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Article

Catalytic performance and synthesis of a Pt/graphene-TiO₂ catalyst using an environmentally friendly microwave-assisted solvothermal method

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ABSTRACT

A Pt/graphene-TiO₂ catalyst was prepared by a microwave-assisted solvothermal method and was characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, cyclic voltammetry, and linear sweep voltammetry. The cubic TiO₂ particles were approximately 60 nm in size and were distributed on the graphene sheets. The Pt nanoparticles were uniformly distributed between the TiO₂ particles and the graphene sheet. The catalyst exhibited a significant improvement in activity and stability towards the oxygen reduction reaction compared with Pt/C, which resulted from the high electronic conductivity of graphene and strong metal-support interactions.

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1. Introduction

A proton exchange membrane fuel cell (PEMFC) can directly convert hydrogen energy into electricity and is considered as a promising power source for portable electronic devices and electric vehicles owing to its high efficiency, high energy density, and low emission [1,2]. However, durability and high cost are the critical issues that have hindered its commercialization and widespread application.

The catalyst support plays a significant role in the activity and durability of the catalyst in a PEMFC. Therefore, the exploration of advanced catalyst supports has been a promising strategy for improving the performance of electrocatalysts [3–6]. Carbon black is a traditional support material for fuel-cell catalysts because of its high electrical and thermal conductivity, high surface area, and porosity [7,8]. However,

carbon black is prone to corrosion under the operating conditions of fuel cells, which results in rapid degradation of the cell performance and durability. Therefore, extensive efforts have been made in the last ten years to develop new carbon-based materials and other alternative support materials for fuel-cell catalysts [9–15]. Transition metal oxides such as TiO₂ [16,17], SnO₂ [18], WO₃ [19], and CeO₂ [20,21] have been employed as alternatives to carbon supports to enhance the stability and durability of electrocatalysts. Among them, TiO₂ is more attractive owing to its inherent stability in an electrochemical environment and strong interactions with other metals [22–25]. However, its low electrical conductivity and small surface area have limited its widespread application in fuel cells. It is very necessary to design new catalyst support materials that can further enhance the electrical conductivity and surface area of TiO₂ when it is used as a catalyst support for fuel cells. Mean-

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while, graphene, a single layer of sp^2 -bonded carbon atoms, has remarkable electrical conductivity and a high surface area [26]. It has been a potential material for fuel cells and other energy conversion and storage devices [27–29]. The high tendency of pristine graphene sheets to agglomerate is inevitable owing to the intense van der Waals forces [30], which lead to the aggregation of the fuel-cell catalysts and reduced performance.

Fortunately, the intercalation of TiO_2 with carbon materials has proven to be a good way to improve the electrochemical performance because of the synergistic effect between the materials [31–38]. For examples, Zhu *et al.* [31] successfully fabricated the nitrogen-doped graphitized carbon/ TiO_2 supports by heat-treatment of polypyrrole/ TiO_2 composites and the addition of nitrate as a graphitization catalyst, and then loading Pt nanoparticles by using a microwave-assisted polyol method in an ethylene glycol solution. The Pt/nitrogen-doped graphitized carbon/ TiO_2 catalyst had high activity for the methanol oxidation reaction compared with the commercial Johnson Matthey catalyst. El-Deen *et al.* [35] prepared an rGO/ TiO_2 composite with different TiO_2 loadings by using the alkaline hydrothermal method. Although these catalysts exhibited higher electrocatalytic performance than Pt/C, the preparation of these catalysts through the above-mentioned methods consumed a lot of time, which is not beneficial for mass production. Recently, some new synthesis methods have been developed. Jiang *et al.* [33] synthesized Pt/ TiO_2 -C catalysts with different particle sizes and TiO_2 content by a microwave-assisted polyol process. Zhao *et al.* [34] synthesized Pt/graphene- TiO_2 hybrid catalysts through a facile one-pot solvothermal method. Ye *et al.* [38] prepared a Pt/ TiO_2 /graphene composite under microwave irradiation. The catalysts showed higher catalytic activity and better tolerance to CO poisoning.

