Enhanced photocatalytic degradation of tetracycline hydrochloride by molecular imprinted film modified TiO₂ nanotubes

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To enhance the photocatalytic activity of TiO₂ nanotubes, tetracycline hydrochloride (TC) molecularly imprinted titania modified TiO₂ nanotubes (MIP-TiO₂) was prepared by liquid phase deposition, which improved the molecular recognition ability of the photocatalyst toward template molecules. This MIP-TiO₂ photocatalyst was characterized by ESEM and XRD, which showed that the imprinted titania was deposited on the nanotube uniformly and was of well-crystallized anatase-type. In the adsorption experiments, MIP-TiO₂ exhibited a high adsorption capacity (about 1.6 times higher than that of TiO₂ nanotubes) for TC mainly because of its imprinted sites and high surface area. Under UV irradiation MIP-TiO₂ showed enhanced photocatalytic activity with an apparent first-order rate constant 1.9-fold that of TiO₂ nanotubes.

liquid phase deposition (LPD), photocatalytic, molecularly imprinting, tetracycline hydrochloride

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TiO₂ has been widely studied for environmental protection applications because of its high photocatalytic (PC) activity, chemical stability, nontoxicity and relatively low price. Many organic pollutants such as persistent toxic substances (PTS), dyes, pesticides and herbicides are degraded by TiO₂ catalysts under UV light irradiation [1–4]. Titania nanotubes can improve the photocatalytic properties compared with other forms of titania because of its excellent PC activity [5,6]. In previous studies, TiO₂ nanotubes prepared by electrochemical anodic oxidation exhibited high PC and photoelectrocatalytic activity during organic pollutant degradation [7]. Their well-formed nanotube array architecture offers the ability to influence the absorption and propagation of light through the architecture and the closely packed vertically aligned crystalline tubes also offer excellent electron percolation pathways for vectorial charge transfer between the interfaces [8–10]. However, PC efficiency still does not fulfill the requirements for practical application in the

treatment of low-level harmful pollutants. The efficiency of TiO₂ photocatalysts for application in wastewater treatment needs to increase.

Molecular imprinting is a promising technique for creating specific molecular recognition sites in solid materials by employing target molecule as a template [11,12]. Since Vlatakis et al. [13] reported theophylline and diazepam molecularly imprinted polymers (MIPs) for mimicking antibody combining sites, interest in the molecularly imprinting technique has increased because of its unique properties of predetermination, selectivity and specific affinity for templates [14–16]. Recently, Shen et al. [17,18] developed a new way to enhance the PC efficiency of TiO₂ nanoparticles by imprinting the target molecule onto a photocatalyst's surface. In our previous work, we found that the photoelectrocatalysis of TiO₂ nanotubes could also be improved and selectivity could be realized by modification with organic imprinted polymers on the substrate of the TiO₂ nanotubes [19]. With the development of molecular imprinting technology, inorganic materials have been preferred for applica-

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tions because of their stability. TiO_2 molecularly imprinted thin layers prepared by liquid phase deposition (LPD) or sol-gel methods show good sensitivity and selectivity for the detection or electrocatalysis of template molecules [20–22]. The preparation procedure of these materials is simple and they are more stable than organic materials. Accordingly, surface molecularly imprinted titania coated onto TiO_2 nanotubes is accessible for the construction of novel hybrid photocatalysis, which retains the specific adsorption ability of the imprinted network and the high PC activity of the nanotubes.

In this study, surface molecularly imprinted titania was prepared on TiO_2 nanotubes by the liquid phase deposition method. Tetracycline hydrochloride (TC, Figure 1) was used as a template and it is a type of broad-spectrum antibiotics that is used in pharmaceuticals and personal care products (PPCPs). The abuse of TC and other antibacterials in aquaculture and farming industry negatively affects the environment and antibiotic residues in water and food results in allergies in humans. The photocatalytic activity of the fabricated MIP- TiO_2 was found to be higher than that of TiO_2 nanotubes.

