH_4$ and ethanol mixture with a pH value of ca. 13 was added dropwise to the suspension. Then, the suspension was vigorously stirred for another 3 h to promote metal NPs uniformly-anchored on the CNTs support. Finally, the catalyst suspension was washed repeatedly with ultrapure water and alcohol to neutral, and dried. By appropriate modulating the atomic ratios between Pd, Ag and Cu, CNT-supported Pd, PdAg (50:50), PdAgCu-A (45:45:10) and PdAgCu-B (35:35:30) catalysts were successfully synthesized via a similar procedure aforementioned.

2.2. Characterization of catalysts

The phase content of catalysts was analyzed using a Bruker-D8-Advance X-ray diffractometer with the Cu Kα radiation (λ = 0.15406 nm) generated at 40 kV and 30 mA. The morphology and chemical composition were characterized using a JEM-2100 transmission electron microscopy and a Bruker-QX-200 energy dispersive X-ray (EDX) analyzer. X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250) were used to detect the surface chemical state of electrocatalyst with monochromatic Al Kα radiation operating at 15 kV and 10 mA.

2.3. Electrochemical measurements

All electrochemical measurements were conducted using a CS-350 Potentiostat at ambient temperature (~25 °C). The preparation scenario of working electrode was as follows: 5 mg of catalyst powder was ultrasonically mixed with 300 μL isopropanol and 100 μL Nafion solution (0.5 wt%) to form a well-dispersed catalyst ink. Afterward, 4 μL of as-obtained catalyst ink was deposited on a polished glassy carbon electrode (GCE, Φ 4 mm). Then, another 4 μL Nafion solution (0.5 wt %) was covered on the surface to protect the pre-loaded catalyst film when the catalyst ink dried. A bright Pt plate and a saturated calomel electrode (SCE) or an Hg/HgO (1.0 M KOH) electrode (MMO) was taken as the counter and reference electrode, respectively. The voltammetric activation was performed in a 0.5 M H_2SO_4 solution and corresponding electrocatalytic activities toward methanol, ethanol and formic acid oxidation were measured in 1.0 M KOH +1.0 M MeOH, 1.0 M KOH +1.0 M EtOH and 0.5 M H_2SO_4 + 0.5 M HCOOH, respectively. The recorded current densities were normalized by equivalent mass of Pd on the GCE surface according to the following equation:

$$m_{Pd} = \frac{5mg_{Catalyst} \times 25\%_{Metal}}{400\mu L_{ink}} \times 4\mu L_{ink} \times Pdwt\cdot\%_{[Pd_xAg_yCu_z]}$$