Pt nanoparticles supported on submicrometer-sized TiO₂ spheres for effective methanol and ethanol oxidation

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Abstract

High electrocatalytic activity for alcohol electrooxidation by Pt nanoparticles supported on submicrometer-sized TiO₂ spheres is achieved. The Pt nanoparticles with a diameter of 8–20 nm are uniformly coated on the surface of the submicrometer-sized TiO₂ spheres with a diameter of 370–500 nm via a simple wet chemical synthesis. The electrocatalytic performances of the Pt/TiO₂ submicrometer-sized TiO₂ spheres for methanol and ethanol in acidic and alkaline media are investigated systematically by electrochemical methods. Compared with the Pt catalyst supported on the commercial carbon black, the Pt/TiO₂ spheres exhibit an excellent enhanced electrocatalytic activity and stability owing to the mesoporous active sites, synergistic effect of Pt/TiO₂, and micro-channels for liquid diffusion and gaseous product to escape.

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1. Introduction

Proton-exchange membrane fuel cells have been receiving extensive attention recently [1–3], especially, direct alcohol fuel cells based on liquid fuels with a much higher energy density than gaseous fuels. The problems of the production, purification and storage of hydrogen do not exist in the direct alcohol fuel cell systems due to the direct injection of liquid alcohol fuel [4]. Among several small organic molecules alcohols, methanol with energy density of 702.32 kJ mol⁻¹ and ethanol with energy density of 1325.31 kJ mol⁻¹ [5] are really attractive because of their low toxicity, abundance and convenience in production. However, the electrocatalytic activity and reaction kinetics of catalysts for alcohol electrooxidation are dependent on many factors. For instance, an excellent dispersion of Pt nanoparticles (NPs), a splendid stability of the combination between Pt NPs and the supporting materials are essential for the catalyst to increase its electrocatalytic activity.

TiO₂, as one of the semiconductive oxides, has been widely studied for its special photoelectric properties. In addition, TiO₂ is chemical stable in both acidic and alkaline solutions, which has shown high catalytic activity for the reduction of some small organic molecules [6]. TiO₂ nanostructures are used as catalyst supports for loading Pt via various processes, including chemical precipitation method [7,8], photochemical deposition [7–9], conventional impregnation techniques [10,11], redox replacement [12–14], sputtering technique [15–17], atomic layer deposition [18], electrodeposition methods [19,20]. Recently, novel submicrometer-sized TiO₂ spheres (SMTS) are reported by Chen et al. [21], indicating that the spheres have a large specific surface area and mesoporous structure which improve the conversion efficiency of TiO₂ based dye-sensitized solar cells. To explore whether such SMTS could be used as a catalyst supports in promoting electrocatalytic activity should be a very interesting work because the mesoporous structures with micro-channels are excellent for liquid diffusion and gaseous product to escape. Besides, the rough surfaces of the SMTS provide quite good sites for loading catalyst NPs. However, to the best of our knowledge, there was no report of the SMTS used as a catalyst support.

Herein, the SMTS is synthesized by the wet chemical synthesis and used as support for the loading of Pt NPs for the electrooxidation of methanol and ethanol in both acidic and alkaline media. Interestingly, the Pt/TiO₂ spheres exhibited significantly increased catalytic activity in the fuel cell in comparison with commercially available carbon black for supporting Pt. It demonstrates that the novel Pt/TiO₂ spheres can be a potential anodic electrocatalyst for direct alcohol fuel cells.

2. Experimental

2.1. Reagents and materials

Tetrabutyl titanate, diethylene glycol, acetone, H₂PtCl₆·6H₂O, NaBH₄, methanol, ethanol, Na₂SO₄·10H₂O, H₂SO₄ and KOH were
purchased from Sinopharm Chemical Reagent Corp., Ltd. Commercial carbon black (CB, Vulcan XC72R) was purchased from CABOT Corp. Nafion® and silver paste were purchased from Sigma–Aldrich and SPI Supplies. Graphite rod electrode, Ag/AgCl electrode and platinum foil electrodes were purchased from Gaoss Union Corp., Wuhan. All chemicals were of analytical grade and were used as received. Deionized water was used throughout.

