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Pd-on-NiCu nanosheets with enhanced electro-catalytic performances for methanol oxidation

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ABSTRACT

For the exploration of catalysts with excellent performance in alkaline fuel cells, high-performance two-dimensional (2D) Pd-on-NiCu nanosheets were synthesized through the kinetics controlling synthesis of NiCu nanosheets followed by Pd nanoparticles (NPs) embedding treatment at room temperature. In which case, well-dispersed Pd NPs with the average diameter of ~4 nm are embedded on NiCu nanosheets (BET surface area of 180.7 m^2g^{-1}). Pd-on-NiCu nanosheets exert remarkable high performance in electrocatalytic activity, methanol-tolerance and stability, the electrocatalytic mass activity of Pd-on-NiCu nanosheets is 1827 $mAmg^{-1}$, which is over 6-fold higher than that of commercial Pd/C (289 $mAmg^{-1}$), and the current density of the electrocatalyst decreases after 300 cycles of only 6%. Therefore, Pd-on-NiCu nanosheets can be considered as one of the most promising candidates for fuel cells applications.

1. Introduction

Fuel cells are attracting increasing attention in the field of new energy in recent years, due to its high energy conversion efficiency, low pollution and extensive fuel sources [1,2]. Particularly, among the vast variety of fuel cells, the alkaline direct methanol fuel cells (ADMFCs) have received more and more attention based on its advantages, including less toxic than the metal anode catalyst, lower potential of cathodic oxygen reduction reaction and so on [3–5]. In spite of many advances in the research of ADMFC, its efficiency and power density still need to be enhanced, which depended on kinetics of the fuel-cells anode reaction and methanol crossover [2,6]. As the small molecule of methanol can easily cross over from the anode to the cathode side through the polymer membranes of ADMFCs [7], the advanced methanol-tolerant catalysts with high performance are of great importance for the practical applications of fuel cells devices [8].

So far, Pt- and Pd-based alloys [9–11] are reported to have shown methanol tolerance and meanwhile retained catalytic activity for the MOR [9,12–14]. However, Pt-based alloy electrocatalysts are available only with low metal loading and thus high costs, which is not desirable for DMFCs application [15]. Owing to high performance and high methanol-tolerance [16], Pd-based catalysts are considered to be a better alternative to Pt-based catalysts for the MOR in alkaline medium [17–20]. On account of the strain and ligand (electronic) influence [21], Pd-M (M = Ni, Co, Cu, etc.) alloy nanocomposite catalysts can produce outstanding catalytic activity besides methanol-tolerance [10,22–26]. However, the activity, selectivity, stability and cost of Pd-included nanoalloy electrocatalyst still need to be further improved to meet the requirements of ADMFC commercialization [26].

Furthermore, the performance of Pd-including nanocatalyst is affected by particle size [27], morphology [28], the properties of carrier material [29], etc. The catalytic activity and selectivity of catalyst can be adjusted by controlling the size and morphology of Pd nanoparticles (NPs) [30,31]. Pd NPs are well dispersed on the surface of an ideal carrier, which can not only increase the performance and stability of the catalyst [29], but also improve the atomic efficiency of Pd. Hence, high specific surface area of carrier materials with excellent properties of electron transportation and adsorption of reaction substrate is also a crucial factor for the improvement of catalytic performance of supported Pd NPs toward MOR [32]. Besides excellent methanol-tolerance, economical hetero-structured Pd-on-NiCu nanocomposites will get remarkable enhancement in terms of electrocatalytic activity toward the MOR in alkaline media due to the synergy of metal component.

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Based on our previous research [26,33], NiCu alloy nanosheets with large surface area were chosen to work as the carrier to support ultra-tiny Pd NPs to gain high catalytic performance, and 2D Pd-on-NiCu nanosheets structures have been synthesized through the dynamics controlling synthesis of NiCu nanosheets followed by Pd NPs (~4 nm) embedding treatment. When applied as electrocatalyst for methanol oxidation reaction (MOR) in alkaline media [26], Pd/$Ni_{70}Cu_{30}$ nanosheets (the mass percent of Pd NPs is 4.4%) showed observably high performance in catalytic activity (1827 $mAmg^{-1}$) and methanol-tolerance, in which case catalytic activity is over 6-fold higher than currently commercialized Pd/C (289 $mAmg^{-1}$). As far as we know, this is the first report about the noble metal NPs supported on alloys nanosheets catalysts exhibit such fantastic catalytic performance towards MOR. As-designed 2D sheet-structured Pd-on-NiCu nanocomposite will not only increase the atomic efficiency of Pd, but also gain high performance in MOR for the fuel cells catalysts applications.

2. Experimental

2.1. Chemicals

Nickel chloride ($NiCl_2 \cdot 6H_2O$, 98.0%), Copper chloride ($CuCl_2 \cdot 2H_2O$, 99.0%), Palladium chloride ($PdCl_2$, 59–60%), Hydrochloric acid (HCl, 36.0–38.0%), CTAC($C_{20}H_{44}ClN$, 97%), ammonia ($NH_3 \cdot H_2O$, 22–25%), Potassium borohydride (KBH_4, 99%), sodium hydroxide (NaOH, 99%), potassium hydroxide (KOH, 82.0%), ethanol (C_2H_5OH, 99.7%), methanol (CH_3OH, 99.5%) were purchased from Shanghai Aladdin Reagent Co. Ltd, China. All the reagents were in analytical purity and used without further purification. The preparation of collodion membranes whose thickness is about 0.20 mm was carried out on a Chemat Technology Spin-Coater KW-4A with a silicon substrate at the rotary speed of 1000 rpm for 20 s. Then the artificial active collodion membranes were allowed to dry naturally in room environment and were peeled for spare.

