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Nitrogen-doped porous carbons supported Pt nanoparticles for methanol oxidation in alkaline medium



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ABSTRACT

Honeycomb-like nitrogen-doped porous carbons (NPCs) have been prepared using ionic liquids 1-butyl-3-methylimidazolium dicyanamide (BMIMdca) as the carbon precursor, and silica spheres as the templates. The obtained NPCs were employed as supports of Pt nanoparticles for methanol oxidation in alkaline medium. The high surface area and the porous structure are beneficial to the uniform dispersion of Pt nanoparticles to increase their utilization. The electrocatalytic activity of methanol oxidation on Pt nanoparticles supported on NPCs (Pt/NPCs) is higher than that of Pt on commercial Vulcan XC-72R carbon (Pt/C). The results showed that NPCs are a potential candidate for application as electrocatalyst supports in alkaline direct methanol fuel cells.

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1. Introduction

Recently, alkaline direct methanol fuel cells have received more and more attentions due to their several potential advantages such as faster kinetics of methanol oxidation reaction (MOR), lower methanol permeability from anode to cathode, and easier water management [1,2].

The supports of electrocatalyst for direct methanol fuel cells (DMFCs) are an important factor owing to the fact that it can reduce the utilization of precious metal catalysts and improve the catalytic activity. Carbon based materials are commonly used as ideal catalyst supports for DMFCs because of their high surface area, excellent electrical conductivity, and corrosion resistance. Many carbon materials such as carbon nanotubes, carbon spheres, and nitrogen modified carbons have been widely used as electrocatalyst supports for DMFCs [3–6]. Among of them, nitrogen-doped carbon materials by doping of nitrogen atoms into carbon materials show interesting properties like high electric conductivity and surface area, excellent thermal and mechanical stability due to that nitrogen has comparable atomic size and contains five valence electrons available to form strong valence bonds with carbon atoms [7,8], which have been widely used as supports of electrocatalyst for MOR [9,10] and oxygen reduction reaction (ORR) [11,12]. However, nitrogen-doped carbon materials usually have been prepared under harsh conditions, such as extreme

temperature, extreme pressure or in the presence of ammonia vapor [13]. Therefore, there was an urgent need to develop a facile method to synthesize nitrogen-doped carbon materials as efficient electrocatalysts for methanol oxidation.

In recent years, ionic liquids (ILs) have attracted much attention due to their unique physical and chemical properties, such as negligible vapor pressure, high electrical conductivity and high thermal stability [14,15]. ILs have been used as suitable precursors to produce functional nitrogen-doped carbon materials [16–20], which have been used in many different fields such as supercapacitors and ORR. However, there have been only a few papers to date on application of nitrogen-doped porous carbons (NPCs) for methanol oxidation in alkaline medium.

In this paper, we report the synthesis of the NPCs using ILs 1-butyl-3-methylimidazolium dicyanamide (BMIMdca) as the carbon precursor, and silica spheres as the hard template. The prepared NPCs are used to support Pt nanoparticles for methanol oxidation in alkaline medium.

2. Experimental

2.1. Preparation of BMIMdca [21]

Firstly, 1-butyl-3-methylimidazolium bromide (BMIMBr) was prepared with equimolar 1-methylimidazole and 1-bromobutane. BMIMBr was obtained after washing and drying. Then, BMIMBr in acetone with $\text{NaN}(\text{CN})_2$ were mixed at room temperature for 24 h.

