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Short communication

Novel spherical TiO_2 supported PdNi alloy catalyst for methanol electroxidation

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ABSTRACT

A novel PdNi/TiO_2 electrocatalyst for methanol oxidation is fabricated using spherical TiO_2 nanoparticles as support. The structural and electrochemical properties of the PdNi/TiO_2 catalyst are characterized by XRD, TEM and electrochemical analysis. The cyclic voltammograms of PdNi/TiO_2 catalyst show that there is a large methanol oxidation peak in about 0.882 V that is much bigger than that of the commercial PtRu/C catalyst in 0.7 V. The composite TiO_2 material has high catalytic activity without UV light illumination. The electrocatalytic activity and anti-poisoning capability of the PdNi/TiO_2 catalyst are promising, which may become a potential candidate for direct methanol fuel cell.

1. Introduction

Anode electrocatalyst is a key material governing the performance of the direct methanol fuel cell (DMFC) [1], in particular the anode catalyst with non-Pt materials or reduced loading of PtRu has attracted increasing attention. Recently, TiO_2 and TiO_2-based materials emerge as supports to reduce the loading of PtRu and enhance the catalytic activity, thanks to its low cost, commercial availability, and higher stability than carbon in oxidizing environments [2–4]. Chen et al. [5], Tian et al. [6] and Kim et al. [7] reported that the presence of TiO_2 could enhance the dispersion of the electrocatalyst particles PtRu on carbon carrier and help the catalyst to better electro-oxidize the methanol. It was found that the methanol oxidation reaction activity depended on the size-controlled PtRu nanoparticles induced by the TiO_2 support [8], and the performance of the PtRu catalyst for methanol oxidation could be improved by TiO_2 without UV excitation [9]. Indeed, TiO_2-based nanowire [10], Pt/TiO_2 nanotube electrode [11], and Pt-Au/CNT@TiO_2 [12] showed excellent catalytic activity and stability. Despite the improvement of catalytic activity, in these previous studies the loading of Pt or PtRu was still high and the loading of TiO_2 was low, because the main function of TiO_2 was enhancing dispersion of the electrocatalyst particles, and it was still the PtRu catalyst which bears the electro-oxidization function.

If the nanometer TiO_2 composite material themselves could contribute to the methanol oxidation, the non-Pt anode catalyst may become a promising candidate for DMFC. Although PdNi/TiO_2 with high catalytic activity and anti-poisoning ability has been successfully prepared in our previous work with TiO_2 nanotube as support [13], the study of non-Pt catalyst (such as the combination of Pd, Ni, Ag, Sn with different TiO_2 as support) for methanol oxidation and its catalytic mechanism is still lacking. Herein, a novel PdNi alloy catalyst supported by spherical TiO_2 nanoparticles is synthesized and its catalytic mechanism for methanol oxidation is elucidated. The spherical TiO_2 supported PdNi alloy catalyst shows promising catalytic activity, and the methanol oxidation mechanism is mainly resulted from the photocatalytic mechanism of the composite TiO_2 material that has a high catalytic activity without UV light illumination.

2. Experimental method

Spherical TiO_2 nanoparticles are obtained from TiO_2 nanopowder by the sol–gel method and by adding surfactant (PEG600 or CTAB) in the precursor solution. Spherical TiO_2 supported PdNi alloy catalyst is synthesized using the surface reductive deposition method [13]. The atomic ratio between Pd and Ni is adjusted as 1:1 and with 3 wt % PdNi loading on the surface of spherical TiO_2. X-ray

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diffraction (XRD) pattern of the sample is collected using a Bruke ADVANCE X-ray diffractometer. The surface morphologies and particles are observed by Transmission Electron Microscopy (TEM, JEOL JEM-1203). The electrochemical measurements are performed on a CHI 660C workstation (American CHI instrument) according to a previous report [13,14].

