

Synthesis of molecular imprinted polymer coated photocatalysts with high selectivity†

Xiantao Shen, Lihua Zhu,* Jing Li and Heqing Tang*

Received (in Cambridge, UK) 20th October 2006, Accepted 2nd February 2007

First published as an Advance Article on the web 15th February 2007

DOI: 10.1039/b615303h

Molecular imprinted polymer coated photocatalysts were prepared *via* polymerization of a proper functional monomer in the presence of TiO₂ nanoparticles and target molecules, which was found to promote the selectivity of TiO₂ photocatalysis.

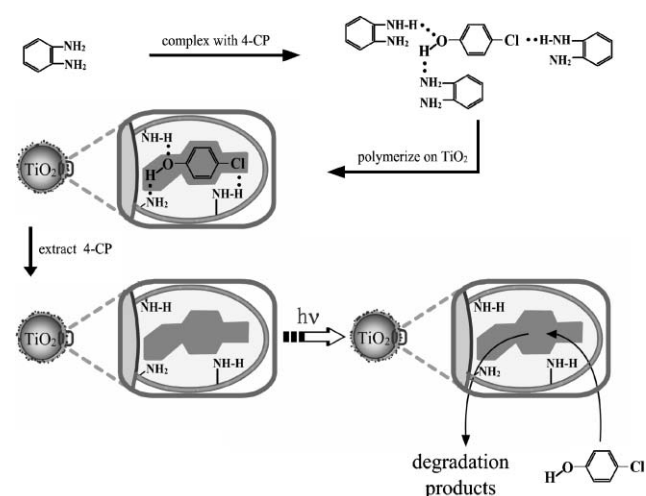
The photocatalytic degradation of pollutants using TiO₂ has been well studied for environmental protection.¹ However, it is as yet difficult to realize selective removal of harmful low-level pollutants in the presence of high-level less harmful pollutants by using this technique, because TiO₂ photocatalyst has very poor selectivity and cannot differentiate between these pollutants. Several approaches towards surface modification have been tried to increase the selectivity of TiO₂, but these methods have been found to be not very effective,² or to give poor stability.³ Composites of TiO₂ and a mesoporous absorbent have been proposed.⁴ One of the best is prepared by constructing organic molecular recognition sites on inert domains.⁵ These composites usually require complicated preparation processes. Molecular imprinted polymers (MIPs) have been extensively studied due to their molecular recognition ability, specific adsorption, and wide applications in separation and sensors.⁶ We expect that their specific adsorption ability favors increasing selectivity of the photocatalyst. Therefore, we will develop a simple way to prepare novel hybrid photocatalysts by *in situ* coating a thin MIP layer of a target pollutant on TiO₂ nanoparticles.

Selection of monomer is critical in the preparation of MIPs. In our new approach, *o*-phenylenediamine (OPDA) is taken as the functional monomer. There are two –NH₂ groups in its molecule. Interaction between the –NH₂ groups in OPDA and the functional groups (such as –OH, –Cl, –NO₂) of the target pollutants (*i.e.*, the templates) may lead to a precursor, which assures the imprinting of the target molecules during polymerization.

As indicated in Scheme 1, our approach consists of three steps. (1) A precursor is prepared *via* a reaction of the monomer OPDA in excess and the target compound (4-chlorophenol (4CP) or 2-chlorophenol (2CP)) as template. The existence of the precursor is assumed only to represent the strong interactions between the monomer and template molecules. (2) A MIP layer is coated on TiO₂ particles *via* an *in-situ* polymerization in the presence of TiO₂ nanoparticles (Degussa P25). (3) MIP-coated photocatalyst is

prepared after chemically removing the template molecules from the polymer layer. In the first step, excess of OPDA and a given amount of the target pollutant is reacted in aqueous solution. Thus, the added monomer exists in two states, *i.e.*, as the above-mentioned precursor or as free molecules. Because the monomer can be adsorbed on the surface of the TiO₂ particles, the polymer is able to coat the surface of TiO₂ *via in-situ* polymerization, leading to the incorporation of the templates into the polymer. During polymerization, the OPDA monomers in both the free state and the precursor state may be coupled in the same way as aniline, producing a polymer with a polyaniline-like structure, which is photochemically stable and favorable to the photocatalytic efficiency of TiO₂-polyaniline under sunlight.⁷ The second –NH₂ group in “free” OPDA molecules may function as cross-linker, enhancing the shape selectivity of the MIP layer.

