Preparation and Catalytic Oxidation of Methanol by Pt/g-C$_3$N$_4$/TNTs Composites

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Abstract. In this paper, g-$C_3N_4$/TNTs composites were in situ prepared based on TiO$_2$ nanotubes (TNTs) and graphitic carbon nitride (g-$C_3N_4$). After deposition of platinum (Pt), Pt/g-$C_3N_4$/TNTs catalytic electrode was used for catalytic oxidation of methanol. SEM and XRD were used to characterize the morphology and crystal of the catalytic electrode. Compared with Pt/g-$C_3N_4$ and Pt/TNTs, Pt/g-$C_3N_4$/TNTs catalyst has better catalytic performance and anti-CO toxicity. Pt/g-$C_3N_4$/TNTs has better anti-CO toxicity ability in catalytic oxidation of methanol, due to higher ratio of forward peak current density and reverse peak current density ratio ($J_f/J_b$). The improved electrocatalytic performance is attributed to the improved CO adsorption resistance of Pt nanoparticles prepared in situ by g-$C_3N_4$/TNTs complex. One possible mechanism is the synergistic effect of g-$C_3N_4$ and TNTs to enable Pt catalysts immobilized in g-$C_3N_4$/TNTs composite to achieve better catalytic performance. The results showed that g-$C_3N_4$/TNTs composites prepared in situ, as a support material, was suitable for preparing Pt base catalyst for electrocatalytic oxidation of methanol.

Introduction

With the increasingly serious environmental pollution, direct methanol fuel cells (DMFCs) have attracted more and more attention due to its clean and high-energy conversion efficiency characteristics [1-3]. Because of its simple structure, light weight, small volume, high specific energy, environmental pollution and so on, DMFCs are ideal power sources for electronic products, electric vehicles. Platinum (Pt) and its alloys can be adopted as anode catalysts for DMFCs [4,5]. But Pt has the disadvantages of insufficient resources and high price, and easily affected by the poisoning of intermediate product CO produced in methanol electrocatalytic oxidation. It is an effective way to promote the commercialization of DMFCs by means of further reducing the catalyst and improving the catalytic performance of methanol oxidation by developing novel and efficient catalyst supports. Carbon materials (porous carbons [6], carbon nanotubes [7] and graphene sheets [8]) were used for constructing Pt-based electrode. The doping of heteroatoms is favorable to remove the absorbed poisoning intermediates and promote the catalytic activity [9]. graphitic carbon nitride (g-$C_3N_4$), as a typical nitrogen-rich carbon materials, has become a hot topic of interest due to its remarkable properties including ideal 2D structure, ultrahigh nitrogen content, excellent chemical and thermal stability, which can be applied in a wide range of areas such as metal-free catalysts for water splitting [10], CO$_2$ fixation [11], organic pollutant degradation [12], and so on.

The combination of TiO$_2$ and Pt can improve the activity of catalysts and reduce the loading of Pt in fuel cell. As one of TiO$_2$, TNTs have large surface area and porous structure that is beneficial to the dispersion of nanosized PdAg on the surface [13]. TNTs as catalysts support, local concentration of methanol around Ni nanoparticles can be enhanced via the adsorption of methanol on TNTs due to its amphiphilic property [14].
In this work, a composite support prepared by g-C₃N₄ and TNTs was used to support Pt catalyst. The obtained Pt/g-C₃N₄/TNTs composites was used as anode electrocatalysts for methanol oxidation. The catalytic performance and stability of Pt/g-C₃N₄/TNTs catalyst is superior to Pt/g-C₃N₄ and Pt/TNTs catalysts for methanol oxidation.

Experimental

Preparation of G-C₃N₄/TNTs

(1) Preparation of TNTs. Ti foil was first washed with acetone, anhydrous ethanol and deionized water for 20 min, respectively. Then Ti foil was anodized in the electrolyte composed of 50 mL ethylene glycol, 12.5 mL deionized water and 0.1 g NH₄F at 45 V for 2 h. The as-anodized sample subsequently was annealed under 400°C for 1 h.