The PdNi/TiO_2 catalyst of 5 mg is mixed completely with paraffin of 30 μL and some VulcanXC-72 in the evaporating dish, followed by evaporation of the water under vacuum. The mixture is finally packed into an electrode cavity of Teflon (3-mm diameter, 5-mm depth). Electrical contact to the paste is established by placing a copper rod into the back of the mixture. The polished and modified electrode is used as the working electrode. The cyclic voltammograms and chronoamperograms are conducted in the solution of 1 mol L^{-1} H_2SO_4 and 1 mol L^{-1} methanol, 2 mol L^{-1} methanol and 4 mol L^{-1} methanol, respectively, at room temperature with the purge of N_2 at a scan rate of 50 mV s^{-1},100 mV s^{-1} and 200 mV s^{-1}. For comparison purpose, a reference commercial catalyst of 20 wt % PtRu/C is acquired from E-TEK.

3. Results and discussion

Fig. 1 shows the XRD patterns of the TiO_2 and PdNi/TiO_2. The XRD patterns of TiO_2 and PdNi/TiO_2 in Fig. 1 exhibits characteristic reflections arising from not only the anatase but also the rutile structure of TiO_2. Indeed, pure TiO_2 and PdNi/TiO_2 catalysts with anatase and rutile structures can make them having higher catalytic activity than that with only anatase or rutile structure [15,16]. In Fig. 1(a), the peaks located at 2θ values of about 25.4°, 37.8°, 48.2° and 54.4° are the (1 0 1), (0 0 4), (2 0 0) and (2 0 4) diffraction peaks of the anatase TiO_2, and the peaks located at 2θ values of about 27.5° and 36.2° are the (1 1 0) and (1 0 1) diffraction peaks of the rutile TiO_2. Compared with the pure TiO_2, the characteristic peak of anatase and rutile in Fig. 1(b) shifts from 25.7° and 27.8° to about 25.4 and 27.5°, respectively, indicating that the deposition of PdNi on the surface of spherical TiO_2 nanoparticles has influenced the structure and catalytic activity of the TiO_2. Two characteristic peaks corresponding to the (1 1 1) and (2 0 0) planes of the face-centered cubic (fcc) crystalline of Pd can be seen in Fig. 1(b). The corresponding 2θ values located at 39.96° and 46.3° are shifted shorter as compared to the 2θ values of 40.1° and 46.4° for the pure fcc Pd. The 2θ values located at 44.46° and 51.9° are associated with the (1 1 1) and (2 0 0) diffraction peaks of Ni, and they are exactly the same as that of pure Ni fcc structure, implying that the PdNi supported nanoparticles have single-phase-disordered structures, and the lattice constants are enlarged because of the Ni substitution in Pd fcc-center.

Fig. 2 shows the TEM image of the PdNi/TiO_2 catalyst, where the overall size of the particles ranges from 20 to 30 nm and the particles exhibit fine spherical feature with some PdNi alloy particles of about 1–2 nm disperse on the surface. The spherical surfaces of TiO_2 have large area which are preferable to the dispersion of PdNi alloy nanoparticles, improving the catalytic activity of PdNi/TiO_2 catalyst. The TEM result is consistent with that of XRD analysis.

The electrochemical oxidation of 1 M H_2SO_4 and 2 M CH_3OH solution is used to test the catalytic activity of PdNi/TiO_2 catalyst. Fig. 3(a) shows the cyclic voltammograms for methanol electro-oxidation of PdNi/TiO_2 and TiO_2 at a scan rate of 100 mV s^{-1}.On the scan to positive potentials from −0.2 V to 1.2 V, the onset of 0.48 V and a large methanol oxidation peak are observed at 0.882 V for the PdNi/TiO_2 catalyst. Compared with the commercial PtRu/C catalyst in Fig. 3(b) whose methanol oxidation peak potential is about 0.7 V, the methanol oxidation peaks potential of the current PdNi/TiO_2 catalyst is higher, indicating that the prepared catalyst has a higher catalytic activity. The result is consistent with our previous study [13] and literature [7,17,18]. In Fig. 3(a), the oxidation and reduction peaks near 0 V are related to the adsorption and desorption peaks of H_2. Several reduction peaks at 0.42 V are also observed due to the reduction of TiO_2 in the methanol oxidation,