2.2. Synthesis of SMTS

The SMTS were prepared by diglycol mediated process [21–24] with minor modification. In a typical experiment, a mixed solution containing 0.3 mL tetrabutyl titanate and 20 mL diethylene glycol was vigorously stirred for 8 h at 25 °C, and then was added dropwise to a 60 mL aceton bath containing 0.38 mL deionized water under stirring for 120 min. The white precipitate was harvested by filtration, and followed by washing. The titanium spheres were completely crystallized and converted into anatase TiO2 by heating for 8 h at 550 °C.

2.3. Preparation of SMTS- or CB-supported Pt catalysts

The preparation of the SMTS-supported Pt catalyst was acquired by chemical precipitation method [5,25] with minor modification. Typically, 7.40 mg of TiO2 spheres was dispersed in 40 mL 2.5 mM H2PtCl6·6H2O aqeous solution. The mixture was vigorously stirred for 3 h. 10 mL of 0.04 M NaBH₄ aqueous solution was added dropwise to the suspension. Finally, SMTS-supported Pt catalyst was obtained by a washing and centrifugation process. After to be dried at 60 °C in a drying oven for 12 h, about 26.90 mg of SMTS-supported Pt catalyst was obtained, demonstrating that all the Pt contained in the H2PtCl6·6H2O aqeous solution are converted to Pt in its elemental state by calculating. To compare the catalysis of the Pt catalyst supported on SMTS with other common Pt-based catalysts, Pt supported on CB was obtained with the loading of Pt [25].

2.4. Characterization of catalysts

FEI Nova 400 field-emission scanning electron microscopy (FE-SEM) was used to characterize the morphology and size of the as-synthesized samples. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were carried out with a JOEL JEM 2100 microscope. X-ray powder diffraction (XRD) pattern of catalysts were recorded on Shimadzu XRD-6000 with Cu Kα radiation.

2.5. Electrode fabrication and electrochemical measurements

Working electrodes were fabricated by casting ethanol-dispersed as-prepared catalyst ink onto a graphite rod electrode (radius, 2.5 mm), which was then be dried at 60 °C in a drying oven. To immobilize the nanostructures on the graphite rod electrode and to enhance the anti-interference ability, 20 μL of 0.5 wt% Nafion® was dropped on the surface of the electrode. The electrode prepared by the SMTS- and CB-supported Pt catalyst is labeled here as Pt/TiO2/G and Pt/CB/G electrode, respectively. The loading of Pt on each electrode was 0.1 mg cm⁻². In a typical case of the fabrication for the Pt/TiO2/G electrode, the working electrode area of the graphite rod electrode is about 0.196 cm². Meanwhile, 19.51 mg Pt was loaded on 7.40 mg SMTs by calculating, which has good agreement between the numerical and experimental results. Then, 6.80 mg of as-prepared SMTS-supported Pt catalyst was dispersed in 5 mL ethanol, 20 μL ethanol-dispersed as-prepared catalyst ink was coated onto the surface of the electrode followed by the drying process and overlaid by Nafion®.

CHI 660C and CHI 660D (CH Instruments, Shanghai Chenhua Instrument Corp., China) electrochemical workstations were employed for electrochemical measurements. A conventional three-electrode electrochemical cell was used. A platinum foil electrode (10 mm x 15 mm x 0.3 mm in length, width and thickness) and Ag/AgCl (saturated KCl) was used as the counter and reference electrode, respectively. Cyclic voltammetry (CVs) were conducted at a rate of 50 mV s⁻¹ in acidic and alkaline aqueous solution. Linear sweep voltammetry (LSVs) were conducted at very slow potential scan rate of 5 mV s⁻¹ in acidic or alkaline aqueous solution. The anamperometric I−t curves were recorded in acidic aqueous solution at 0.7 V or in alkaline aqueous solution at −0.2 V for 2000 s. The electrochemical impedance spectroscopy (EIS) is recorded in 0.1 M Na₂SO₄ aqueous solution at frequency ranging from 0.5 Hz to 100,000 Hz with amplitude at 5 mV. All the experiments were carried out at room temperature (25 °C).