In comparison with conventional methods of MIP preparation, there are two additional merits in our method. One is that the polymerization is initiated photocatalytically by UV light illumination on TiO₂ nanoparticles without using any other chemical initiator or cross-linker. The other is that the template can be removed from the polymer layer by UV light illumination for an appropriate period of time, leading to the final products of MIP-coated TiO₂. The application of the photocatalyst was little affected by the treatment types, but the operation of the photocatalytic treatment is simpler than the Na₂CO₃ treatment. The combination of the two merits allowed us to easily control the



Scheme 1 The route for preparation of MIP-coated photocatalyst and its use in photocatalytic degradation. Here, 4-chlorophenol is used as a representative of the target pollutants.

Department of Chemistry, Huazhong University of Science and Technology, Wuhan, 430074, P. R. China.

E-mail: lh Zhu63@yahoo.com.cn (Zhu); hqtang62@yahoo.com.cn (Tang); Fax: (+86) 27 87543632; Tel: (+86) 27 87543632

† Electronic supplementary information (ESI) available: TEM image, UV-visible absorption spectra and FTIR spectra of photocatalysts, and accumulation of intermediates. See DOI: 10.1039/b615303h

thickness of the MIP layer, assuring both the molecular recognition ability and the photocatalytic efficiency.

In this work, 4CP or 2CP was used as the target pollutant, and the resultant MIP-coated photocatalysts are referred to as 4CP-P25 and 2CP-P25, respectively.† If neither 4CP nor 2CP was used in the preparation, the obtained catalyst is named as NIP-P25.

The TEM image indicated that MIP-P25 was composed of TiO₂ particles partially coated with a layer of MIP having a thickness of ~5 nm. In the UV–visible absorption spectra of the photocatalysts, the MIP layer yielded absorption in the visible region with a maximum absorption at ~440 nm. FTIR spectra of MIP-coated TiO₂ were measured in comparison with that of neat TiO₂ and the polymer of OPDA. The main characteristic absorption bands of the polymer of OPDA can be found in the spectrum of MIP-coated TiO₂. The stretching bands of –NH₂ appeared at wavenumbers of 3448 cm⁻¹ and 3310 cm⁻¹, and the strong absorption band at 1525 cm⁻¹ was ascribed to the bending mode of the –NH– bond. The stretching vibration of the =C–H bond on the benzene ring occurred at 3187 cm⁻¹, and the absorption bands at 1359 cm⁻¹ and 1233 cm⁻¹ are attributed to the =C–N bond on the benzene ring. The FTIR measurements indicated that the MIP layer had the structure of the polymer of OPDA.

Fig. 1 shows the adsorption isotherms for 2CP and 4CP over the photocatalysts in aqueous suspensions. It is easily seen from Fig. 1 that due to the MIP layer, 2CP-P25 (or 4CP-P25) gives stronger adsorption toward the target 2CP (or 4CP), relative to both P25 and NIP-P25. This is in good agreement with the intrinsic molecular recognition ability and selective adsorption ability of MIP. Because of the important role of the organic pollutant's adsorption on the photocatalyst's surface, we could expect that the MIP-coated photocatalysts have high selectivity toward the photodegradation of the target pollutants.

The photodegradation of 2CP, 4CP and phenol over the photocatalysts in the present work was found to follow a pseudo first-order reaction in kinetics.§ The measured apparent rate constants (*k*) and their ratios are used to evaluate the influence of the MIPs on the degradation rate of pollutants and the selectivity of various photocatalysts. In the degradation of single target or non-target pollutant(s) with *c*₀ = 20 mg L⁻¹, we found that relative to P25 as a control, 4CP-P25 increased the *k* value for the target 4CP from 0.02449 min⁻¹ to 0.03494 min⁻¹ by a factor of 143%, and decreased that for the non-target 2CP from 0.02032 min⁻¹ to 0.00810 min⁻¹ by a factor of 39.8%. When 2CP was treated as the target, the photocatalyst 2CP-P25 increased the *k* value for the

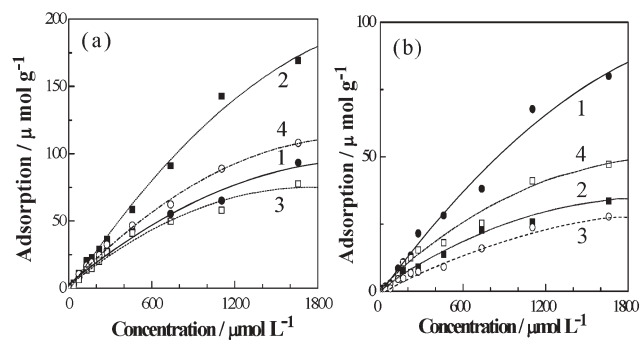


Fig. 1 Adsorption of 2CP (a) and 4CP (b) on photocatalysts 4CP-P25 (1), 2CP-P25 (2), NIP-P25 (3) and neat P25 (4).