In this work, a more convenient, facile, and rapid method for preparing the catalyst Pt/graphene- TiO_2 is proposed. A graphene- TiO_2 composite support material and Pt catalyst were successfully prepared. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were carried out to determine the crystalline structure and composition. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques were also used to examine the electrochemical performance of the Pt/graphene- TiO_2 catalysts.

2. Experimental

2.1. Materials

All chemicals including graphite powder (100 μm , Qingdao Henglide Graphite Co., Ltd.), $KMnO_4$, KNO_3 , H_2SO_4 ((95–97) wt%), H_2O_2 30 wt% (*m/m*), $K_2S_2O_8$, P_2O_5 , tetrabutyl titanate (TBT), deionized (DI) water, acetic acid (HAc), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmin]BF₄), and $H_2PtCl_6 \cdot 6H_2O$ were purchased from Sinopharm, China. The Nafion solution (5 wt%) was purchased from Dupont. All chemicals were of analytical grade and used as received.

2.2. Synthesis of graphene oxide (GO)

The graphene oxide (GO) was synthesized using a modified Hummer's method [39]. Briefly, 5 g of graphite powder was pre-oxidized in a mixture of 4.2 g $K_2S_2O_8$, 4.2 g P_2O_5 , and 60 mL H_2SO_4 at 80 °C for 4.5 h. The pre-oxidized sample was added into 120 mL H_2SO_4 at 0 °C, and then 2.5 g KNO_3 and 16 g $KMnO_4$ were slowly added. After the mixture was stirred for 2 h at 35 °C, 250 mL DI water was added, followed by the addition of 30 mL 30 wt% H_2O_2 . The resultant mixture was washed with DI water, and then filtrated with HCl solution (1 mol/L) until the filtrate was almost neutral. Finally, the filter cake was dried at 60 °C in air.

2.3. Synthesis of cubic TiO_2

Anatase titanium dioxide [40] was prepared using a microwave-assisted ionothermal method. Specifically, 1 mL [bmin]BF₄, 2.5 mL H_2O , and 40 mL HAc were mixed well and then 1 mL TBT was added. The solution appeared light white and turned colorless and transparent after ultrasonic treatment for 30 min. The solution was then transferred into a microwave reactor (Explorer48, CEM) with a volume capacity of 50 mL and heated at 180 °C for 25 min. When it was cooled to room temperature, the white precipitate was isolated by centrifugation, rinsed several times with DI water and ethanol, and dried in a vacuum oven at 100 °C for 6 h.

2.4. Synthesis of Pt/graphene- TiO_2 catalyst

Pt/graphene- TiO_2 catalysts with different TiO_2 content were synthesized by using a microwave-assisted hydrothermal method. Typically, a calculated amount of GO and TiO_2 were dispersed into a mixture of ethylene glycol (EG) under ultrasonic treatment for 30 min, and kept stirring for 20 min. Then, the H_2PtCl_6 -EG solution was added into the solution with agitation for 30 min. The pH of the solution was then adjusted to approximately 13 and the solution was transferred into a microwave reactor with a volume capacity of 50 mL and heated at 140 °C for 3 min. After cooling to room temperature, the pH of the solution was adjusted to 4. The mixture was washed repeatedly with ultrapure water. The obtained Pt/graphene- TiO_2 catalysts were dried at 80 °C in a vacuum oven for 5 h and subsequently treated in a reductive atmosphere at 150 °C for 2 h.

The TiO_2 content in the catalysts was relative to the total mass of the mixed support. For the sake of convenience, Pt/graphene- TiO_2 catalysts with 20 wt%, 40 wt%, and 60 wt% TiO_2 were denoted as Pt/graphene- TiO_2 -20%, Pt/graphene- TiO_2 -40%, and Pt/graphene- TiO_2 -60%, respectively. The Pt metal loading of the hybrid catalysts was approximately 20 wt%. The metal loading of the samples was determined by burning off the carbon support and verifying the metal content by XRD. Samples of 50–100 mg were prepared to ensure good reproducibility and to minimize any errors.

