Inorganic-Framework Molecularly Imprinted CdS/TiO₂ for Selectively Photocatalytic Degradation of Di (2-ethylhexyl) phthalate

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Summary: In order to improve the photocatalytic efficiency and selectivity of di (2-ethylhexyl) phthalate (DEHP) under solar-driven, the inorganic-framework molecularly imprinted CdS/TiO₂, named as MIP-CdS/TiO₂, was prepared by using DEHP as template molecule and tetrabutyl titanate as titanium source and functional monomer. The as-prepared MIP-CdS/TiO₂ was characterized by scanning electron microscopy (SEM), X-ray energy spectrum (EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), UV-Vis Spectroscopy (UV-vis), X-ray photoelectron spectroscopy (XPS) and photoluminescence spectrum (PL). And the specific recognition and photocatalytic selectivity of MIP-CdS/TiO₂ to DEHP were investigated. The results show that inorganic-framework molecular imprinting on the surface of CdS/TiO₂ can result in existence of specific recognition sites of DEHP, extend and intensify the absorption visible light of CdS/TiO₂, inhibit the recombination of the photo-induced electron-holes pairs. MIP-CdS/TiO₂ has a specific recognition to DEHP. The binding selectivity coefficients of DEHP relative to its analogues DBP and DMP are 2.78 and 2.60, respectively. Compared with CdS/TiO₂, MIP-CdS/TiO₂ exhibits higher photocatalytic activity and selectivity for DEHP. Under simulated solar light irradiation, the degradation efficiency of DEHP photocatalyzed by MIP-CdS/TiO₂ is 75.5%, which is 1.63 times as high as that of DEHP photocatalyzed by CdS/TiO₂.

Keywords: Photocatalyst; Molecular imprinting; Di (2-ethyl) phthalate; Titanium dioxide; Cadmium sulfide.

Introduction

Di (2-ethylhexyl) phthalate (DEHP) is the widely used phthalates [1, 2]. It is usually used as plasticizers during production of polyethylene plastic, rubber, food packaging materials, medical blood bags and hoses, children's toys, cleaning agents and daily care products, *etc.* [3, 4]. Due to non-covalent combination between DEHP and plastic monomer molecule, DEHP is not strongly bonded to the plastic. So it is easy for DEHP to migrate from plastic matrix to the environment [5]. At present, DEHP has been detected in various environments around the world, such as rivers, lakes, soil, seabed sediments and so on [7-9].

DEHP is reproductively toxicity [10]. Low dosage of DEHP can induce anti-androgen effects, and high dosage of DEHP will result in testicular histopathological changes [11]. It has been found that DEHP and its metabolite mono-2-ethylhexyl phthalate (MEHP) are highly relevant with female abortion [12]. At present, DEHP has been listed as an environmental priority pollutant in many countries including China and Philippines [13]. Therefore, it is of great significance to control DEHP pollution.

Photocatalysis has been considered as a desirable technology to remove organic pollutants because of its advantages, such as high efficiency, thorough degradation of pollutants and so on [14-16]. Titanium dioxide (TiO₂) and cadmium sulfide (CdS) are two kinds of widely studied semiconductor photocatalyst. TiO₂ is characteristic of low toxicity, high catalytic activity, no secondary pollution and high stability [17]. However, TiO₂ has a relatively wide band gap (3.2 eV). Only the light with a wavelength of less than 387 nm can excite its valence band electron-guided band transition. So, small portion (3-5%) of solar spectrum can be utilized by TiO₂, which limits its application in practice [18, 19]. CdS has narrow band gap (2.4ev) and intense absorption of visible light [20]. However, photochemical corrosion resulting from oxidization of sulfur in CdS by photo-induced hole can bring about reduced activity and short service life of CdS. Therefore, CdS/TiO₂ composite has been prepared by the combination of TiO₂ and CdS, which can not only extend the spectral response of TiO₂ to increasing the quantum yield, but also facilitate separation of photoelectron-hole to weaken the photochemical corrosion of CdS and enhance photocatalytic activity

[21-23]. Nevertheless, CdS/TiO₂ has no selectivity to target pollutant. When CdS/TiO₂ is employed to treat wastewater containing organic pollutants, the coexistent nutrient in wastewater can perhaps quickly adsorbed on the surface of catalyst and preferentially be degraded. On the contrary, organic pollutants that need really to be removed cannot be adequately degraded [24]. It is essential to improve the selectivity of CdS/TiO₂ in order that the degradation of organic pollutants can be performed selectively.