Table 1 Values of *k* and *k*_{target}/*k*_{non-target} obtained from the photodegradation of the mixture of 2CP (2 mg L⁻¹), 4CP (2 mg L⁻¹) and phenol (50 mg L⁻¹) over different photocatalysts

	2CP-P25	4CP-P25	P25
<i>k</i> _{2CP} (min ⁻¹)	0.09731	0.06357	0.01499
<i>k</i> _{4CP} (min ⁻¹)	0.05369	0.12464	0.02247
<i>k</i> _{phenol} (min ⁻¹)	0.01167	0.00606	0.00259
<i>k</i> _{2CP} / <i>k</i> _{4CP}	1.81	—	0.667
<i>k</i> _{2CP} / <i>k</i> _{phenol}	8.34	—	5.78
<i>k</i> _{4CP} / <i>k</i> _{2CP}	—	1.96	1.50
<i>k</i> _{4CP} / <i>k</i> _{phenol}	—	20.6	8.68

target 2CP from 0.02032 min⁻¹ (over P25) to 0.02579 min⁻¹ by a factor of 122%, and decreased that for the non-target 4CP from 0.02449 min⁻¹ (over P25) to 0.01895 min⁻¹ by a factor of 77.3%. Similarly, the promoted photodegradation of the targets over MIP-coated P25 was also observed in the mixtures of 4CP and 2CP (*c*₀ = 20 mg L⁻¹ for both 4CP and 2CP). Therefore, the MIP-coated P25 markedly enhanced the photodegradation of the target and inhibited the degradation of the non-target. Even though 4CP and 2CP have very similar chemical structures and molecular sizes, the MIP layer can differentiate them.

Table 1 compares the rate constants for the photodegradation of 2CP, 4CP and phenol over different photocatalysts in the degradation of their mixture. Generally, the degradation rate of the target compound is much faster than that of the non-target ones. The ratio of *k*_{4CP}/*k*_{phenol} is 20.6 over 4CP-P25, much greater than 8.68 over P25. Similarly, the ratio of *k*_{2CP}/*k*_{phenol} is 8.34 over 2CP-P25, greater than 5.78 over P25. This confirms that the MIP coating significantly increases the catalyst's ability to differentiate the mixed pollutants, and the selectivity of MIP-coated catalysts is increased greatly as the differences between the pollutants are increased. Such high selectivity allows us to selectively remove low-level target compounds (2 mg L⁻¹) using MIP-coated TiO₂ in the presence of high-level non-target compound (50 mg L⁻¹ phenol). This was further confirmed in the photodegradation of the mixture of 2 mg L⁻¹ 4CP and 500 mg L⁻¹ phenol over 4CP-P25. When such a low level of 4CP was degraded in the presence of 500 mg L⁻¹ phenol, the target 4CP was rapidly degraded with a half-time *t*_{1/2} of ~8 min, while the relative concentration (*c*/*c*₀) of phenol apparently remained almost unchanged (Fig. 2).

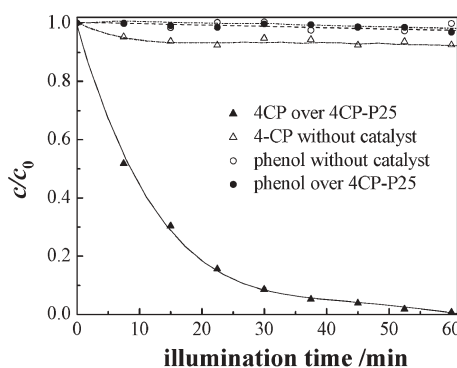


Fig. 2 Degradation kinetics for 4CP (triangles) and phenol (circles) in their mixtures (*c*₀ = 2 mg L⁻¹ for 4CP and 500 mg L⁻¹ for phenol) under UV light illumination in the absence (open) and presence (solid) of 4CP-P25 as photocatalyst.

Because direct photolysis of chlorophenols has been reported,⁸ the direct photolysis may make a contribution to the measured values of k . When only 4CP (or 2CP) was present in solution, we indeed observed the direct photocatalysis of 4CP (or 2CP). This resulted in a high accumulation of aromatic intermediates (such as 2-hydroxy-1,4-benzoquinone, 1,4-hydroquinone and 1,4-benzoquinone), which were very difficult to degrade further in the absence of any photocatalyst. In contrast, the photocatalytic degradation of 4CP is faster, leading to very small accumulations of the aromatic intermediates, which can be degraded completely. In consideration of possible contributions of direct photolysis to the measured k values, all of our conclusions were based on a comparison between the experimental results obtained over MIP-coated P25 and over the neat P25 as a control. Furthermore, as shown in Fig. 2, we found that the direct photolysis of 4CP is inhibited almost completely when a high level of phenol coexists in solution, because the UV-light-absorption ability of 4CP is relatively decreased when a low level of 4CP is mixed with other high levels of UV-light-absorbing substances, such as phenol and MIP-coated P25. Therefore, we can safely conclude that the MIP-coated catalysts can increase the selectivity of TiO₂ photocatalysis toward the photocatalytic degradation of the target chlorophenols.