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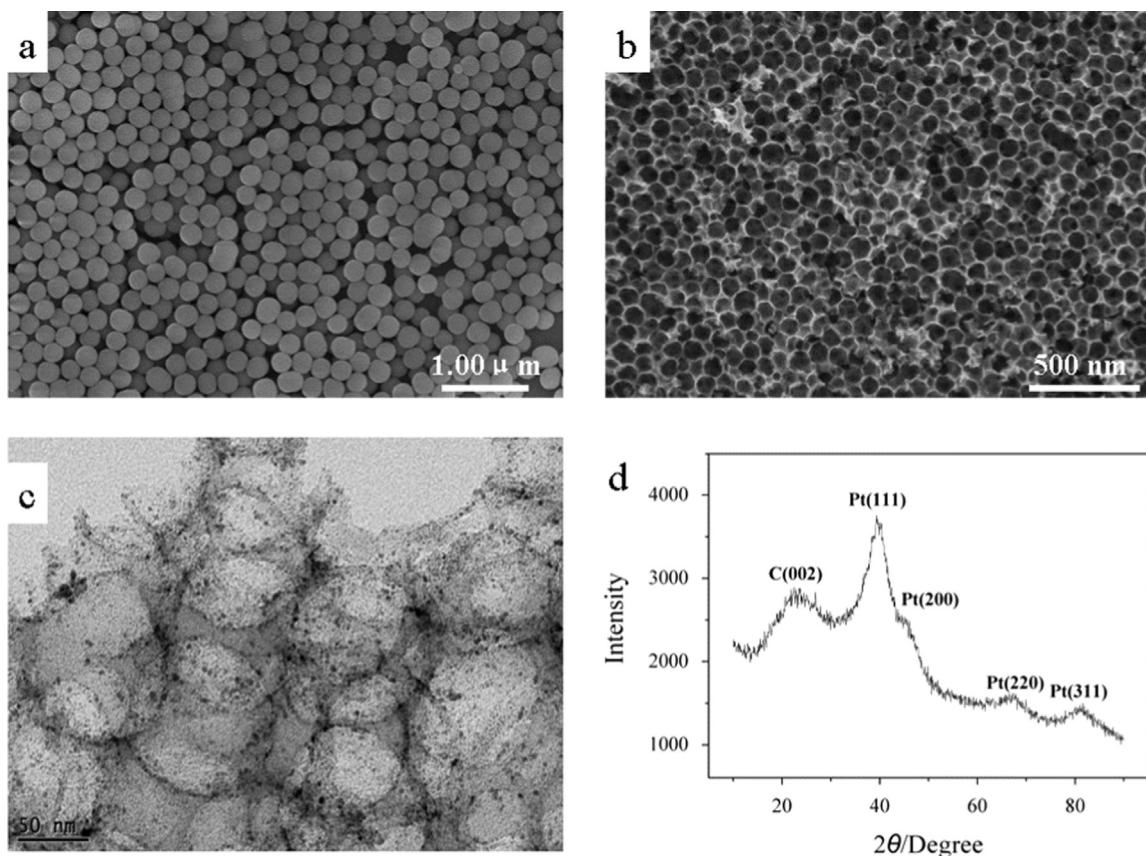


Fig. 1. SEM images of SiO₂ spheres(a) and NPCs(b); TEM images of Pt/NPCs(c); XRD patterns of the Pt/NPCs(d).

After filtrating, washing and drying, BMIMdca was obtained. ¹H NMR (400 MHz, acetone) δ 9.80 (s, 1H), 7.86 (s, 1H), 7.79 (s, 1H), 4.42 (t, 2H), 4.09 (s, 3H), 1.98–1.88 (m, 2H), 1.45–1.32 (m, 2H), 0.94 (t, 3H).

2.2. Preparation of NPCs

NPCs were synthesized using ILs BMIMdca as the precursors and SiO₂ spheres as the hard template. Firstly, SiO₂ spheres with a diameter of 300 nm were synthesized using the Stöber method [22]. 20 mL of ethanol and 3 mL of aqueous ammonia solution (28 wt%) were mixed with stirring for 20 min to make uniform. 4 mL of tetraethylorthosilicate and 30 mL of ethanol were added into above mixtures. After stirring for 4 h at room temperature, the products were collected by centrifugation and washed. The SiO₂ spheres were obtained through drying at 70 °C for 24 h. Then, 1.0 g SiO₂ spheres and 1.0 g BMIMdca were mixed with 50 ml water under ultrasonic treatment for 30 min, and then stirred at room temperature for 4 h. The mixtures were heated to 100 °C to remove the water. The products were carbonized by heating to 800 °C with a rate of 10 °C min⁻¹ under nitrogen atmosphere, and maintained for 3 h. The obtained black powders were treated with 10 wt% HF solution to remove the silica template. The NPCs were filtered, washed, and finally dried at 80 °C for 12 h.