1 Experimental

1.1 Chemicals and materials

Titanium sheets were purchased from Tianjin Gerui Co. Ltd. Tetracycline hydrochloride (TC) was obtained from Johnson Matthey. $(\text{NH}_4)_2\text{TiF}_6$ was from Tianjin Fuchen Chemical Reagent Co. H_3BO_3 was from Shenyang NO.5 Chemical Reagent Factory. All the other chemicals were of analytical grade and used as received. Ultrapure water was used for the preparation of all aqueous solutions.

1.2 Preparation of the TiO_2 nanotubes

The TiO_2 nanotubes were prepared by anodic oxidation according to literature in a two-electrode electrochemical cell [7]. To induce crystallinity, the initially amorphous as-anodized layers were annealed at 500°C for 2 h at a rate of $3^\circ\text{C}/\text{min}$ during the heating processes and then cooled to

room temperature at a rate of $3^\circ\text{C}/\text{min}$.

1.3 Synthesis of imprinted titania modified TiO_2 nanotubes

The liquid phase deposition of imprinted titania onto the TiO_2 nanotubes was carried out by mixing 5 mL 0.1 mol/L $(\text{NH}_4)_2\text{TiF}_6$ with 5 mL 0.3 mol/L H_3BO_3 followed by adding 10 mg of TC. The TiO_2 nanotube substrate was placed vertically into the deposition solution and the temperature was maintained at 20°C in a water-bath for a certain deposition time. Molecularly imprinted titania modified TiO_2 nanotubes (MIP- TiO_2) were thus prepared after the template molecule was removed by thoroughly rinsing with water. Non-imprinted TiO_2 nanotubes (LPD- TiO_2) were used as a control sample and were prepared by the same method but in the absence of TC in the deposition solution and the same procedures were used as for MIP- TiO_2 .

1.4 Characterization and photocatalytic experiments

The morphological characterization of the samples was carried out using an environmental scanning electron microscope (ESEM; Quanta 200 FEG). X-ray diffraction (XRD) analysis was carried out using a diffractometer with $\text{Cu K}\alpha$ radiation (Shimadzu LabX XRD-6000) to determine the crystalline structure of the samples.

The adsorption of TC onto LPD- TiO_2 and MIP- TiO_2 was performed by placing the sample in solutions containing 20 mg/L TC. The whole process was carried out with continuous magnetic stirring for 2 h at 20°C in a water bath. The amount of adsorbed TC was determined by measuring the difference between the total amount of TC and the residual amount in solution.

The photocatalytic oxidation of TC was carried out in a single quartz photochemical reactor. The lamp was placed vertically outside the reactor with an illumination intensity of $1.0 \text{ mW}/\text{cm}^2$. All experiments were carried out with continuous magnetic stirring. The TC aqueous solution with an initial concentration of 20 mg/L was sampled periodically during the reaction and the absorbance was measured at 275 nm as a function of reaction time using a UV-7504 spectrophotometer.

2 Discussion

2.1 Mechanism of the LPD procedure

Liquid phase deposition is a soft-wet chemical and self-assembling process for the preparation of oxide films. The principle of the LPD process is the formation of oxide thin films by the slow hydrolysis of a metal-fluoro complex by fluoride scavengers [6,21,23]. $[\text{TiF}_6]^{2-}$ is hydrolyzed to $[\text{TiF}_{6-n}(\text{OH})_n]^{2-}$ groups and HF molecules. The hydrolysis accelerates after HF is captured by H_3BO_3 . A mechanism

Figure 1 Chemical structure of tetracycline hydrochloride.

for the preparation of the LPD-TiO₂ film can be expressed as the reactions (1) and (2). After the consumption of F in [TiF_{6-n}(OH)_n]²⁻, [Ti(OH)₆]²⁻ is formed in solution. The formation of a -Ti-O-Ti- structure is achieved upon the loss of a water molecule from [Ti(OH)₆]²⁻.

