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Polyaniline-functionalized TiO_2–C supported Pt catalyst for methanol electro-oxidation

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ABSTRACT

The hybrid support titania–carbon black (TiO_2–C) is used as catalyst support and functionalized by polyaniline (PANI) to further improve the electro-catalytic activity and stability of platinum/titania–carbon black (Pt/TiO_2–C) for methanol electro-oxidation for the first time. Pt nanoparticles have been successfully assembled on PANI-functionalized TiO_2–C by chemical reduction method in aqueous solutions. PANI may act as a binder to fix the Pt nanoparticles on the TiO_2–C support. The catalysts were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and electrochemical measurements. It is observed that with the PANI functionalization, the Pt nanoparticles are smaller in size and more uniformly dispersed on the surface of TiO_2–C than those of Pt/TiO_2–C. Electrochemical measurements show that the electro-catalytic activity and stability of the novel platinum–polyaniline/titania–carbon black (Pt–PANI/TiO_2–C) catalyst are really improved, compared to the Pt/TiO_2–C catalyst. The significantly enhanced electro-catalytic activity and stability of Pt–PANI/TiO_2–C are mainly ascribed to: (1) the bridging position of PANI between Pt and TiO_2–C with the forming of Pt–N bonding; (2) highly dispersed Pt nanoparticles with narrowly distributed particle sizes. These studies indicate that the Pt–PANI/TiO_2–C catalyst will become a new type of catalyst for methanol electro-oxidation and may be a promising electrode material for direct methanol fuel cell (DMFC).

1. Introduction

Direct methanol fuel cell (DMFC) is considered as a prospective power source for a variety of applications, due to its high-energy efficiency, low-temperature operation, environmentally friendly nature, fast start-up and convenient manipulation over other power sources [1–4]. At present, carbon supported Pt-based catalysts are commonly used as anode catalysts for methanol electro-oxidation in DMFC [5–12]. However, because of the weak interactions between Pt nanoparticles and carbon supports, the electrochemical corrosion of carbon supports and the dissolution of platinum nanoparticles, the low electro-catalytic activity and short-term stability of these catalysts in the methanol electro-oxidation still hamper the widespread commercialization of DMFC [13].

To solve these problems, extensive efforts have demonstrated that the incorporation of novel support material (such as SiC [14,15], TiO_2 [16–20], CeO_2 [21–23], etc.) and carbon as the hybrid support is an efficient way to improve both the electro-catalytic activity and stability of Pt-based catalysts. Among them, the unique physical and chemical properties of TiO_2 [24] have made it draw increasing attention as an alternative catalyst support due to its excellent mechanical resistance and anti-corrosion ability in acidic and oxidative environments. There are many papers which have demonstrated that Pt-based catalysts used TiO_2–C as the hybrid support can enhance the electro-catalytic activity and stability of catalysts [16–20]. For example, Jiang et al. [19] has reported that the Pt/TiO_2–C catalyst synthesized by a microwave-assisted polyol process has substantially enhanced stability and identical activity as compared to Pt/C prepared by the same procedure. Lv et al. [20] has pointed that the electro-catalytic activity and stability of Pt/TiO_2–C for methanol electro-oxidation were both markedly improved compared with those of Pt/C. Therefore, the incorporation of TiO_2 and carbon as the hybrid support for Pt-based catalysts becomes more reasonable.

On the other hand, to date, many of the studies have focused on the surface treatment of supports with surfactants and functional polymers [25–31]. Among them, polyaniline (PANI) is one of the

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most studied conducting polymers because of its good electrical conductivity, environmental and chemical stability, low cost and relative easy synthesis [32]. Besides, it was reported that PANI could be a good conducting matrix to improve the dispersion of Pt nanoparticles, and then enhance electro-catalytic activity and stability [33–41]. For example, He et al. [40] has also reported that highly dispersed Pt nanoparticles are loaded onto the carbon nanotube with narrowly distributed particle sizes due to the polymer stabilization and existence of Pt—N bonding. The Pt–PANI/carbon nanotube catalyst is electroactive and exhibits excellent electrochemical stability in comparison with Pt/carbon nanotube; Zhang et al. [41] has reported that Pt nanoparticles have been successfully assembled on PANI-functionalized graphite nanoplatelet, and with PANI functionalization, the Pt nanoparticles are smaller in size and more uniformly dispersed on the surface of graphite nanoplatelet than those of Pt/graphite nanoplatelet catalyst. These results may be explained as follows: the presence of PANI, on the one hand, provides nitrogen atom nucleation centers for the Pt nanoparticles to tightly anchor onto the surface of the catalyst supports, which can bind a Pt atom with the lone pair of electrons on the N atom of PANI; on the other hand, the PANI chain extends the adsorption sites of the Pt nanoparticles, prevents the Pt nanoparticles from aggregating with each other, effectively improves the distribution of the Pt nanoparticles and reduces the size of the Pt nanoparticles [31,40,41]. Therefore, it seems more reasonable to use PANI to functionalize catalyst supports to improve the dispersion of Pt nanoparticles and then enhance electro-catalytic activity and stability.