2.3. Preparation of Pt/NPCs

Pt supported on nitrogen-doped porous carbons (Pt/NPCs) and Vulcan XC-72R (Pt/C) were synthesized by the ethylene glycol (EG) method according our previous work [5]. As added into the Vulcan XC-72R slurry, the equivalent solution of H₂PtCl₆ in EG was slowly added into the NPCs slurry. The theoretical content of Pt was

controlled 20 wt% by adjusting the amount of H₂PtCl₆.

2.4. Characterization of the materials

The scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM, FEI Tecnai G20) were used to determine the morphologies of the electrocatalysts. N₂ sorption analysis was conducted on a Quadrasorb SI (Quantachrome), equipped with an automated surface areas using the Brunauer–Emmett–Teller (BET) method. BET surface area of NPCs (1515 m² g⁻¹) is far larger than the surface area of commercial Vulcan XC-72R (254 m² g⁻¹). The energy dispersive X-ray (EDX) spectra was employed to identify the existent and content of element in NPCs. The content of N, C, and O was 2.92 wt%, 90.97 wt%, and 6.11 wt%, respectively. The powder X-ray diffraction (XRD) pattern was recorded on Bruker D8A with parallel Cu Kα radiation.

2.5. Electrochemical measurement

Electrochemical measurements were carried out using a CHI660D electrochemical workstation (Shanghai Chenhua Instrument Corporation, China) with a standard three-electrode cell. A modified glassy carbon electrode was used as a working electrode. The working electrode was prepared as follows: 3.0 mg Pt/NPCs were ultrasonically mixed with 2.7 ml isopropanol and 0.3 ml Nafion solution (5 wt%, DuPont) for 30 min to obtain catalyst ink. Then, 35 μl of the catalyst ink was dropped onto the clear glassy carbon electrode (3 mm in diameter), and dried at room temperature. The working electrode had the loading mass of Pt 0.1 mg cm⁻². A platinum wire was used as a counter electrode, and Ag/AgCl as a reference electrode. The potential range was from

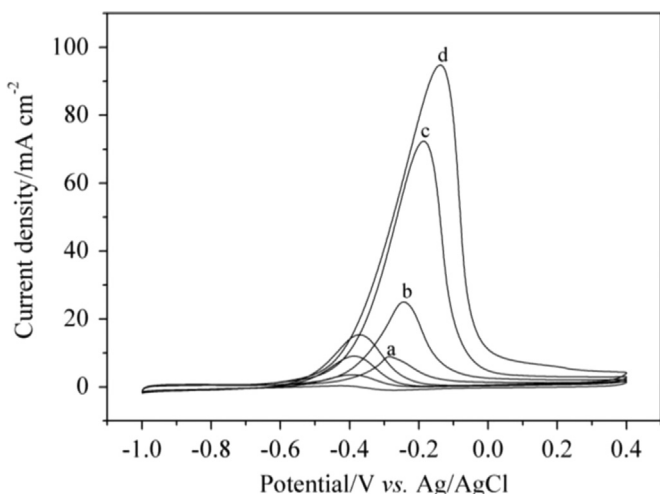


Fig. 2. Cyclic voltammograms of the Pt/NPCs in 1 M NaOH solution with (a) 0.1 M; (b) 0.5 M; (c) 1.0 M; (d) 2.0 M methanol solution at scan rate of 50 mV s⁻¹.