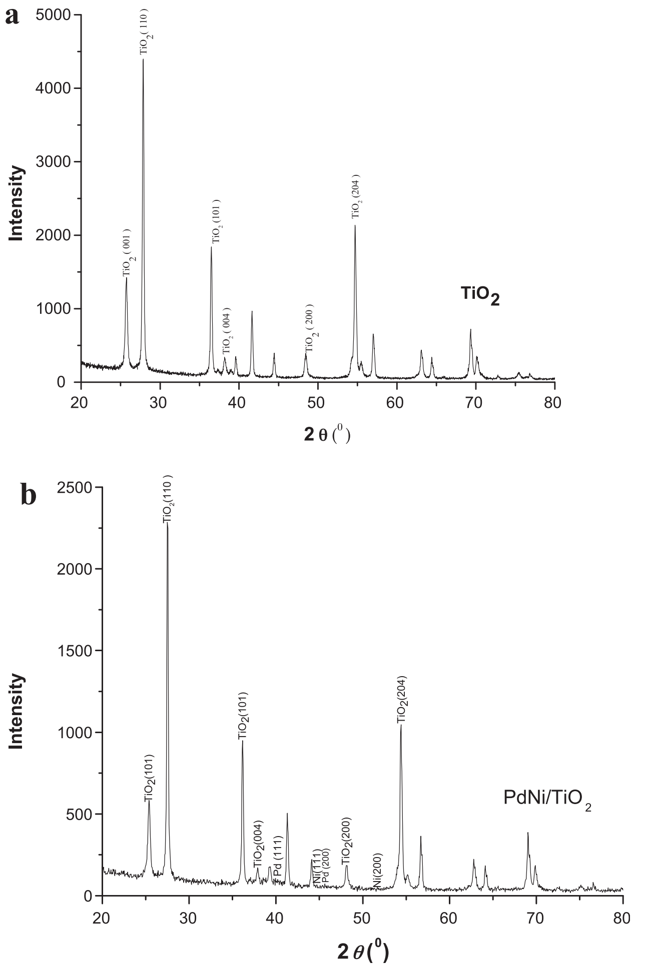

Fig. 1. XRD patterns of the TiO_2 and PdNi/TiO_2 catalyst (a) TiO_2 (b) PdNi/TiO_2.

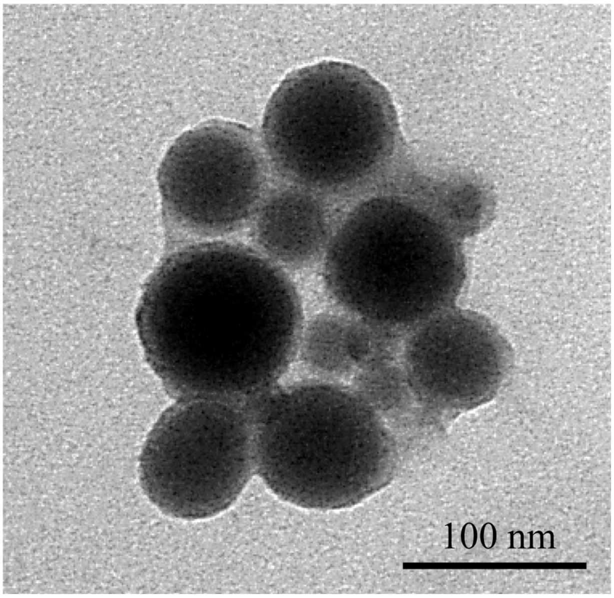

Fig. 2. TEM image of the PdNi/TiO_2 catalyst.