Preparation and electrochemical performance of manganese porphyrin /titanate intercalated nanocomposite

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Abstract. A new nanocomposite of manganese porphyrin/titanate (MnPP-Ti₄O₉) was prepared successfully by delamination/reassembling (DR) method, with layered titanate as the host material, manganese porphyrin (MnPP) as the guest material. The microstructure of MnPP-Ti₄O₉ was characterized by XRD, UV-Vis, SEM and TEM. MnPP molecules were closely tilted against the host nanosheets at an inclined angle of 42.7°, by simple geometric calculation. The electrochemical performance of the nanocomposite was measured using cyclic voltammetry (CV). It was found that MnPP-Ti₄O₉ modified glassy carbon electrode (MTGCE) showed desired electrochemical performance and good catalytic activity for oxygen reduction.

1. Introduction

Inorganic layered compounds have a two-dimensional spatial structure, of which the distance between neighbor layers is at the molecular level. There is a strong covalent bond inside the layer, while the layers are stacked together by the weak force. If the layers are electrically neutral, such as graphite, the force is Van der Waals’ force; if charged, it turns to electrostatic force [1]. According to the structural features of the layer, many nanocomposites can be fabricated by inserting different kinds of functional guest molecules into the layer space by appropriate methods [2-4]. Although some methods, such as direct-reaction method, ion-exchange method and direct-embedding method have been reported to accomplish successful intercalations, the uses of them are limited due to either the high charge density of the host layers or the size of guest molecules or the host layer spacing, which may lead to a long reaction period or failing intercalation [5-6]. Delamination/reassembling (DR) method, which is a relatively new method, has been proved feasible in fabricating intercalated nanocomposite recently [7]. This method can effectively overcome the steric hindrance of the layer spacing, thus the reaction time is remarkably reduced, compared with the previous methods which may have a reaction period of several months. What’s more, intercalated materials prepared by this method seem to show a larger specific surface area than those prepared by other methods, which may lead to a better catalytic performance.

Intercalated nanocomposite not only exhibits some advantages of both layered host and functional guest molecules, but also show some differences in catalytic, adsorption, electrical and magnetic properties, compared with single component, which has potential applications in providing the new
material system of building photoelectric devices, chemical and biological sensors, and in the field of molecular recognition and catalysis [8-9]. Titanate is a class of layered compounds, having regular layer structure and properties of layer-swellable and ion-exchangeable, which makes it an ideal material as good support for functional guest molecules [10]. Metalloporphyrins are a well-known kind of naturally-occurring compounds that represent many important enzymes. In this paper, the nanocomposite of MnPP-Ti$_4$O$_9$ is fabricated by DR method with layered potassium titanate (K$_2$Ti$_4$O$_9$) as the host body, MnPP as the guest, and the electrochemical performance of the nanocomposite is studied.

2. Experimental

K$_2$Ti$_4$O$_9$ was synthesized by solid-state reaction at 800°C for 20h with K$_2$CO$_3$ and TiO$_2$ in the mole ratio of 1:1. The product was acidified 5 times with 3M HCl for 12h. The protonated product (H$_2$Ti$_4$O$_9$) was washed with distilled water to remove Cl$^{-}$ and dried in the vacuum. The resulting product was treated with tetrabutylammonium hydroxide (TBAOH) to exfoliate titanate. H$_2$Ti$_4$O$_9$ (0.2g) was firstly dispersed evenly into the distilled water, then a 10 wt% TBAOH aqueous solution was added slowly to the suspension until pH value reached 9.7. The exfoliated product was obtained after stirring for 2 weeks at room temperature. The colloidal suspension was centrifuged at 2000rpm for 30minutes to remove the particles that were not exfoliated, and the colloidal suspension containing titanate nanosheets was collected. The addition of MnPP aqueous solution to the colloidal suspension resulted in immediate aggregation of the nanosheets as precipitates. The final product MnPP-Ti$_4$O$_9$ was obtained after washed with distilled water 3 times and dried in the vacuum at 60°C overnight.

Powder X-ray diffraction (XRD, XRD-6100), scanning electron microscope (SEM, JSM-5600), transmission electron microscope (TEM, JEM-2010) and ultraviolet-visible spectroscopy (UV-Vis, UV-2550) were employed to the characterization of the products. The electrochemical performance was performed on CHI 660C electrochemical workstation, with a saturated calomel electrode as the reference electrode, a platinum electrode as the auxiliary electrode, and a glassy carbon electrode (GCE) as the working electrode. The MTGCE was prepared by an absorption method, with 10 μL MnPP-Ti$_4$O$_9$ aqueous suspension coated on a GCE and dried for at least 24h. All electrochemical tests were performed at 25°C.