2.5. Physical characterization

The XRD patterns of the as-prepared catalysts were obtained with a D/max-RB diffractometer (Japan) using a $Cu K\alpha$

X-ray source operating at 45 kV and 100 mA and a scanning rate of $4^\circ/\text{min}$ with an angular resolution of 0.05° of the 2θ scan. A scanning electron microscope (JSM-6510, JEOL, Japan) coupled with an energy dispersive spectrometer (EDS) was used to examine the surface morphology and elemental composition of the samples. TEM images were acquired to characterize the morphology of the samples using a Tecnai-20 G2 transmission electron microscope (USA), which was operated at 200 kV. The samples were finely ground and ultrasonically dispersed in alcohol, and a drop of the resultant dispersion was deposited and dried on a standard copper grid coated with a carbon film.

2.6. Electrochemical measurements

Electrochemical experiments were carried out on a potentiostat (Solatron 1287, Associate Scribner) with a three-electrode-type cell. A glassy carbon (GC) disk with a geometrical area of 0.1256 cm^2 was used as a working electrode. A saturated calomel electrode (SCE) and platinum wire were used as reference and counter electrodes, respectively. The working electrodes in the electrochemical experiments were prepared as follows. The catalyst (8 mg) and 80 μL Nafion aqueous solution were dispersed in a solution of 1500 μL DI water and 420 μL ethanol and then the ink was ultrasonicated for 30 min. Ten microliters of this dispersion was pipetted onto the GC substrate of the disc and dried at room temperature. Prior to any electrochemical measurements, the working electrode was cycled in the potential range from 0 to 1.3 V with respect to SCE at a sweep rate of 50 mV/s to activate the sample. The rotating disk electrode (RDE) was rotated at 1600 r/min throughout the experiment at a sweep rate of 5 mV/s. The CV and LSV measurements were performed in solutions containing 0.5 mol/L aq. H_2SO_4 saturated with N_2 and O_2 . All the experiments were conducted at room temperature and all the potentials shown in this paper were converted to the reversible hydrogen electrode (RHE) scale.

3. Results and discussion

3.1. Physical characteristics of the Pt/graphene-TiO₂ catalysts

The XRD patterns of the GO, TiO₂ and Pt/graphene-TiO₂ catalysts are shown in Fig. 1. The pattern in Fig. 1(1) displays a sharp diffraction peak at 11.4° , which was attributed to GO (001) plane reflection and indicated that GO was successfully prepared through the chemical oxidation of the graphite powder. The XRD pattern of TiO₂ shown in Fig. 1(2) was perfectly indexed with anatase TiO₂ in JCPDS card (84-1285). All the peaks in the spectrogram were extremely sharp and exactly straight lines. These characteristics indicated that the TiO₂ was highly crystallinity and were very consistent with a single-crystalline structure [39]. As shown in Fig. 1(3), the diffraction peak at 25° was owing to the carbon (002) plane. Fig. 1(4) and (5) possess a broad diffraction peak at 25° corresponding to the (002) plane of graphene and the sharp diffraction peak at 11.4° disappears, indicating that the GO was reduced to gra-

Fig. 1. XRD patterns of GO (1), TiO₂ (2), Pt/C (3), Pt/graphene (4), and Pt/graphene-TiO₂ (5).

phene. From Fig. 1(3), (4), and (5), it is clear that the diffraction peaks at 40° , 46° , and 67.5° represent the Pt (111), (200), and (220) planes observed in the spectrogram, which suggested that the prepared Pt exhibited a face-centered cubic (fcc) crystal structure [34]. Moreover, the characteristic diffraction peak of anatase TiO₂ is clearly evident in Fig. 1(5), which demonstrated that TiO₂ was integrated with the graphene sheets.