For the preparation of MIP-TiO₂, the template can interact with [TiF_{6-n}(OH)_n]²⁻ groups and form noncovalent bonds with TiO₂ molecules (Figure 2). To remove the loose imprinted material and the adsorbed HBF₄ and NH₄⁺, MIP-TiO₂ was washed with water. MIP-TiO₂ was then be used to rebind the TC molecules.

2.2 Morphology of the imprinted titania modified TiO₂ nanotubes

Figure 3 shows top-view ESEM images of TiO₂ nanotubes that were fabricated using MIP-TiO₂ over different deposition times and upon LPD-TiO₂ liquid phase deposition over 5 h. As shown in Figure 3(a), the diameter range of the TiO₂ nanotubes is about 60 to 90 nm with wall thicknesses of about 20 nm. After liquid phase deposition, the molecular imprinted titania film was uniformly deposited onto the surface of the TiO₂ nanotubes. The film thickness increased with an increase in deposition time and simultaneously the inner radius decreased gradually (Figure 3(b)–(d)). For a deposition time of up to 21 h the whole TiO₂ nanotubes surface was covered by the molecular imprinted titania film, and an obvious crack appeared because of the over-covered molecular imprinted titania film. Therefore, in this study the imprinted titania that was deposited for 5 h was chosen for further investigation to determine the requirements for a high photocatalysis efficiency. Based on a comparison between the morphology of LPD-TiO₂ (Figure 3(f)) and MIP-TiO₂ (Figure 3(c)), which was deposited over 5 h it is reasonable to deduce that the template molecules that were added during the imprinting process had little influence on the morphology of the MIP-TiO₂.

Figure 2 Schematic of a molecularly imprinted titania modified TiO₂ nanotube (MIP-TiO₂) formed by liquid phase deposition.

Figure 3 ESEM image of (a) TiO₂ nanotubes and MIP-TiO₂ deposition over (b) 3 h, (c) 5 h, (d) 7 h and (e) 21 h, and (f) non-imprinted titania modified TiO₂ nanotubes (LPD-TiO₂) deposited over 5 h.

2.3 XRD analysis

Figure 4 shows the XRD patterns obtained for the TiO₂ nanotubes, MIP-TiO₂ and LPD-TiO₂. Well-crystallized anatase-type TiO₂ films without any other phase characteristics were formed on the TiO₂ nanotubes after annealing at 500°C. Both MIP-TiO₂ and LPD-TiO₂ are in anatase form. Neither contains the rutile phase, which is a polymorph that is less

Figure 4 XRD analysis of (a) TiO₂ nanotubes, (b) MIP-TiO₂ and (c) LPD-TiO₂.

photoactive than anatase [24,25]. The strength of the peaks in the MIP-TiO₂ and LPD-TiO₂ samples are a little weaker than that for TiO₂ nanotubes, which is due to the loose density of the deposited samples. The XRD patterns indicate that a modification of the deposited layer on the TiO₂ nanotubes does not affect its crystallization and its photocatalytic ability is retained.

2.4 Adsorption properties of the TiO₂ nanotubes, LPD-TiO₂ and MIP-TiO₂

The adsorption of TC onto LPD-TiO₂ and MIP-TiO₂ was performed by placing the sample in solutions containing 20 mg/L TC. The amount of adsorbed TC was determined by measuring the difference between the total amount of TC and the residual amount in solution. The adsorption ability of the TiO₂ nanotubes for TC was determined under the same conditions. As shown in Table 1 the imprinting effect was confirmed by the fact that MIP-TiO₂ showed a higher adsorption capacity for TC than the TiO₂ nanotubes and LPD-TiO₂. The maximum adsorption capacity under equilibrium conditions was about 1.3 ng for the 20 mg/L TC solution, which was 1.6 times higher than that of the TiO₂ nanotubes and 1.2 times of LPD-TiO₂. The effective imprinted sites of the MIP-TiO₂ that was produced at the wall or the inner surface of the nanotubes contributed to the improved adsorption capacity for the target molecule. It is expected that MIP-TiO₂ will have a high TC photodegradation efficiency.