3. Results and Discussion

3.1. Microstructure characterization

Figure 1(a) shows the XRD patterns of K$_2$Ti$_4$O$_9$, protonated product (H$_2$Ti$_4$O$_9$), and intercalated product MnPP-Ti$_4$O$_9$, respectively. It can be found that the (200) peak of K$_2$Ti$_4$O$_9$ shifts slightly to the lower angle side after the acidification process, with 2θ angle changing from 10.14° to 10.07°, corresponding to the increase of layer spacing. This is due to that H$^+$ is inserted into the layers in hydrated state, of which the ion volume is bigger than K$^+$. The delamination occurs after the addition of the TBAOH molecules, driven by the force of neutralization reaction. The reassembling process is considerably fast, and the intercalated deposition can be observed immediately when adding metalloporphyrin aqueous solution to the nanosheets suspension. After the process, the (200) peak significantly shifts to lower angle after the reassembling process, which suggests MnPP is inserted successfully into the layers and the distance between neighbor layers is further expanded. The thickness of titanate, as described previously, is 0.5nm and the size of MnPP molecule is 1.80×1.80×0.75 nm$^3$ (estimated by Chem 3D for an optimized structure) [10]. With these datum, it can be speculated that MnPP molecules are closely tilted against the host nanosheets at a specific inclined angle whose value is 42.7°, by simple geometric calculation.

Figure 1(b) shows the UV-Vis absorption spectrum of homogeneous MnPP and the nanocomposite of MnPP-Ti$_4$O$_9$. It can be found, both have two absorption bands in the wavelength range from 300 to 800 nm, where strong absorption bands correspond to the Soret absorption band and weak absorption
bands are Q band absorption bands. The maximum absorption wavelength of homogeneous MnPP in Soret absorption band is at 462nm, while that of MnPP-Ti$_4$O$_9$ changes to 480nm. This phenomenon may be caused for that the terminal substituents of MnPP are distorted due to the restriction of the layer spacing in nanoscale. As a result, the coplanar effect between substituents and the porphyrin rings increases, leading to the formation of the big $\pi$ Bond, thereby reducing the energy level difference [11]. This further indicates that the MnPP molecules are tilt-arranged between the titanate layers, because only in this way can MnPP molecules be closely packed.

TEM and SEM images of the intercalated nanocomposite are shown in figure 2(a) and figure 2(b), respectively. It is obvious titanate still keeps the layer structure and the layers are still orderly-arranged after acidizing, exfoliating and resembling processes. These suggest MnPP molecules can be successfully inserted into titanate layers, while the two-dimensional spatial structure of the host body is retained. The structural model of MnPP-Ti$_4$O$_9$ nanocomposite is shown in figure 3, according to the analyses above.

![XRD pattern and UV-vis spectrum](image)

**Figure 1.** (a) XRD patterns of K$_2$Ti$_4$O$_9$, H$_2$Ti$_4$O$_9$ and MnPP-Ti$_4$O$_9$ and (b) UV-vis spectrum of pure MnPP and the nanocomposite of MnPP-Ti$_4$O$_9$.

![SEM and TEM images](image)

**Figure 2.** SEM (a), TEM(b) images of the nanocomposite of MnPP-Ti$_4$O$_9$. 
Figure 3. Model of the nanocomposite of MnPP-Ti₄O₉.

3.2. Electrochemical performance

The bare GCE is put into a $3 \times 10^{-4}$ mol L$^{-1}$ MnPP+0.1 mol L$^{-1}$ KCl, N₂ saturated aqueous solution. CV tests are carried out in the voltage range of $-0.5$-$0.5$ V at the scanning rate of 50 mV s$^{-1}$. The results are shown in figure 4(a). The oxidation peak potential ($E_{pa}$) is located in $-0.188$V, while the reduction peak potential ($E_{pc}$) is in $-0.258$V, and the half maximum peak potential of $E_m$ is $-0.223$V. The peak separation value of $\Delta E_p$ is 69 mV, which is greater than that of the single electron transfer theory value (59mV), suggesting the electrode reaction is quasi-reversible reaction, in accordance with the previously reported redox couple of Mn$^{III}$PP$^{5+}$/Mn$^{II}$PP$^{4+}$[12].

The MTGCE is fabricated by a absorption method. The CV curves of the MTGCE are shown in figure 4 (a). The electrode shows good redox activity, of which the waveform is similar to the bare GCE in homogeneous MnPP aqueous solution, suggesting it also has good redox properties. $E_{pa}$ is located in $-0.177$V, while $E_{pc}$ is in $-0.256$V which is almost identical with the bare GCE. The ratio of reduction peak current and oxidation peak current ($I_{pc}/I_{pa}$) is 1.9, showing a worse reversibility than homogeneous MnPP. This is due to the electron transfer process is somewhat hampered by host layers who possess semi-conductor properties. Both $I_{pc}$ and $I_{pa}$ of the MTGCE increase, which indicates that the concentration of MnPP between layer spacing is larger than that in the homogeneous MnPP aqueous solution, which results in a stronger electrochemical response current.