The SEM images of graphene, TiO₂, graphene-TiO₂-20%, graphene-TiO₂-40% and graphene-TiO₂-60% and the corresponding particle size distributions of TiO₂ are shown in Fig. 2. As shown in Fig. 2(a), the GO was transparent and consisted of a lamellar nanosheet with wrinkles. Fig. 2(b) shows anatase TiO₂, which forms well-dispersed cubes with good uniformity in size distribution. As shown in Fig. 2(c), (d) and (e), the TiO₂ cubes were uniformly distributed on the graphene sheets.

The corresponding histograms of the TiO₂ particle size distribution are shown in Fig. 2, which quantitatively reveals the particle size distribution of the catalyst support. Clearly, most of the cubic TiO₂ particle size was 60 nm in size. Highly dispersed and narrowly distributed TiO₂ cubes were obtained. After mixing with graphene, there was no change in the particle size of TiO₂, which implied that the crystallinity, uniformity, and cubic shape of TiO₂ were well-preserved during the microwave treatment.

Fig. 3 shows the TEM and HRTEM images of the Pt/graphene-TiO₂ catalysts. From Fig. 3(a), it is clear that Pt and TiO₂ were uniformly deposited on the graphene sheets. More interestingly, Fig. 3(b) shows that most of the Pt nanoparticles seem to preferentially anchor between TiO₂ and graphene and form a unique triple junction structure, which indicated that there was a strong interaction between TiO₂ and the precious metal. Fig. 3(c) shows the high-resolution TEM image of the Pt and TiO₂ particles. Regular lattice fringes with a spacing of 0.35 nm and 0.22 nm are clearly evident, which was extremely consistent with the (101) plane of the anatase TiO₂ and (111) plane of Pt, respectively. The TEM images and particle size distributions of the Pt nanoparticles are shown in Fig. 3(d–f). Highly dispersed, homogeneous, and spherical metal

Fig. 2. SEM images of graphene (a), TiO₂ (b), graphene-TiO₂-20% (c), graphene-TiO₂-40% (d), and graphene-TiO₂-60% (e), and the corresponding particle size distributions of TiO₂.

Fig. 3. TEM images (a, b, d, e, f) and HRTEM images (c) of Pt/graphene-TiO₂-20% (a, b, c, d), Pt/graphene-TiO₂-40% (e), and Pt/graphene-TiO₂-60% (f), and the corresponding particle size distributions of Pt.

clusters were anchored on the composite support. The average particle size of the Pt particles in Pt/graphene-TiO₂-20%, Pt/graphene-TiO₂-40%, and Pt/graphene-TiO₂-60% was 2.4, 2.3, and 2.4 nm, respectively. The average size of the Pt was

almost the same, which could not exert any influences on their activity [34]. The EDS analysis of the Pt/graphene-TiO₂ catalyst further proved the coexistence of Pt and TiO₂, as shown in Fig. 4. The content of each element is listed in the inset table.

Fig. 4. EDS images and the content of elements of the Pt/graphene-TiO₂ catalyst. (a) Pt/graphene-TiO₂-20%; (b) Pt/graphene-TiO₂-40%; (c) Pt/graphene-TiO₂-60%.

3.2. Electrochemical characteristics of Pt/graphene-TiO₂ catalyst

The CV technique is very useful for obtaining information about the stability in the reaction media and the participation of the active sites on the electrode surfaces [32]. Fig. 5 shows the CV curves of Pt/C, Pt/graphene-TiO₂-20%, Pt/graphene-TiO₂-40%, and Pt/graphene-TiO₂-60% electrocatalysts in the N₂-saturated 0.5 mol/L aq. H₂SO₄ at a scan rate of 50 mV/s in the potential region of 0 and 1.3 V (vs. RHE). It is clear that all the catalysts show peaks related to hydrogen adsorption/desorption between 0.05 and 0.35 V (vs. RHE). The electrochemical surface area (ECSA) was 72.21, 77.36, 22.23, and 12.34 m²/g for Pt/C, Pt/graphene-TiO₂-20%, Pt/graphene-TiO₂-40% and Pt/graphene-TiO₂-60%, respectively. The Pt/graphene-TiO₂-20% showed the highest ECSA among these catalysts, which indicated that the addition of cubic TiO₂ can mitigate the aggregation of the Pt particles and more Pt sites were available for the oxygen reduction reaction compared with the Pt/C catalyst. The ECSA significantly decreased with increasing TiO₂ content as a result of high electronic resistance.