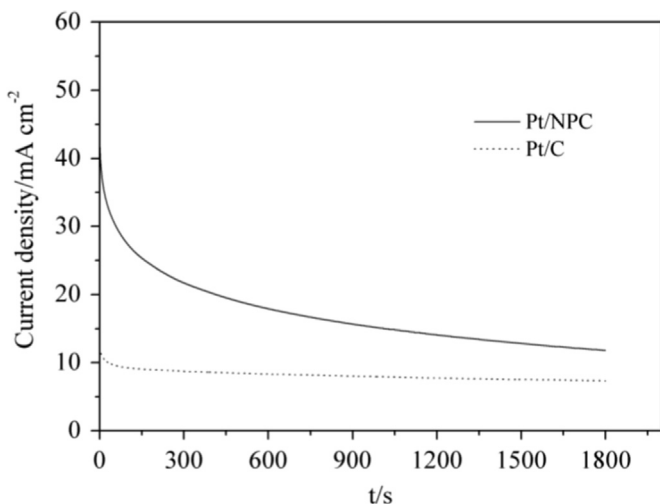


Fig. 3. Chronoamperometric results of Pt/NPCs and Pt/C at -0.2 V.

-1.0 to 0.4 V (*vs.* Ag/AgCl) and the scan rate was 50 mV s⁻¹. All the electrochemical experiments were carried out at room temperature.

3. Results and discussion

Fig. 1a presents SEM image of SiO₂ spheres with diameter about 300 nm, which are basically uniform in size and morphology. The SEM image of NPCs (see Fig. 1b) indicates that the obtained NPCs were honeycomb-like monolith after the removal of silica template. From Fig. 1c, Pt nanoparticles were uniformly spread on the surface of the porous of NPCs. Fig. 1d shows the XRD patterns of Pt/NPCs. The diffraction peak at 2θ of 39.6°, 45.3°, 67.3°, and 81.1° correspond to (110), (200), (220), and (311) crystalline planes of face-centered cubic structure of Pt, respectively. The diffraction peak at about 22.6° observed can be attributed to the C(002) facet of graphitic carbon.

The performance of methanol oxidation on Pt/NPCs electrocatalysts was characterized in 1.0 M NaOH solution containing different concentrations of methanol (0.1–2.0 M), as shown in Fig. 2. It can be seen that the peak current density for methanol electro-oxidation increased obviously with methanol concentration, and the peak potentials for methanol electrooxidation shift positively with

increasing methanol concentration. Moreover, the peak current density for methanol oxidation on Pt/NPCs is 71 mA cm⁻² in 1.0 M NaOH + 1.0 M CH₃OH, which is about 4 times as high as that on Pt/C (17 mA cm⁻²) reported in our previous work [5] under the same testing conditions (3 mm in diameter glassy carbon electrode, 0.1 mg cm⁻² Pt loading, and scan rate of 50 mV s⁻¹), indicating that the Pt/NPCs has higher electrocatalytic activity.

The electrocatalytic oxidation of methanol on the Pt/NPCs and Pt/C catalysts under the same Pt loading (0.1 mg cm⁻²) is also investigated by chronoamperometry in 1.0 M NaOH + 1.0 M CH₃OH at a potential of -0.2 V for 1800 s and the results are shown in Fig. 3. It can be seen that the current density of both the catalysts initially exhibited a gradual decay and then achieved a relatively stable current. During the entire test, the current density of Pt/NPCs electrocatalysts is higher than that of Pt/C electrocatalysts. The results indicate that the Pt/NPCs have higher electrocatalytic stability for the oxidation of methanol.

4. Conclusions

In summary, nitrogen-doped porous carbons (NPCs) with honeycomb-like structures have been successfully synthesized through a facile method using ILs BMIMdca as the carbon precursor, and silica spheres as the templates. The high surface area and the porous structure make NPCs as suitable supports for Pt electrocatalysts. In comparison with Pt/C, the Pt/NPCs show higher electrocatalytic activity and improved stability for methanol oxidation in alkaline medium, suggesting potential application as electrocatalyst supports in alkaline direct methanol fuel cells.

Acknowledgments

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