3. Results and discussion

3.1. Characterization of the SMTS and Pt/SMTS

Fig. 1 shows the XRD patterns of the SMTS and Pt/SMTS catalyst. All the peaks for the SMTS can be indexed to anatase phase TiO2 (JCPDS No. 89-4921). The 2-theta of 39.76, 46.24 and 67.45 for the Pt/SMTs correspond to the (1 1 1), (2 0 0) and (2 2 0) of cubic phase Pt (JCPDS No. 04-0802). The results indicate that anatase phase TiO2 and cubic phase Pt are all observed in the Pt/SMTS sample. EDS (inset in Fig. 1) results are consistent with those of XRD, demonstrating the Pt is distributed on the SMTS (the peak of silicon is from the substrate).

Fig. 2a shows a typical SEM image of the TiO2 spheres with diameter of 370–500 nm. After being coated with Pt NPs the diameter of the SMTS is 400–550 nm as shown in Fig. 2b. The rough surface of the SMTS provides quite good sites for the adsorption of Pt NPs. Fig. 2c shows that the morphology of the Pt/CB nanostructures is irregular particle–like. TEM images of the SMTS are shown in Fig. 2d and e, from which we can see that the sphere consists of interconnected nanocrystals with diameter of 19–21 nm, which is consistent with the evaluation from XRD according to Scherrer formula. The Pt NPs on the SMTS can be clearly observed as shown in Fig. 2f and g, indicating that the Pt NPs about 8–20 nm in diameter are well supported on the surface of the SMTS.

To further examine the structure of the SMTS and the detail of Pt/SMTS structure, as-prepared samples were characterized by
HRTEM. Fig. 3a shows HRTEM image of the SMTS, from which the lattice pattern is clearly observed, indicating that these crystals have high crystallinity. A lattice spacing of 0.35 nm belongs to the (1 0 1) plane of the anatase phase. Fig. 3b–d further illustrates the composite architectural structure of the SMTS and Pt NPs. The single crystalline structure of the Pt NPs is demonstrated too. Lattice pattern of Pt NPs and Pt–TiO$_2$ interface is clearly observed from the HRTEM analysis that the crystal lattice image of cubic Pt and anatase TiO$_2$ are complete and distinct, in which 0.22 nm is for (1 1 1) plane of cubic Pt and 0.23 nm is for (1 1 2) plane of anatase TiO$_2$. To investigate the stability of the combination of the SMTS and Pt NPs, an ultrasonic treatment was employed, by which the
composite architectural structure did not break up, even for as long as 30 min.

3.2. Electrochemically active surface (EAS)

Fig. 4 presents the CVs of the Pt/TiO2/G and Pt/CB/G electrodes recorded in 0.5 M H2SO4 (a) and 1.0 M KOH (b) aqueous solutions. In acidic media, there are two hydrogen desorption peaks at −0.102 V and 0.047 V in positive scan and reduction peak at 0.581 V in negative scan for the Pt/TiO2/G electrode. And in alkaline media, there exist similar peaks at −0.739 V, −0.645 V and −0.259 V. For comparison, the Pt/CB/G electrode was also studied. Obviously, the peaks on the Pt/TiO2/G electrode are much stronger than that of the Pt/CB/G electrode, which proves a better catalytic activity on the Pt/TiO2 catalyst than that on the Pt/CB catalyst. The EAS can be calculated according to the area of hydrogen adsorption/desorption peaks [26,27]. In this case, the EASs of these two electrodes with the same loading of Pt are in the order of Pt/TiO2/G > Pt/CB/G. This result implies that the SMTS with the interconnected nanocrystals provides a larger three-phase interface. The mesoporous structure create pores and channels that allow the liquid fuel to diffuse into the inside and the gaseous product (CO2) to escape from the catalyst layer more easily. Moreover, studies are already proven that CB is an amorphous powder with a low degree of graphitization [25,28–31]. CB forms a large percentage of micropores within its structure due to its wider size distribution and irregular morphology. This character makes CB to be a possible candidate for supporting noble metal, but unfortunately, this irregular morphology cannot fully utilize the Pt just because the reactants are inaccessible to Pt NPs anchored inside the aggregated carbon particles, and also increases the transfer resistance of reactants, intermediates and products.

