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Mixed ionic liquids/graphene-supported platinum nanoparticles as an electrocatalyst for methanol oxidation

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ABSTRACT

A kind of mixed ionic liquids (ILs) of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4], IL_1) and hexafluorophosphate ([bmim][PF_6], IL_2) was introduced to the functionalization of graphene (GN) nanosheets, which was used to the synthesis of platinum nanoparticles (Pt NPs) to obtain the Pt/IL_1-IL_2/GN nanocomposite. The interaction between mixed ILs and GN achieved a stable performance due to the excellent electronic and interfacial property of the fabricated nanocomposites, which was favorable for effective loading of Pt NPs on the IL_1-IL_2/GN support. The as-prepared Pt/IL_1-IL_2/GN composites exhibited highly electrocatalytic activity (764.3 mA $mg^{-1}{}_{Pt}$ at 0.6 V vs. SCE) and stability toward methanol oxidation, demonstrating their promising potential as the anode catalyst for direct methanol fuel cells (DMFCs).

1. Introduction

Direct methanol fuel cells (DMFCs), which provide a promising way to convert chemical energy directly into electrical energy, have attracted extensive attention as green power sources for vehicles and portable electronics. However, the practical application of DMFC is still hindered by the high cost of Pt catalyst and the sluggish methanol oxidation reaction [1,2]. Recently, developing novel carbon materials to support catalyst has been demonstrated as one effective way to enhance the catalytic activity and reduce the usage of Pt-based catalysts. Such support materials can not only maximize the availability of surface area of the nanosized electrocatalyst for electron transfer but also provide better mass transport of reactants to the electrocatalyst. Graphene, a two-dimensional carbon material with single (or a few) atomic layer, has attracted great attention for both fundamental science and applied research. The combination of the extremely high specific surface area (theoretical value of 2630 $m^2\ g^{-1}$), particular electronic conductivity and unique graphitized basal plane structure [3–5] makes graphene a promising candidate as anode catalyst support in DMFCs. However, the effective loading of Pt NPs with well-controlled dimensions and morphologies on graphene is still a challenge. Recently, several works reported that the surface functionalization of the carbon supports has a large effect on the synthesis of catalysts. Wietecha et al. covalently functionalized graphene by N-(trimethoxy-silylpropyl) ethylenediamine triacetic acid (EDTA-silane), which was used as support for Pt NPs growth [6]. They found that Pt NPs could be evenly distributed on the functionalized graphene surface and proved that the chelating groups of EDTA-silane could enhance the catalytic activity of Pt-NPs towards methanol oxidation. Luo et al. reported that poly(diallyldimethylammonium chloride) (PDDA) functionalized graphene could provide considerably higher density and homogeneity of surface functional groups, which was beneficial to evenly deposit Pt NPs on this functionalized graphene surface [7]. Finally the obtained catalyst exhibited higher catalytic activity and CO-tolerance for methanol oxidation.

In recent years, room temperature ionic liquids (RTILs) have attracted great interest in multidisciplinary areas due to their unique physicochemical properties, such as high thermal stability, negligible vapor pressure, relatively high ionic conductivity and good electrochemical stability [8]. Wu et. al and Yang et. al have recently reported the methods by using imidazolium ionic liquids (ILs) as medium for the formation and stabilization of catalytically active transition-metal nanoparticles [9,10]. It can be interpreted that the outstanding exchange ability for anions of ILs could enable Pt precursors with negative charge to be enriched on the surface of supporting materials, which will facilitate the

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preparation of high-density Pt NPs. Additionally, the intrinsic high charge of imidazolium salts, which creates an electrostatic colloid-type protection (DLVO-type stabilization) [11] for the transition-metal nanoparticles similar to those proposed for quaternary ammonium salts. Therefore, the combination of IL and graphene would provdie a broader scope of graphene-based composite applications [12–14]. For example, Li et. al designed a novel electrochemical detection platform based on Pt/IL/graphene composites, which can be used to simultaneously determine ascorbic acid (AA) and dopamine (DA) by cyclic voltammetry [15]. However, the current investigations on the IL/graphene based support for the synthesis of nanoparticles were restrained by using only one kind of IL. The combination of different ILs for the fabrication of nanocomposites is rarely explored.

In this work, a kind of mixed ILs of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4], IL_1) and hexafluorophosphate ([bmim][PF_6], IL_2) was employed to one pot synthesis of Pt NPs supported on graphene (GN). The fabricated Pt/IL_1-IL_2/GN nanocomposites exhibited excellent electrochemical performance, which hold great promise as an electrocatalyst for methanol oxidation.

2. Experimental

2.1. Materials

Graphite was provided by Qingdao Fujin graphite Co., Ltd. Friendly (China). 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) and hexafluorophosphate ([bmim][PF_6]) were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. $H_2PtCl_6{\cdot}6H_2O$, H_2SO_4 and methanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the reagents were of analytical grade and used without further purification. Doubly distilled water was employed throughout the experiment.

