Preparation and photoelectrocatalytic performance of N-doped TiO₂/NaY zeolite membrane composite electrode material
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ABSTRACT
A novel composite electrode material based on a N-doped TiO₂-loaded NaY zeolite membrane (N-doped TiO₂/NaY zeolite membrane) for photoelectrocatalysis was presented. X-ray diffraction (XRD), scanning electron microscopy (SEM), UV–visible (UV-vis) and X-ray photoelectron spectroscopy (XPS) characterization techniques were used to analyze the structure of the N-doped TiO₂/NaY zeolite membrane. The XRD and SEM results verified that the N-doped TiO₂ nanoparticles with the size of ca. 20 nm have been successfully loaded on the porous stainless steel-supported NaY zeolite membrane. The UV-vis result showed that the N-doped TiO₂/NaY zeolite membrane exhibited a more obvious red-shift than that of N-TiO₂ nanoparticles. The XPS characterization revealed that the doping of N element into TiO₂ was successfully achieved. The photoelectrocatalysis performance of the N-doped TiO₂/NaY zeolite membrane composite electrode material was evaluated by phenol removal and also the effects of reaction conditions on the catalytic performance were investigated. Owing to exhibiting an excellent catalytic activity and good recycling stability, the N-doped TiO₂/NaY zeolite membrane composite electrode material was of promising application for photoelectrocatalysis in wastewater treatment.

Key words | electrode material, N doping, photoelectrocatalysis, TiO₂, zeolite membrane

INTRODUCTION
The combined technology involving use of photocatalytic and electrochemical processes for the removal of harmful organic compounds in wastewater has been rapidly developed in recent years (Ferraz et al. 2013; Gupta & Subramanian 2014). Photoelectrocatalysis (PEC) shows an advantage over photocatalysis since it applies a potential across a photoanode on which the catalyst is supported. This configuration allows for a more effective separation of the charges generated (e⁻/h⁺) in the process, thus increasing the lifetime of the electron–hole pairs (Carneiro et al. 2005). The actual implementation of PEC technology is critically dependent on semiconductor electrode materials. Among the various electrode materials studied, TiO₂ is the most common candidate for the destruction of organic pollutants due to its high photocatalytic activity, good stability, non-toxicity and low cost. Therefore, many composite electrode materials involving TiO₂ have been studied, such as TiO₂/SrTiO₃ (Huang et al. 2014), WO₃/TiO₂ (Zhang et al. 2014), Ti/TiO₂ annotate (Ferraz et al. 2013), Bi₂Ti₂O₇ (Gupta & Subramanian 2014), Au-NPs/TiO₂ annotate (Wu et al. 2015) and Cr-doped TiO₂ annotate (Yang et al. 2014). The doping with nonmetal elements in the TiO₂ nanostructure has shown encouraging results for the development of visible light-active photoelectrocatalysts (Hong et al. 2005; Lu et al. 2007; Wu et al. 2008). To achieve pre-concentration of pollutants and resolve the difficult separation of TiO₂ particles, immobilization of TiO₂ on an adsorbent or an inert support to form integrated photocatalytic adsorbents (IPAs) has been advised (Yeung & Han 2014). Using IPAs, removal of pollutants can be achieved by the simultaneous effects of physical adsorption by the adsorbent and photochemical removal by the immobilized TiO₂. To realize this, TiO₂ particles are typically dispersed on supports with high surface area such as activated carbon (Shan et al. 2010; Su et al. 2015) and zeolite (Basha et al. 2011).