3.3. Electrooxidation of methanol and ethanol

Fig. 5 shows the typical CVs of 1.0 M methanol (a) and 1.0 M ethanol (b) electrooxidation in 0.5 M H2SO4 on the two electrodes. And the electrooxidation of 1.0 M methanol and 1.0 M ethanol in 1.0 M KOH on the two electrodes is shown in Fig. 5c and d, respectively. To make a clear comparison, current densities are calculated by the specific mass of the loading of Pt. Table 1 shows the comparisons of the electrochemical performances on the two electrodes in both acidic and alkaline media. With the apparent geometric area, the Pt/TiO2/G electrode has a much higher current density than the Pt/CB/G electrode in all the four kinds of media which consists with the results of EAS. Compared these two electrodes, the Pt/TiO2/G electrode reveals not only a great enhancement of the current density of the electrooxidation, but also obvious lower the onset potentials which will be discussed below. Meanwhile, I/Ib can be used to evaluate the tolerance to carbonaceous species accumulation between different kinds of catalysts [32], where I is the forward scan peak current density and Ib is the backward scan peak current density. I/Ib presents the electrochemical oxidation reaction of the freshly chemisorbed species coming from media. Ib is primarily related with removal of carbonaceous species which are not completely oxidized in the forward scan. That means a higher I/Ib ratio indicates a better oxidation of alcohol to CO2 and relatively less carbonaceous residues generated. The I/Ib ratios are shown in Table 1. In this study, the Pt/TiO2 catalyst exhibits higher ratio than the Pt/CB catalyst in all four kinds of media. Besides, both peak current density and I/Ib ratio of the Pt/TiO2 catalyst in alkaline media reveal better performances than those in acidic media.

LSVs at a very slow potential scan rate of 5 mV s−1 are employed to further study the catalysis, as shown in Fig. 6. The negative shifting onset potential of the Pt/TiO2/G electrode is obviously observed, indicating that the electrooxidation is more readily on the Pt/TiO2/G electrode than that of the Pt/CB/G electrode. This negative shift also demonstrates the improvement of the reaction kinetics due to synergistic effect by the interaction between Pt and SMTS [33]. The negative shifting onset potential on the Pt/TiO2/G electrode is fairly easy to be observed in both Figs. 5 and 6 with the similar trend which could be a fine feature for practical applications. The onset potentials shift to a more negative direction for the Pt/TiO2/G electrode than that for the Pt/CB/G electrode in either the acidic media or alkaline media for both kinds of alcohol, indicating

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<td>Comparisons of the peak potential, peak current density (I_p) and I/Ib ratio on the Pt/TiO2/G and Pt/CB/G electrode in both acidic and alkaline media.</td>
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<td>Electrode</td>
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that the former electrode is more active for alcohol electrooxidation. In addition, the peak current densities observed here are in agreement with the CV studies. Therefore, these quasi-steady-state polarization curves give evidences that the composite architectural structure of Pt/SMTS can greatly enhance the electrocatalytic activity towards methanol and ethanol oxidation.

3.4. The electrocatalytic stability

The electrocatalytic stability of the Pt/TiO₂/G electrode and Pt/CB/G electrode for methanol and ethanol electrooxidation in acidic media (a) and alkaline media (b) has been investigated by amperometric i–t curves and the corresponding curves are shown in Fig. 7. All these catalysts show a rapid current density decay within the first few minutes, followed by a fairly constant current density for a long time. Obviously, the ultimate steady current density on the Pt/TiO₂/G electrode is larger than that on the Pt/CB/G electrode for both methanol and ethanol oxidation in acidic and alkaline media. The blocking of the surface with COₐd species is the result of the current density decay [6]. Meanwhile, this decay is also caused by the time dependent adsorption of the strongly bound irreversible OHₐd species in alkaline media [34]. COₐd species could be more effectively oxidized and removed by the Pt NPs on the Pt/TiO₂/G electrode than that on the Pt/CB/G electrode, so that the Pt/TiO₂/G electrode performs a better catalytic effect and also exhibits higher stability.