2.5 Photocatalytic activities

The photocatalytic degradation of TC by TiO₂ nanotubes, LPD-TiO₂ and MIP-TiO₂ was determined under UV light irradiation. The results are shown in Figure 5. The PC removals of TC for LPD-TiO₂ and MIP-TiO₂ are much higher than that for the TiO₂ nanotubes (Figure 5(a)). The kinetics of TC degradation in this study for the direct photolysis (DP) and photocatalytic degradation by the TiO₂ nanotubes, LPD-TiO₂ and MIP-TiO₂ follows pseudo first order kinetics, as shown in Figure 5(b). The apparent first-order rate constant k was evaluated according to $\ln(C_0/C)=kt$, where C represents the TC concentration at time t and C_0 is the initial concentration. The corresponding kinetic constants and regression coefficients of TC by direct photocatalysis and photocatalysis by TiO₂, LPD-TiO₂ and MIP-TiO₂ are also given in Figure 5(b). The presence of LPD-TiO₂ and MIP-

Figure 5 (a) Variation of TC concentrations and (b) variation of $\ln(C_0/C)$ with degradation time in the DP and PC processes involving TiO₂ nanotubes, LPD-TiO₂ and MIP-TiO₂ with a TC concentration of 20 mg/L.

TiO₂ photocatalysts increases the rates of TC removal giving apparent constants of 0.163 and 0.218 h⁻¹, respectively. The rate constant for TC photodegradation by MIP-TiO₂ is about 1.9 times higher than that for the TiO₂ nanotubes.

3 Conclusions

In conclusion, using TC as a template and TiO₂ nanotubes as a support, a molecularly imprinted titania modified TiO₂ photocatalyst was prepared by liquid phase deposition. A MIP layer provided specific molecular recognition sites leading to a high absorption ability towards the target pollutant. Photodegradation experiments confirmed that the photocatalytic activity of the TiO₂ photocatalyst can be enhanced by combining molecularly imprinted titania with TiO₂ nanotubes. This is an alternative way to increase the PC activity of TiO₂ by a molecularly imprinted film fabricated by liquid phase deposition.

Table 1 Amounts of TC adsorbed by the TiO₂ nanotubes, LPD-TiO₂ and MIP-TiO₂ at 20°C over 2 h