Zeolites consisting of three-dimensional structures of SiO₄ and AlO₄, tetrahedrally linked by oxygen atoms to
form a cage structure, have good adsorption abilities, uniform channels and regular pores. Thereby, TiO$_2$ can be facilely supported in the existing channels or surface of the zeolite particles. Recently, those studies involving TiO$_2$/zeolite IPAs have exhibited a good photocatalytic performance for the removal of organic compounds such as dyes (Li et al. 2005; Wang et al. 2011; Kuo et al. 2012), humic acids (Liu et al. 2014) and pharmaceutical compounds (Kanakaraju et al. 2015). This should be attributed to the advantages of IPAs. In addition, zeolite-modified electrodes as active anode exhibited some good features, such as fast, easy and cheap, for electrooxidation of formaldehyde (Abrishamkar & Kakhkeshi 2013), oxidation of ascorbic and uric acid (Mazloum Arkadani et al. 2006; Rohani & Taher 2009) and cysteine (Nezamzadeh-Ejhieh & Hashemi 2012). Zeolite membranes, as the intergrown material of zeolite crystals, have potential advantages in many applications, including electrocatalysts and electrolyte membrane for fuel cells (Yeung & Han 2014). So far, a study on electrode material based on zeolite membrane-supported N-doped TiO$_2$ used in PEC has not been found. This work prepared a novel PEC electrode material based on N-doped TiO$_2$-loaded NaY zeolite membrane, and studied its photoelectrocatalytic performance for phenol removal.

**EXPERIMENTAL**

**Preparation of zeolite membrane-based electrode material**

A porous stainless steel disc (diameter of 20 mm and thickness of 2 mm) with a porosity of 75% and an average pore size of 0.2 μm was polished with sandpaper, treated in an aqueous solution of sodium hydroxide (10 mol L$^{-1}$) for 12 h, dried at 120 °C for 24 h and then transferred into a desiccator for further use. The preparation of Y-type zeolite membrane is described in our previous work (Cheng et al. 2003). The precursor of N-doped TiO$_2$ was synthesized using the sol–gel method and n-butylamine as the doping N source. The N-doped TiO$_2$-coated porous stainless steel or the N-doped TiO$_2$-loaded NaY zeolite membrane was prepared by using the dip-coating method. One side of the porous stainless steel or the supported NaY zeolite membrane was dipped in the precursor of N-doping solution for 30 s, and the procedure was repeated at least three times. After drying in air at 60 °C, the supported NaY zeolite membrane was calcined at 300 °C, 400 °C, 500 °C and 600 °C for 6 h, respectively. After cooling down the resulting N-doped TiO$_2$-loaded NaY zeolite membrane was washed several times with deionized water until neutrality and dried at room temperature. The N-doped TiO$_2$ (N-TiO$_2$) nanoparticles with the size of ca. 20 nm was prepared by the sol–gel method (Papoulis et al. 2010).

**Material characterization**

The formation of zeolite membranes was confirmed by X-ray diffraction (XRD) using a Bruker-AXS D8 powder diffractometer with Cu Kα ($\lambda = 0.154$ nm) radiation (40 kV and 30 mA). The surface morphology was examined by scanning electron microscopy (SEM) (S4800, Hitachi) at an acceleration voltage of 15 kV. The UV–visible (UV-vis) light absorption spectrum was obtained from a Varian Cary 5000 spectrophotometer equipped with an integrating sphere assembly. The X-ray photoelectron spectroscopy (XPS) analysis was carried out using an ESCALAB 250Xi spectrometer (Thermo Scientific). The chemical oxygen demand (COD) value of phenol solution was detected with a rapid determination instrument (5B-1) and the total organic carbon (TOC) value was measured with a TOC-VCPH instrument (Shimadzu company).

**Measurement of catalytic performance**

The photoelectrocatalytic activity of the prepared electrode material was studied by using phenol as probe pollutant under simulated solar-light radiation flux (source: xenon lamp, PLS-SXE300, 300 W, 200–2,500 nm wavelength band, Beijing Trusttech Co. Ltd, China) and power with an electric field of 8 V. Herein, the supported N-doped TiO$_2$-loaded NaY zeolite membrane composite electrode material was used as anode, and the cathode was the porous stainless steel disc. The distance between the electrodes was kept at 5 cm. The adsorption–desorption equilibrium was established by keeping the catalyst-loaded phenol in the dark under stirring for half an hour. The falling value of phenol concentration was no more than 3% as a result of zeolite adsorption. The removal rate of phenol was calculated by measuring the varying value of the concentration of phenol before and after reaction using a UV-vis spectrophotometer (Lambda 850, PE company). The evaluation was performed for a 100 mL phenol solution with the initial concentration of 90, 100, 110 and 120 mg/L (denoted c$_0$) under magnetic stirring, respectively. Upon each interval time, the concentration of phenol (denoted c$_i$) was measured. After the ending, the N-doped TiO$_2$/NaY zeolite membrane was regenerated by calcination at 500 °C. The stability was evaluated by reusing the electrode material several times. In most cases, the pH value of the initial phenol solution
was kept at alkaline condition to prevent the iron in stainless steel from dissolving. The photoelectrocatalytic evolution was carried out as shown in Figure 1.