(2) In situ preparation of g-C₃N₄/TNTs. The prepared TNTs was inserted into the solution of melamine. The temperature of 60°C was kept to evaporate water. The composite was heated in an alumina crucible with a cover in a muffle furnace at 4°C/min until reaching 550°C and held for 2 h. G-C₃N₄/TNTs composite prepared in situ was ground into power and stored for later use.

Preparation of Catalytic Electrode

The electrodeposition of Pt onto the supports was performed in a standard three-electrode system, including a KCl-saturated Ag/AgCl electrode as the reference electrode, a Pt plate as the counter electrode and TNTs, g-C₃N₄ and g-C₃N₄/TNTs as the working electrode, respectively. The electrodeposition was carried out at room temperature under -0.2 V for 450 s. All the reagents used were of analytical grade and were used without further purification. The obtained electrodes were denoted as Pt/TNTs, Pt/g-C₃N₄ and Pt/ g-C₃N₄/TNTs, respectively.

Characterization

The morphology of the samples was characterized using EVO MA10 SEM. The X-ray diffractometer (XRD) were obtained from a Bruker D8 X-ray diffractometer using Cu Kα radiation source and λ = 1.5406 Å. The electrochemical dates were recorded on a CHI660E electrochemical workstation.

Electrocatalytic Oxidation of Methanol

The electrochemical performances for catalytic oxidation of methanol were studied by cyclic voltammetry curve (CV) and chronoamperometry using a CHI660E electrochemical workstation with a conventional three-electrode system. Pt/TNTs, Pt/g-C₃N₄ and Pt/g-C₃N₄/TNTs were used as the working electrode, and a KCl-saturated Ag/AgCl electrode as the reference electrode, a Pt plate as the counter electrode, respectively.

Result and Discussion

Figure 1 shows the SEM images of TNTs, g-C₃N₄/TNTs and Pt/g-C₃N₄/TNTs, respectively. Figure 1A shows TNTs prepared by anodic oxidation under the best conditions (oxidation voltage 45 V, oxidation time 2 h). It can be seen that the surface nanotubes are evenly arranged and the structure is clear. After in-situ loading of g-C₃N₄, many pieces of g-C₃N₄ appeared on the surface (Figure 1B). The SEM image of Pt/g-C₃N₄/TNTs for deposition of 180 s was shown in Figure 1C. Few white spherical Pt particles appear in the Figure. After the deposition time increased to 450 s, a few Pt microspheres were found on the surface of g-C₃N₄/TNTs (Figure 1D). This kind of microsphere has a larger specific surface area, which can guarantee the better catalytic performance of Pt/g-C₃N₄/TNTs.

Figure 2 shows the XRD patterns of TNTs, g-C₃N₄/TNTs and Pt/g-C₃N₄/TNTs, respectively. The peaks at 25.24°, 38.2° and 40.18° of all the samples can be indexed to the anatase phase of TiO₂ (101), (004) and (200), respectively. According to the literature, g-C₃N₄ spectrum (marked as ○), located in 27.4° is the characteristic peak of interring stacking surface (002). However, the peak value of the
characteristic peak is small, maybe the amount of g-C₃N₄ is very small. In addition, the diffraction angle of 2θ is 46.4°, which is the diffraction peak of Pt (200) crystal plane.

Figure 1. SEM images of TNTs (A), g-C₃N₄/TNTs (B), Pt/g-C₃N₄/TNTs (C,D).

Figure 2. XRD of TNTs (a), g-C₃N₄/TNTs (b), Pt/g-C₃N₄/TNTs (c).