C (mg/L)	Adsorption of TC (ng)		
	TiO ₂	LPD-TiO ₂	MIP-TiO ₂
20	0.48	1.1	1.3

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- 1 Sun B, Reddy E P, Smirniotis P G. Visible light Cr(VI) reduction and organic chemical oxidation by TiO₂ photocatalysis. *Environ Sci Technol*, 2005, 39: 6251–6259
- 2 Tachikawa T, Fujitsuka M, Majima T. Mechanistic insight into the TiO₂ photocatalytic reactions: Design of new photocatalysts. *J Phys Chem C*, 2007, 111: 5259–5275
- 3 Liu Z Y, Zhang X T, Nishimoto S, et al. Efficient photocatalytic degradation of gaseous acetaldehyde by highly ordered TiO₂ nanotube arrays. *Environ Sci Technol*, 2008, 42: 8547–8551
- 4 Zheng R Y, Lin L, Xie J L, et al. State of doped phosphorus and its influence on the physicochemical and photocatalytic properties of P-doped titania. *J Phys Chem C*, 2008, 112: 15502–15509
- 5 Mor G K, Varghese O K, Paulose M, et al. A review on highly ordered, vertically oriented TiO₂ nanotube arrays: Fabrication, material properties, and solar energy applications. *Sol Energ Mater Sol Cells*, 2006, 90: 2011–2075
- 6 Zhang J D, Zheng Y Q, Jiang G D, et al. Electrocatalytic evaluation of liquid phase deposited methylene blue/TiO₂ hybrid films. *Electrochem Comm*, 2008, 10: 1038–1040
- 7 Quan X, Yang S G, Ruan X L, et al. Preparation of titania nanotubes and their environmental applications as electrode. *Environ Sci Technol*, 2005, 39: 3770–3775
- 8 Albu S P, Ghicov A, Macak J M, et al. Self-organized, free-standing TiO₂ nanotube membrane for flow-through photocatalytic applications. *Nano Lett*, 2007, 7: 1286–1289
- 9 Frank A J, Kopidakis N, Lagemaat J. Electrons in nanostructured TiO₂ solar cells: Transport, recombination and photovoltaic properties. *Coord Chem Rev*, 2004, 248: 1165–1179
- 10 Mor G K, Shankar K, Paulose M, et al. Use of highly-ordered TiO₂ nanotube arrays in dye-sensitized solar cells. *Nano Lett*, 2006, 6: 215–218
- 11 Xie C G, Zhang Z P, Wang D P, et al. Surface molecular self-assembly strategy for TNT imprinting of polymer nanowire/nanotube arrays. *Anal Chem*, 2006, 78: 8339–8346
- 12 Sibirian-Vazquez M, Spivak D A. Molecular imprinting made easy. *J Am Chem Soc*, 2004, 126: 7827–7833
- 13 Vlatakis G, Andersson L I, Müller R, et al. Drug assay using antibody mimics made by molecular imprinting. *Nature*, 1993, 361: 645–647
- 14 Sellergren B. Imprinted polymers with memory for small molecules, proteins, or crystals. *Angew Chem Int Ed*, 2000, 39: 1031–1037
- 15 Percival C J, Stanley S, Galle M, et al. Molecular-imprinted, polymer-coated quartz crystal microbalances for the detection of terpenes. *Anal Chem*, 2001, 73: 4225–4228
- 16 Haupt K, Mosbach K. Molecularly imprinted polymers and their use in biomimetic sensors. *Chem Rev*, 2000, 100: 2495–2504
- 17 Shen X T, Zhu L H, Liu G X, et al. Enhanced photocatalytic degradation and selective removal of nitrophenols by using surface molecular imprinted titania. *Environ Sci Technol*, 2008, 42: 1687–1692
- 18 Shen X T, Zhu L H, Li J, et al. Synthesis of molecular imprinted polymer coated photocatalysts with high selectivity. *Chem Commun*, 2007, 11: 1163–1165
- 19 Lu N, Chen S, Wang H T, et al. Synthesis of molecular imprinted polymer modified TiO₂ nanotube array electrode and their photoelectrocatalytic activity. *J Solid State Chem*, 2008, 181: 2852–2858
- 20 Feng L, Liu Y J, Hu J M. Molecularly imprinted TiO₂ thin film by liquid phase deposition for the determination of L-glutamic acid. *Langmuir*, 2004, 20: 1786–1790
- 21 Li C Y, Wang C F, Wang C H, et al. Development of a parathion sensor based on molecularly imprinted nano-TiO₂ self-assembled film electrode. *Sens Actuator B-Chem*, 2006, 117: 166–171
- 22 Lahav M, Kharitonov A B, Katz O, et al. Tailored chemosensors for chloroaromatic acids using molecular imprinted TiO₂ thin films on ion-sensitive field-effect transistors. *Anal Chem*, 2001, 73: 720–723
- 23 Niesen T P, De-Guire M R. Review: Deposition of ceramic thin films at low temperatures from aqueous solutions. *Solid State Ion*, 2002, 151: 61–68
- 24 Hoffmann M R, Martin S T, Choi W, et al. Environmental applications of semiconductor photocatalysis. *Chem Rev*, 1995, 95: 69–96
- 25 Zhao H M, Chen Y, Quan X, et al. Preparation of Zn-doped TiO₂ nanotubes electrode and its application in pentachlorophenol photoelectrocatalytic degradation. *Chin Sci Bull*, 2007, 52: 1456–1461

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