We also noted from Table 1 that the phenol removal rate was increased in the cases of both MIP-modified TiO₂ catalysts (2CP-P25 and 4CP-P25). This is possibly related to the increment in the phenol adsorption, which is possibly due to (1) similar space structure and molecule size of phenol to those of the template molecules, and (2) similar reaction sites of phenol molecules to the bulky MIP (the benzene ring and the existence of an -OH group).

We observed that the selectivity of the MIP-coated TiO₂ gradually worsened during a long period of UV-light illumination if there was only a low level of the target pollutant in solution. From the next experiments, however, we find that these new catalysts have a good lifetime, if there are other coexisting organic pollutants in solution. We photo-degraded the target pollutant 4CP of 2 mg L⁻¹ over 4CP-P25 in the presence of 50 mg L⁻¹ phenol for successive cycles. In each cycle, about 80% of added 4CP was degraded, then a part of 4CP was freshly added and the next degradation cycle started. The rate constant k_{4CP} was measured as 0.08975, 0.08716, 0.08848, 0.08198, 0.08104 and 0.08154 min⁻¹ for the first six cycles, being ~3 times that over P25 (0.02757 min⁻¹). In another experiment, the photodegradation of 2CP (20 mg L⁻¹) was performed for 15 min over 2CP-P25, then 2000 mg L⁻¹ of 4-nitrophenol was added and the photodegradation was continued for 12 h, followed by a filtration with a 0.22 μm filter. After being vacuum dried, the collected photocatalyst was again suspended into a fresh solution of 20 mg L⁻¹ 2CP, and the photodegradation of 2CP was repeated for several cycles as described above. The k_{2CP} values in the first four cycles were almost the same as before the 12-h photodegradation of 4-nitrophenol. These suggest that the MIP-coated TiO₂ is quite stable during the operation.

In conclusion, we first developed a very simple approach to prepare MIP-coated photocatalysts *via* an *in-situ* polymerization of OPDA in the presence of target molecules and TiO₂ nanoparticles. Using a photocatalytic treatment with the novel hybrid photocatalysts, we can selectively remove low-level target pollutants in the presence of high-level less toxic pollutants.

The authors thank the National Science Foundation of China (grants No. 20677019 and 30571536) for financial support. The Analytical and Testing Center of Huazhong University of Science and Technology is also thanked for its help in the characterization of photocatalysts.

Notes and references

‡ Details for the preparation of MIP-coated photocatalysts are as follows. In a typical preparation, 0.24 g OPDA and 0.1 g 2CP were dissolved into 40 mL distilled water, and the solution was stirred for 20 min, followed by addition of 1 mL of 6 M HCl and 0.4 g P25 and then a 3-min ultrasonication. Polymerization was conducted for 24 h after being initiated with a 30-min irradiation with UV light using a 250-W Hg lamp as light source. Then, 0.13 g L⁻¹ Na₂CO₃ was added into the suspension, followed by stirring for 20 min and filtration. The obtained solids were washed five times by using Na₂CO₃ solution and distilled water, respectively. Alternatively, the polymer-coated particles resulting from the polymerization could be photocatalytically treated *in situ* by UV-light illumination for 15–20 min, followed by filtration. After the Na₂CO₃ treatment or the photocatalytic treatment, the solids were thoroughly vacuum dried and powdered, leading to 2CP-P25. Similarly, 4CP-P25 was prepared by using 4CP instead of 2CP, and NIP-P25 was obtained when neither 4CP nor 2CP was used in the preparation.

§ To evaluate the photocatalytic selectivity of photocatalysts, the degradation of organic(s) was carried out in a jacketed quartz reactor filled with 250 mL of the test solution in the presence of the catalyst (25 mg) by using a 9-W UV lamp (Philips, λ_{max} = 253.7 nm) as light source. Prior to illumination, the suspension was stirred for 20 min to favor the pollutant's adsorption onto the catalyst surface, followed by determination of the concentration of the pollutant(s) as the initial concentration c_0 . The remaining concentration of pollutant(s) in the suspension at given intervals of irradiation was measured on a JASCO PU-2089 HPLC. The adsorption of 4CP and/or 2CP was monitored on the MIP-coated P25 nanoparticles, and the amount of the adsorption was found to cause no decrease of the chlorophenol to be degraded.

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