Fig. 6 presents the CV curves before and after the accelerated potential cycling test (APCT) in the N₂-saturated 0.5 mol/L

Fig. 5. Cyclic voltammograms of Pt/C, Pt/graphene-TiO₂-20%, Pt/graphene-TiO₂-40%, and Pt/graphene-TiO₂-60% catalysts in H₂SO₄ solution (0.5 mol/L).

aq. H₂SO₄ at a scan rate of 50 mV/s in the potential range from 0 to 1.3 V (vs. RHE). Fig. 6(a) shows that there is a sharp decline in the hydrogen adsorption/desorption area of the Pt/C catalyst after 400 cycles because of agglomeration of the Pt nanoparticles and corrosion of the carbon powder [39]. However, as shown in Fig. 6(b, c, d), the attenuation in ECSA of the Pt/graphene-TiO₂ catalysts was not distinct compared with that of the Pt/C catalyst. To check the stability of the four catalysts, the ECSAs of these catalysts were calculated after APCT. After 2000 cycles, the ECSA degraded by 95% and 55% for Pt/C and Pt/graphene-TiO₂-20%, respectively. The decay rate of the Pt/graphene-TiO₂-40% and Pt/graphene-TiO₂-60% catalysts was almost the same, but slightly lower than that of the Pt/graphene-TiO₂-20%. The stability of the catalyst was indeed improved with increasing TiO₂ content. This indicated that the Pt/graphene-TiO₂ catalysts exhibited higher stability than the Pt/C catalyst, which was attributed to the excellent durability of the TiO₂ in acidic media and the strong metal-support interactions between the Pt particles and cubic TiO₂, mitigating the agglomeration of Pt metal particles [41–43]. The graphene with a single layer of carbon atom array structure also exhibited higher chemical stability than carbon powder [26–29]. In addition, the uniform dispersion of cubic TiO₂ nanoparticles on graphene sheets could offer more durable passages for ion and electrolyte transport [40].

The oxygen reduction reaction (ORR) curves for the Pt/graphene-TiO₂ catalysts and Pt/C in the O₂-saturated 0.5 mol/L aq. H₂SO₄ are presented in Fig. 7. Fig. 7(a) shows that the initial voltage for ORR on the Pt/C, Pt/graphene-TiO₂-20%, Pt/graphene-TiO₂-40%, and Pt/graphene-TiO₂-60% catalyst was 0.95, 0.99, 0.99 and 0.99 V, respectively. The limiting current of the Pt/graphene-TiO₂-20% was much closer to that of the Pt/C catalyst, whereas the limiting currents of the other two catalysts were much lower than that of Pt/C because of the high electrical resistance resulting from the high loading of TiO₂. As presented in Fig. 7(b), the onset potentials for ORR on Pt/C, Pt/graphene-TiO₂-20%, Pt/graphene-TiO₂-40%, and Pt/graphene-TiO₂-60% catalysts were 0.90, 0.99, 0.99, and 0.99 V after 2000 cycles, respectively. The negative shift of the LSV curve of the Pt/graphene-TiO₂ catalysts was much lower than that of the Pt/C catalyst. Hence, the Pt/graphene-TiO₂ catalyst was more durable than Pt/C. In our work, Pt/graphene-TiO₂ with 20 wt% TiO₂ exhibited the highest activity and stability.

Fig. 6. Cyclic voltammograms of Pt/C (a), Pt/graphene-TiO₂-20% (b), Pt/graphene-TiO₂-40% (c), and Pt/graphene-TiO₂-60% (d) in 0.5 mol/L H₂SO₄ solution during the APCT.