Figure 4. (a) CV grams of GCE in $3 \times 10^{-4}$ mol L$^{-1}$ MnPP + 0.1 mol L$^{-1}$ KCl, N₂ saturated aqueous solution and MTGCE in 0.1 mol L$^{-1}$ KCl, N₂ saturated aqueous solution, at a scanning rate of 50 mV s$^{-1}$, pH=7.0, T=25°C; (b) CV grams of MTGCE in 0.1 mol L$^{-1}$ KCl, N₂ saturated aqueous solution, at the scanning rate: 50, 100, 150, 200, 250, 300, 350 and 400 mV s$^{-1}$, respectively, pH=7.0, T=25°C.

Further researches on the CV behaviors of the MTGCE at different scanning rates are shown in
figure 4(b). With the increase of the scanning rate, the position of $E_{pa}$ and $E_{pc}$ gradually change to the positive and negative sides, respectively. Besides, both $I_{pc}$ and $I_{pa}$ are gradually increasing, and the value of $\Delta E_p$ has also shifted from 54 mV to 108 mV, which further indicates that the host layers with semi-conductor properties have a negative effect on the electron transfer process of the reaction, and the effect is extremely significant at a high scanning rate. Two straight lines can be obtained by drawing the relationship diagrams between the peak current ($I_{pa}$ or $I_{pc}$) and the square root of the scanning rate. This means there is a linear relationship between peak current ($I_{pa}$ or $I_{pc}$) and the square root of scanning rate, which can be described by two regression equations.

$$I_{pa}(\mu A) = -1.3941 + 0.05466v^{1/2} (mV s^{-1})^{1/2} \quad (r = 0.9832)$$  \hspace{1cm} (1)

$$I_{pc}(\mu A) = -0.6327 - 0.05530v^{1/2} (mV s^{-1})^{1/2} \quad (r = 0.9921)$$  \hspace{1cm} (2)

Where $r$ is referred to correlation coefficient. This suggests that the electrochemical reaction of the active substance in the modified electrode is diffusion-controlled.

The stability of the MTGCE is studied on the same modified electrode for continuous 7 days, 40 times a day, using CV tests, in 0.1 mol L$^{-1}$ KCl, N$_2$ saturated aqueous solution, at a scanning rate of 50 mV s$^{-1}$. Figure 5(a) is the relationship gram between peak potential and time while figure 5(b) is the relationship gram between peak current and time. It is obvious the peak potential almost has no change, while the peak current has only decreased by 8%, indicating that the nanocomposite can be well absorbed by the GCE and the nanocomposite has better stability than homogeneous metalloporphyrin which decompose easily in the oxidation process and has difficulty in recovery [13-15].

Based on the excellent electrochemical performance and stability of the MTGCE, the application of the MTGCE in the catalytic reduction of oxygen is researched using CV, in O$_2$ saturated phosphate buffer solution, the result is shown in figure 6. It is obvious that the reduction peak of the MTGCE has shifted positively by 260 mV, compared with the bare GCE in the same solution, what’s more, it is observed that the peak has also sharpened and there is a upward trend in the reverse scanning curve. All of these suggest that the MTGCE has good catalytic activity for oxygen reduction, which results in a stronger electrochemical response current.

**Figure 5** (a) The relationship gram between peak potential and time, and (b) the relationship gram between peak current and time
Figure 6. CV gram of MTGCE in O$_2$ saturated phosphate buffer solution, at a scanning rate of 50 mV s$^{-1}$, pH=7.0, T=25°C. Built-in gram is the CV test of bare GCE in O$_2$ saturated phosphate buffer solution, at a scanning rate of 50 mV s$^{-1}$, pH=7.0, T=25°C.

4. Conclusions

The nanocomposite of MnPP-Ti$_4$O$_9$ is fabricated by DR method. XRD, SEM and TEM images reveal that the insertion of MnPP into titanate layers is successful, and MnPP molecules show close tilt arrangement against the host nanosheets at an inclined angle of 42.7°, which is further supported by UV-Vis. CV tests show that titanate layer structure has litter impact on the electrochemical property of the nanocomposite and the electrochemical reaction is diffusion-controlled. What’s more, the MTGCE has good catalytic activity for oxygen reduction and potential for applications in the field of electrochemical catalysis.

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