2.2. Apparatus

UV-Vis and FT-IR spectra were obtained on a Unico UV-2800 spectrophotometer (Shanghai, China) and a Nicolet-5700 spectrophotometer (Madison, USA), repectively. SEM and TEM images were taken by JEOL JSM-7001F and JEOL JEM-2100, respectively. Cyclic voltammetric (CV) and amperometric measurements were carried out on a CHI 660 C electrochemical workstation (Shanghai, China) with a conventional three-electrode system. The composite films coated glass carbon electrode was used as working electrode, while a saturated calomel electrode (SCE) and a platinum wire were used as reference and counter electrode, respectively. All the potentials reported in this work were with respect to the SCE reference electrode.

2.3. Preparation of Pt/IL/GN nanocomposite

Graphite oxide (GO) were synthesized by a modified Hummers method [16]. As to synthesis of the composite catalyst, firstly, 50 mg GO was dissolved in 30 mL of a mixed solution of methanol and water under stirring, followed by the addition of 50 mg ionic liquid mixture of [bmim][BF_4] (IL_1) and [bmim][PF_6] (IL_2) with a volume ratio of 1:1. It is important to note that the ionic liquid mixture had been stirred for 24 h to form a homogeneous system. Then 2 mL of 38 mM H_2PtCl_6 was added dropwise under vigorous stirring. The pH of the resulting solution was adjusted to 11.0 by 0.5 M KOH. Then, 200 mg of $NaBH_4$ was slowly added to the mixture, afterwards stirring for 24 h under room temperature. The resulting black precipitate was filtered, washed several times with methanol-water solution, and collected after vacuum drying at 50 °C for 24 h to obtain the Pt/IL_1-IL_2/GN nanocomposites. As controls, Pt/IL_1/GN and Pt/IL_2/GN ware also synthesized by the same procedures except for just adding one kind of IL in the composite.

2.4. Electrochemical performance of Pt/IL/GN nanocomposite

Electrochemical experiments were performed at a CHI-660 C electrochemical workstation with a conventional three-electrode cell. The working electrode was prepared as follows: catalyst powder was ultrasonically dispersed in 0.5% Nafion + C_2H_5OH solution to generate a homogeneous black ink with a content of 1 mg mL^{-1}. 3 μL of this ink was pipetted onto the glass carbon electrode (3 mm in diameter) and dried using an IR lamp.

The electrochemically active surface area (ECSA) of Pt nanoparticles on IL/GN was calculated from the hydrogen adsorption/desorption curve, which was recorded in 0.5 M H_2SO_4 solution saturated with nitrogen at 50 mV s^{-1}. The electrocatalytic performance of Pt/IL/GN toward methanol oxidation was studied in 0.5 M CH_3OH + 0.5 M H_2SO_4 at 50 mV s^{-1}. The catalytic stability of the Pt/IL/GN was evaluated by CA at an applied potential of 0.60 V for 1000 s. CV was also conducted for 1000 cycles to evaluate the cycling stability of Pt/IL/GN for methanol oxidation. The temperature of the electrolytes during the experiments was kept at 15 ± 1 °C

3. Results and discussion

The compositions of the composites were investigated by UV-Vis (Fig. 1A) and FT-IR (Fig. 1B). It can be seen from Fig. 1 A that besides the bands of graphene at 270 nm [17], the appearance of the bands at 220 nm is corresponding to the characteristic absorption of the aromatic system of imidazole [18], demonstrating the existence of both IL and graphene in the composite. Particularly, as for the IL-graphene composite a red shift of the bonds of graphene is observed, which can be ascribed to the π-π conjugation of graphene and imidazole ring within IL. Moreover, the red shift is much larger for Pt/IL_1-IL_2/GN (Fig. 1A, red curve c), indicating a more effective π-delocalization extended within this composite framework, which signifies the peculiar role of IL hybrid in regulating the inner-structure of graphene-based materials. Additionally, FT-IR were also performed to confirm the structure and composition of the as-prepared composite (Fig. 1B). Similarly, in addition to the bands of graphene, the bands at 1150 and 1550 cm^{-1} are corresponding to the specific stretching vibrations within the aromatic system of imidazole. Especially, the bands at 820 cm^{-1} and 1030 cm^{-1} are corresponding to the stretching vibrations of P-F and B-F, further indicating the successful attachment of IL to GN [19]. As well consistent with the UV-Vis results, the aforementioned bands for Pt/IL_1-IL_2/GN (Fig. 1B, red curve d) shift to lower wavenumbers due to potentially more robust π-π stacking interactions between the imidazolium rings of IL_1-IL_2 and the conjugation of GN, which plays a significant role in preventing the disassociation of IL from GN and improving the adhesion of Pt NPs. The strong π-π conjugation and improved stability can be reasonably interpreted as a collaborative effect of electron transfer and ionic interaction (as shown in Fig. 2). On one hand, distinguishing from the aspect of electronegativity, the moiety B (electronegativity, 1.96) and P (electronegativity, 2.24) in the IL will interact with each other through forming guest-host electron scaffold. Thus, the trend of electron contributing is relieved from the conjugated π systems derived from imidazole and graphene, thereby improving the density of π-electron cloud and elevating the π-π conjugation degree and the stability of these conjugated π systems. On the other hand, the electrostatic repulsion of IL_1 and IL_2 will increase ionic spacings along the GN surface, which is favorable for extending the π-π conjugation region and consequently improving the stability.