In Figure 3A, Pt/g-C₃N₄ (a), Pt/TNTs (b) and Pt/g-C₃N₄/TNTs (c) showed a pair of obvious redox peaks between 0.25 V and 0.45 V. As can be seen from the Figure, Pt/g-C₃N₄/TNTs had the maximum redox peak current. The main reason may be the synergistic effect of TNTs and g-C₃N₄. Figure 3B shows the CV curves of Pt/g-C₃N₄ (a), Pt/TNTs (b) and Pt/g-C₃N₄/TNTs (c) in 0.5 M H₂SO₄ solution. Pt/g-C₃N₄ had a pair of absorption/desorption peaks at -0.5 V and 0.05 V, Pt/TNTs had a pair of absorption/desorption peaks at -0.11 V and 0.014 V, and Pt/g-C₃N₄/TNTs had a pair of absorption/desorption peaks at -0.11 V and 0.04 V, respectively. Pt/g-C₃N₄/TNTs had the larger peak value than that of Pt/g-C₃N₄ and Pt/TNTs, indicating that Pt/g-C₃N₄/TNTs had the best catalytic performance.

Figure 4A shows the CVs recorded for the electrocatalytic oxidation of methanol at a scan rate of 100 mV s⁻¹ for Pt/g-C₃N₄, Pt/TNTs and Pt/g-C₃N₄/TNTs in 0.5 M H₂SO₄ containing 1 M CH₃OH. The improved catalytic activity was observed for Pt/g-C₃N₄/TNTs evidenced by the lower onset potential and obviously higher oxidation current in the forward sweep. The oxidation peak generated in the reverse scan is associated with the oxidation of adsorbed CO in the forward scan. The stability of catalyst was studied by chronoamperometric method. The results of Figure 4B show that the Pt/g-C₃N₄/TNTs has a higher steady-state current compared to Pt/TNTs and Pt/g-C₃N₄ at an applied potential of 0.5 V. The final state current (c, 98.02 μA) measured for Pt/g-C₃N₄/TNTs is 1.35 times and 11.22 times of Pt/TNTs (b, 72.62 μA) and Pt/g-C₃N₄ (A, 8.74 μA), respectively. The initial rapid
The decline was due to the accumulation of intermediate products such as CO on the surface of Pt, leading to the decrease of active sites of Pt. Therefore, Pt/g-C₃N₄/TNTs catalyst has better stability.

![Figure 3](image1.png)

**Figure 3.** CVs of Pt/g-C₃N₄ (a), Pt/TNTs (b), Pt/g-C₃N₄/TNTs (c) in 0.1 M KCl solution containing 5 mM [Fe(CN)₆]³⁻/⁴⁻ (A) and 0.5 M H₂SO₄ solution (B).

![Figure 4](image2.png)

**Figure 4.** CVs (A) and Chronoamperometric curves (B) of Pt/g-C₃N₄ (a), Pt/TNTs (b), Pt/g-C₃N₄/TNTs (c) in 0.5 M H₂SO₄ containing 1 M CH₃OH.

The ratio of the forward anodic peak current (Iₕ) to the reverse anodic peak current (Iᵦ) can reflect the anti-toxicity ability of the catalyst. A high Iₕ/Iᵦ ratio shows a strong anti-toxicity ability. As can be seen from Table 1, the Iₕ/Iᵦ value of Pt/g-C₃N₄/TNTs catalyst is the highest, that is, it has the strongest anti-toxicity ability. Therefore, modification of g-C₃N₄ on TNTs can improve the anti-toxicity ability.

**Table 1.** Catalytical performance of Pt/g-C₃N₄, Pt/TNTs, Pt/g-C₃N₄/TNTs.

| catalyst          | Iₕ (mA) | Iᵦ (mA) | Iₕ/Iᵦ |
|-------------------|---------|---------|-------|
| Pt/g-C₃N₄        | 0.05    | 0.25    | 2.0   |
| Pt/TiO₂          | 0.29    | 0.26    | 1.1   |
| Pt/g-C₃N₄/TiO₂  | 0.79    | 0.36    | 2.2   |

**Conclusion**

In this paper, we have fabricated Pt based catalysts anchored on in-situ prepared g-C₃N₄/TNTs successfully. Owing to the unique characteristics, including high electroactive surface area, high nitrogen content, and good electrical conductivity, the obtained Pt/g-C₃N₄/TNTs composites show excellent electrical electrocatalytic performance combined with high electrocatalytic activity, strong anti-toxicity ability, and stability using as anode electrocatalysts for DMFCs.
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