RESULTS AND DISCUSSION

Characterizations of N-doped TiO$_2$/NaY zeolite membrane composite electrode material

Figure 2 shows the XRD patterns of the as-synthesized NaY zeolite membrane (a) and the N-doped TiO$_2$/NaY zeolite membrane (b). The obtained as-synthesized NaY membrane is of the standard peak of FAU-type structure (JCPDF: 39–1380) as shown in Figure 2(a), confirming that the as-synthesized NaY zeolite membrane has successfully grown on the porous stainless steel disc. After loading with TiO$_2$ precursor and then calcination, the substrate-supported NaY zeolite membrane has fresh peaks at 20–25.3’ and 37.8’, which were attributed to the anatase crystal structure of TiO$_2$. This suggests that the TiO$_2$ particles have been successfully loaded on the NaY zeolite membrane. Figure 3 shows SEM images of zeolite membrane before and after loading with TiO$_2$. It can be observed that the as-synthesized NaY zeolite membrane consists of flower-like intergrown crystals (Figure 3(c)); however there still exists some small defect holes. In contrast to the magnification images of before and after the N-TiO$_2$ loading, the NaY zeolite membrane is fully coated by TiO$_2$ nanoparticles with the size of ca. 20 nm (Figure 3(d)). Owing to existing massive natural nanopores in the zeolite crystal, a certain amount of TiO$_2$ nanoparticles was encapsulated in those nanopores.

Figure 4 shows the UV-vis spectra of the TiO$_2$, the N-TiO$_2$ and the N-doped TiO$_2$/NaY zeolite membrane. Besides the typical UV absorption band, the visible absorption bands of the N-TiO$_2$ and the N-doped TiO$_2$/NaY zeolite membrane both appear as a distinct red-shift in the visible range of between 400 nm and 600 nm compared to the TiO$_2$, and furthermore the latter exhibits a more obvious red-shift than the former. This verifies that there is the existing of N—Ti bonding in N-TiO$_2$. This is likely to be ascribed to the effect of the electrostatic field of the zeolite nano-pore cavity. Figure 5 shows the survey and N1s XPS spectra of N-doped TiO$_2$/NaY zeolite membrane. In addition to a stronger Ti2p peak, there appears a weak N1s peak in the
survey XPS spectra (Figure 5(a)). Most importantly, the N1s spectra includes a \( \beta \)-N1s peak, which was considered to be evidence of the Ti–N bond (Diwald et al. 2004; Sakthivel et al. 2007). These results verify that the N element has been successfully doped into the crystal structure of TiO\(_2\). It suggests that the N-doped TiO\(_2\)/NaY zeolite membrane should be of a visible-light photocatalytic activity.

**Photoelectrocatalysis performance of N-doped TiO\(_2\)/NaY zeolite membrane composite electrode material**

Figure 6 shows the comparison of catalytic activity of the N-doped TiO\(_2\)/NaY zeolite membrane in 90 mg/L phenol solution under different catalysis patterns. For the electrocatalysis pattern, the removal of phenol on the N-doped TiO\(_2\)/NaY zeolite membrane shows a lower level. However, the catalytic activity of the N-doped TiO\(_2\)/NaY zeolite membrane is obviously stimulated by the photocatalysis pattern under simulated solar light. The removal rate is about two times larger than that of the electrocatalysis pattern after reaction time of 60 min. This is assumed to be the effect of N-doped TiO\(_2\). Under the PEC pattern, the N-doped TiO\(_2\)/NaY zeolite membrane for the removal of phenol exhibits the best catalytic activity, removing phenol by 80% and 89% after 90 min and 180 min of reaction times, respectively. Interestingly, these are about 10–20% higher than the sum of the removals of electrocatalysis and photocatalysis patterns. It presents an enhancing synergistic effect of the N-doped TiO\(_2\) and the NaY zeolite membrane. The mechanism can be assumed to be that a part of the N-TiO\(_2\) nanoparticles occupying the defect pores of the zeolite membrane has the ability of the conduction electron and the other part of the N-TiO\(_2\) nanoparticles encapsulated in zeolite nanopores under the affect of the electrostatic field can promote the anode electron conduction, which enhanced the electrocatalysis of the N-doped TiO\(_2\)/NaY zeolite membrane composite electrode material.