Fig. 7. Oxygen reduction reaction (ORR) polarization curves of Pt/C, Pt/graphene-TiO₂-20%, Pt/graphene-TiO₂-40%, and Pt/graphene-TiO₂-60% in O₂-saturated 0.5 mol/L H₂SO₄ at 1600 r/min (a) before and (b) after 2000 cycles.

4. Conclusions

The Pt/graphene-TiO₂ hybrid catalyst was synthesized through an environmentally friendly and novel microwave-assisted solvothermal method. The microstructure, composition, and electrochemical performance of the prepared catalyst were examined by physical and electrochemical tech-

niques. The integration of graphene sheets and cubic TiO₂ enhanced the activity and stability of the Pt nanoparticles, which was attributed to the strong metal-support interactions and the synergetic effect between TiO₂ and graphene.

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Graphical Abstract

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Catalytic performance and synthesis of a Pt/graphene-TiO₂ catalyst using an environmentally friendly microwave-assisted solvothermal method

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An environmentally friendly microwave-assisted method was developed for the synthesis of Pt/graphene-TiO₂ catalysts. The improved activity and stability of the nano-Pt catalysts were attributed to the high electronic conductivity and strong metal-support interactions.

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微波辅助溶剂热法制备Pt/石墨烯-TiO₂及其催化性能

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摘要: 质子交换膜燃料电池具有比能量高、结构简单、工作温度低、高效清洁和安静无摩擦等优点, 是一种非常具有发展前景的电源。燃料电池借用催化剂把燃料与氧化剂中的化学能转化为电能, 通常采用碳粉负载的Pt催化剂。在燃料电池的工作环境下, 碳粉载体容易腐蚀和团聚, 降低了催化剂活性和稳定性, 进而降低了燃料电池的使用寿命。因此, 探索高稳定性的催化剂载体有利于提高催化剂的稳定性, 促进燃料电池的实用化进程。

为增强催化剂载体的抗腐蚀能力, 一些金属氧化物如SnO₂, WO₃, CeO₂和TiO₂等被用作催化剂载体。其中, TiO₂因具有稳定的化学性能以及与金属之间的“强相互作用”而备受研究者关注。但TiO₂载体比表面积小和导电能力弱等缺点限制了它在燃料电池中的应用。石墨烯具有卓越的导电性和比表面积, 却容易发生团聚。利用TiO₂与碳材料间存在的协同作用, 将TiO₂与石墨烯复合来制备复合载体, 能够增强TiO₂的导电能力, 抑制石墨烯的团聚, 提高催化剂载体的化学稳定性和比表面积。

本文采用微波辅助溶剂热法制备了石墨烯-TiO₂复合载体和Pt/石墨烯-TiO₂催化剂, 研究了TiO₂含量对催化剂活性和稳定性的影响。采用X射线衍射(XRD)、扫描电子显微镜(SEM)和透射电子显微镜(TEM)对制备的样品进行了微观结构和成分表征。结果表明, Pt/石墨烯-TiO₂催化剂中TiO₂为立方状纳米颗粒, 粒径约为60 nm, 均匀地分布在石墨烯上; Pt纳米粒子倾向于锚定在TiO₂与石墨烯之间, 而且分布均匀。采用线性伏安扫描(LSV)和循环伏安法(CV)测试了不同TiO₂含量的Pt/石墨烯-TiO₂催化剂的活性和稳定性。发现TiO₂的加入确实能够提高催化剂的稳定性, 随着TiO₂含量的提高, 催化剂稳定性增加。当TiO₂含量为20%时, 催化剂的起始电压与极限电流均与Pt/C催化剂接近。经过循环伏安扫描3000圈的快速老化测试后, Pt/石墨烯-TiO₂催化剂起始电压的负移明显低于Pt/C催化剂, 呈现了优良的稳定性和催化活性。

关键词: 微波辅助溶剂热法; 立方状二氧化钛; 石墨烯-二氧化钛; 氧还原反应

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