In this work, we use PANI to functionalize hybrid support (TiO_2–C) to further improve the electro-catalytic activity and stability of Pt/TiO_2–C for methanol electro-oxidation for the first time. As we know, there have been no reports of hybrid support (TiO_2–C) functionalized by PANI as catalyst support so far. The hybrid support (TiO_2–C) was first functionalized by PANI, and then Pt nanoparticles were assembled on PANI-functionalized TiO_2–C by chemical reduction method in aqueous solutions. Moreover, the physical properties of catalysts were studied by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The electrochemical properties of catalysts were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry test. This work represents a new type of electro-catalyst with several important benefits. For one thing, the procedure is very simple and can be performed at mild conditions using commercially available reagents. For another, the Pt nanoparticles are anchored tightly and evenly on the surface of hybrid supports by the functionalization of PANI. The resulting Pt–PANI/TiO_2–C catalyst exhibits enhanced electro-catalytic activity and stability for methanol electro-oxidation in comparison with Pt/TiO_2–C catalyst.

2. Experimental

2.1. Materials

Aniline (AR), ammonium peroxydisulfate (APS, AR), sulfuric acid (H_2SO_4, AR), methanol (CH_3OH, AR), formic acid (HCOOH, 88%, AR), isopropanol (AR) and ethanol were all purchased from Chuandong Chemical Reagent Company (Chengdu, China). Titania nanoparticles (TiO_2, average 20 nm, AR) were obtained from Chengdu Aike Da Chemical Reagents Co., Ltd. Vulcan XC-72 carbon black was purchased from Cabot Company. Hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, AR) was purchased from The First Regent Factory, Shanghai, China. Nafion solution was purchased from Dupont China Holding Co., Ltd. Distilled water was produced by water purification system. All chemicals were used as received without further purification.

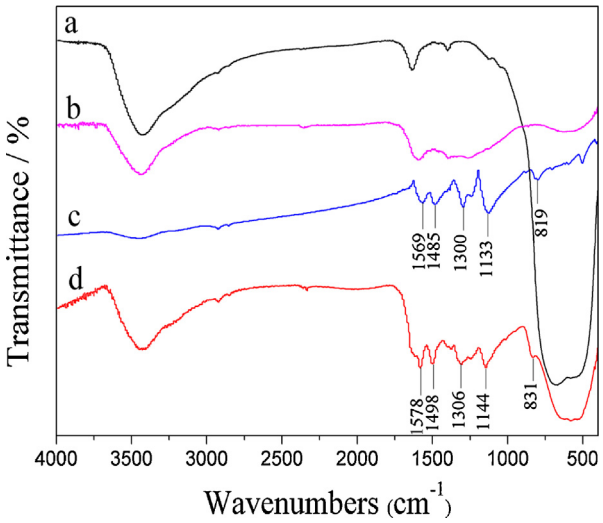

Fig. 1. FTIR spectra of TiO_2 (a), XC-72 (b), PANI (c) and Pt–PANI/TiO_2–C (d).

2.2. Preparation of polyaniline/titania–carbon black (PANI/TiO_2–C) composites

0.1 g TiO_2 and 0.15 g Vulcan XC-72 carbon black (the mass ratio of TiO_2 to Vulcan XC-72 carbon black was 2:3) were added into 50 mL 1.0 M H_2SO_4 solution, stirred and ultrasonically treated for 1 h each at room temperature, then 98 μL aniline monomer was added into it and ultrasonically treated for 1 h to uniformly disperse around TiO_2 and Vulcan XC-72 carbon black. After that, the mixture was taken out and placed in ice bath, then a definite amount of ammonium peroxydisulfate (APS) dissolved in 50 mL 1.0 M H_2SO_4 solution (the molar ratio of aniline to APS was 1:1) was added drop-wise within 1 h under vigorous stirring. The reaction solution was continuously stirred for 8 h after the addition of APS–H_2SO_4 solution. When the polymerization was completed, the resulted black dispersion was filtered and washed with ethanol and 0.5 M H_2SO_4 solution for several times till the filtrate became

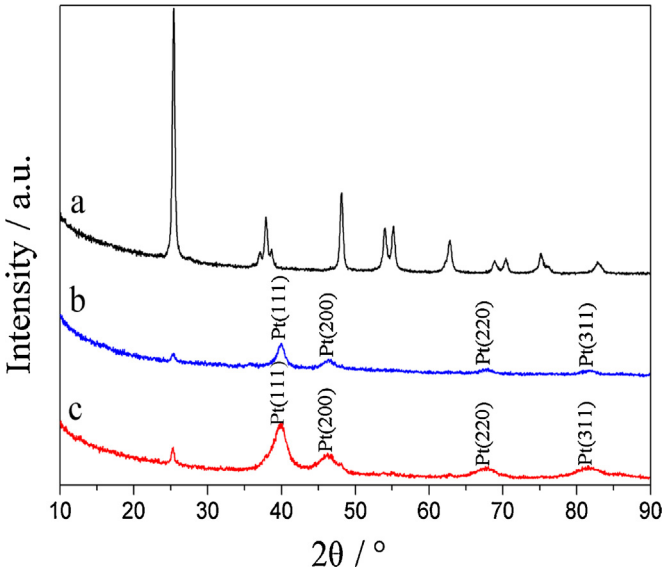

Fig. 2. XRD patterns of anatase TiO_2 (a), Pt/TiO_2–C (b), and Pt–PANI/TiO_2–C (c).