Figure 7 shows the effect of the initial concentration of phenol on the N-doped TiO\(_2\)/NaY zeolite membrane for phenol removal under PEC pattern. It can be seen that the removal rate of phenol is decreased with the increasing of the initial concentration of phenol at the same reaction time. This suggests that the phenol removal efficiency of the N-doped TiO\(_2\)/NaY zeolite membrane is dependent on the initial concentration of phenol.
Figure 8 gives the effect of the initial pH value of solution on the N-doped TiO$_2$/NaY zeolite membrane for phenol removal under PEC pattern. The phenol removal rate attains 81% at the pH value of 5.0, which is slightly higher than that at the pH value of 8.0. The result suggests that the initial solution with the acidic condition is more favorable to the phenol removal. However, because the porous stainless steel support corrodes more easily under the acidic condition, the pH value of the initial solution was set to 8.

Figure 9 shows the effect of the calcination temperature of the N-doped TiO$_2$/NaY zeolite membrane composite electrode material to phenol removal. As the calcination temperature increases from 300 °C to 600 °C, the phenol removal rate of the N-doped TiO$_2$/NaY zeolite membrane composite electrode material firstly increases and afterwards decreases. The N-doped TiO$_2$/NaY zeolite membrane composite electrode material after calcination at 400 °C exhibits the best catalytic activity for phenol removal.

For verifying the recycling performance of the N-doped TiO$_2$/NaY zeolite membrane composite electrode material, the recycling times also were investigated under the PEC pattern as shown in Figure 10. After being recycled five times, the removal rate of the N-doped TiO$_2$/NaY zeolite membrane slightly decreases from 89 to 75%, still exhibiting a good stability.
Figure 11 gives the UV-vis spectra of phenol removal via the N-TiO$_2$/porous stainless steel and the N-TiO$_2$/NaY zeolite membrane composite electrode materials after reaction for 180 min. As can be observed, there are two typical feature peaks of the phenol solution at 220 nm and 270 nm. For N-TiO$_2$/porous stainless steel without supported zeolite membrane, the intensities of the typical feature peaks of phenol decrease by about 20% compared to phenol solution. Most of all, the typical feature peaks of phenol almost disappear when the N-TiO$_2$/NaY zeolite membrane composite electrode material was employed. Table 1 lists the removal results obtained by UV-vis, COD and TOC measurements after the reaction time of 180 min, respectively. Under alkaline condition, the porous stainless steel electrode material only has a 3.1% removal rate for phenol, whereas the removal rate of the N-TiO$_2$/porous stainless steel electrode material is 20.3%. But for the N-TiO$_2$/NaY zeolite membrane composite electrode material, the removal rate has attained 89.0%, which is consistent with the UV-vis result. For each electrode material, the removal rates for phenol (UV-vis measurement), COD and TOC are similar. This verifies that most of the phenol should be decomposed to CO$_2$ and H$_2$O through the N-TiO$_2$/NaY zeolite membrane composite electrode material under PEC pattern.

**CONCLUSION**

In this paper, a novel composite electrode material based on N-doped TiO$_2$-loaded NaY zeolite membrane was achieved. The N-doped TiO$_2$/NaY zeolite membrane composite electrode material for the removal of phenol exhibits a high PEC activity and good recycling stability, removing phenol by 89% after 180 min of reaction times. It provides a promising photoelectrocatalytic material for practical application in the removal of organic compounds.

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