2.2. Preparation of NiCu nanosheets

2D NiCu nanosheets were fabricated using a simple aqueous solution method: 10 mL solution of $NiCl_2$ (5 $mmolL^{-1}$) and $Cu(NH_3)_4Cl_2$ (2 $mmolL^{-1}$) in a molar ratio of 7:3 and PVP solution (1 $mLmg^{-1}$) were added into a 25 mL glass tube under an argon atmosphere with the bottom sealed by collodion membrane, $Cu(NH_3)_4Cl_2$ were synthesized by $CuCl_2$ and $NH_3 \cdot H_2O$, then a 10 mL of KBH_4 (30 $mmolL^{-1}$) was added into a 150 mL glass beaker [33]. The pH of the reaction solution was ~10. After reacting for 3 h, the black products were collected selectively from the side of the metal ion solution and washed thoroughly with distilled water for twice and then ethanol successively. Then the black products were dissolved in 5 mL ethanol for storage.

2.3. Synthesis of the Pd NPs

As mentioned in previous articles [34], the small sized Pd NPs were synthesized as follows: 44.5 mg $PdCl_2$ were dissolved in a 25 mL 0.2 $molL^{-1}$ HCl solution to obtain 0.01 M H_2PdCl_4, the solution of H_2PdCl_4 (0.01 M, 0.25 mL) was first mixed with CTAC (0.1 M, 9.75 mL). And then a freshly prepared ice-cold (~0 °C) $NaBH_4$ solution (0.01 M, 0.60 mL) was added under vigorous stirring. After being stirred for 20s, the resultant solution was kept undisturbed for 3 h at room temperature. The final precipitate was filtered, washed thoroughly with deionized water and ethanol, and then dried at 60 °C for 12 h.

2.4. Preparation of the Pd-on-NiCu nanosheets catalyst

2 mL of NiCu nanoalloy (2 $mgmL^{-1}$ ethanol) and 100 μg of Pd NPs were mixed under vigorous stirring, the mixture was ultrasonicated for 3 h and then filtered and dried for 4 h at 333 K in the vacuum oven to yield the Pd-on-NiCu catalysts. 1 mg Pd-on-NiCu catalysts were added into a 25 mL stainless steel autoclave with Teflon liner followed by adding 15 mL triethylene glycol. Then autoclave was ultra-sonicated for a further 30 min and then slowly heated up to 453 K and maintained at this temperature for 8 h. Finally, the autoclave was naturally cooled down in room ambient, the yielded black products were purified by three more centrifugation, rinsing and dispersion steps with deionized water and absolute ethanol, and then dried under vacuum at 333 K for 4 h for further usage or direct preservation in ethanol.

2.5. Characterization

Transmission electron microscopy (TEM, JEOL JEM-1200EX) was used to characterize the morphologies, size, and selected-area electron diffraction (SAED) pattern of the sample. Energy dispersive X-ray (EDX) analysis for composition was conducted by Field-emission scanning electron microscopy (FESEM, JEOL, S-4800) at 5 Kev on a TN5400 EDX instrument (Oxford). An inductively coupled plasma atomic emission spectrometer (ICP-AES) from Agilent Technologies (USA) was employed to confirm the component of Pd, Cu, and Ni in the as-prepared product. Prior to the ICP-AES measurements, the NiCu nanoalloy and Pd-on-NiCu nanomaterials were dissolved in 2% HNO_3. X-Ray powder diffraction (XRD) was carried out using a Bruker D8 (German) diffractometer with a Cu Kα radiation source ($\lambda = 0.154056$ nm). For further element measurement, X-ray photoelectron spectroscopy (XPS) experiment was carried out on an RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with Al Kα radiation ($h\nu = 1486.6$ eV). Binding energies were calibrated by using the containment carbon (C*1s* = 284.6 eV) and an electrochemical analyzer was used to evaluate the electrochemical characteristics.

2.6. Fabrication of electrodes and electrocatalytic measurement

Small aliquots (c.a.5 μL) of the Pd-on-NiCu nanomaterial solutions were dropped onto a clean glassy carbon electrode (CH Instruments, Inc.) with a diameter of 3 mm. Then, the electrode had been air-dried for 1 h at room temperature. Three-electrode electrochemical cells were prepared using the modified electrode as the working electrode, a Pt wire as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrocatalytic activities of the synthesized Pd-on-NiCu nanomaterial in the three electrode cells were measured using a CHI 660E electrochemical workstation (Shanghai, China). A electrochemical cleaning process was applied in an argon saturated 0.5 M H_2SO_4 solution by performing cyclic voltammetry scanning at −0.2–1.0 V for 30 cycles until stable voltammograms were obtained [35]. Chronoamperotry curves were measured on fixed potential at −0.2 V in 0.5 M KOH containing 0.5 M methanol.

3. Results and discussion

3.1. Fabrication mechanism of Pd-on-NiCu nanosheets

The synthesis of Pd-on-NiCu nanosheets proceeded as shown in Scheme 1. In the first reaction stage, NiCu nanosheets were fabricated through the dynamics controlling reaction process [33]. The kinetics controlling of alloy reduction was carried out by collodion membrane. The mixture aqueous of $NiCl_2$ & $[Cu(NH_3)_4]Cl_2$ together