Fig. 5. CVs of the Pt/TiO₂/G (i) and Pt/CB/G (ii) electrode in 0.5 M H₂SO₄ aqueous solution containing 1.0 M methanol (a) or 1.0 M ethanol (b), and 1.0 M KOH aqueous solution containing 1.0 M methanol (c) or 1.0 M ethanol (d) at sweep rate of 50 mV s⁻¹.  

Fig. 6. LSVs of the Pt/TiO₂/G (i) and Pt/CB/G (ii) electrode in 0.5 M H₂SO₄ (a) or 1.0 M KOH (b) aqueous solution containing 1.0 M methanol or 1.0 M ethanol at sweep rate of 5 mV s⁻¹.
3.5. Solution/electrode interface processing analysis

EIS technique is well known as a powerful tool for characterizing the electrochemical processes occurring at the solution/electrode interface. The Nyquist plot includes a semicircle region which is related to the electron-transfer-limited process lying on the $Z_{re}$ axis observed at higher frequencies, followed by a linear part which is related to the diffusion-limited process at the lower frequencies. Usually, the semicircle diameter equals to the electron transfer resistance, which is affected obviously by the surface modification of the electrode [5,35,36]. Fig. 8 shows the Nyquist plots of the two electrodes. As shown in Fig. 8, the $Z_m$ starts at 11.63 $\Omega$ for the Pt/TiO$_2$/G electrode and 21.71 $\Omega$ for the Pt/CB/G electrode, indicating that the electron-transfer resistance of the Pt/TiO$_2$/G electrode is less than that of the Pt/CB/G electrode because the semicircle diameter for the Pt/TiO$_2$/G electrode should be smaller than for that for the Pt/CB/G electrode by fitting the curves. This demonstrates that the composite architectural structure formed by the Pt and SMTS can enhance the conductivity of the electrode owing to its faster interfacial charge carrier transfer as a result of higher specific area of submicrometer-sized sphere morphology that increases the Pt utilization in comparison with the irregular morphology of the CB. Besides, the synergistic effect by the interaction between Pt and SMTS is another reason caused the reduced electron-transfer resistance. Usually, conductivity and surface activity are the two most important factors for judging an analytical electrode among many other factors [37,38]. As the Pt/SMTS structure not only provides a larger three-phase interface and forms pores and channels for the liquid fuel to diffuse into the inside and the gaseous product (CO$_2$) to escape from the catalyst layer more easily, but also retains faster electron-transfer speed on the interface between liquid and electrode. Therefore, the Pt/TiO$_2$/G electrode exhibits excellent performance in electrooxidation of both methanol and ethanol in acidic and alkaline media.

4. Conclusion

A novel electrocatalysts of the Pt nanoparticles supported on SMTS have been prepared by wet chemical synthesis. The composite architectural structure Pt/TiO$_2$ sphere catalyst with uniform distribution of Pt NPs on the surface of the TiO$_2$ spheres exhibits a highly catalytic oxidation activity to both methanol and ethanol in acidic and alkaline media. A series electrochemical measurement demonstrates that the submicrometer-sized TiO$_2$ sphere structure provides larger three-phase interface and forms pores and channels for the liquid fuel to diffuse into the inside and the gaseous product (CO$_2$) to escape from the catalyst layer more easily. The catalyst retains faster electron-transfer speed on the interface between liquid which is very pivotal for the enhancement of alcohols electrooxidation. Our work suggests that the Pt/TiO$_2$ sphere electrocatalysts could be a potential candidate as excellent catalyst material for proton-exchange membrane fuel cells anode.

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