Molecularly imprinted polymers (MIP) have cavities and adsorption sites that match with the template molecules and can achieve specific recognition to the template molecules. They are widely used in biosensors, biological receptors, separation techniques [25, 26]. In recent years, organic molecularly imprinted polymers were coated on the surface of the catalyst to enhance the photocatalytic selectivity to the target contaminants [27-30]. However, the molecularly imprinted polymers coating on the surface of the catalyst can hinder the transmission of light and may be degraded during photocatalysis, resulting in short service life of the catalyst. Furthermore, the preparation of photocatalysts coated by molecularly imprinted polymers is cumbersome [31-33]. To overcome such drawbacks, some researchers have been focused on inorganic-framework molecularly imprinted photocatalysts without a layer of organic molecularly imprinted polymers. Wu et al. have synthesized an inorganic-framework molecularly imprinted TiO₂ by using 4-nitrophenol as a template molecule. Xu has synthesized inorganic imprinted photocatalyst Fe₃O₄ @ SiO₂ @ imprinted TiO₂. But, these inorganic molecularly imprinted TiO2 only respond to UV light. Therefore, it is urgent to synthesize inorganicframework molecularly imprinted photocatalysts that can be driven by visible light.

In this work, inorganic-framework molecularly imprinted CdS /TiO2 was synthesized by using tetrabutyl titanate as functional monomer and titanium source. During the preparation of MIP-CdS /TiO₂, imprinted cavities formed after the template molecules were removed by calcinations. The asprepared molecularly imprinted CdS /TiO₂ displays high adsorption amount and selectively photocatalytic activity under solar light irradiation.

Experimental

Materials

Dimethyl phthalate (DMP), di(2-ethylhexyl)

phthalate (DEHP), dibutyl phthalate (DBP), methanol, anhydrous ethanol, glacial acetic acid and tetrabutyl titanate were purchased from Sinopharm Chemical Reagent Co., Ltd.(Shanghai, China). Cadmium chloride was obtained from Shanghai Jinshan Pavilion New Chemical Reagent Co., Ltd. (Shanghai, China). Sodium thiosulfate was supplied by Shanghai Pilot Chemical Corporation (Shanghai, China). Of the above chemicals, methanol was of HPLC chromatographic grade and the other chemicals were of analytical reagent grade. All Reagents were used as received without purification.

Preparation of MIP-CdS / TiO₂

Cadmium chloride (0.3666 g) and sodium thiosulfate (1.9854 g) were dissolved in 20 mL deionized water and stirred for 30 min. The mixtures were ultrasonically dispersed for 10 min and were then heated in the microwave reactor (MAS-II, Shanghai Xinyi Microwave Chemical Technology Co., Ltd.) with the operating power of 500 W and working temperature of 100 $^{\circ}$ C for 40min under vigorous stirring. After final products were cooled into room temperature, they were collected by centrifugation, washed with the deionized water for several times, dried at 60 $^{\circ}$ C for 6 h. Cadmium sulfide (CdS) was obtained.

Tetrabutyl titanate (10 mL), acetic acid (2 mL) and DEHP (1.2 mL) were respectively dissolved in 13 mL of anhydrous ethanol, and then the asprepared cadmium sulfide (0.041 g) was dispersed in above solution to obtain the solution A. Under stirring, the mixed solution containing 4 mL of water, 6 mL of ethanol and 6 mL of acetic acid was added dropwise in the solution A and then kept on stirring for 2 h. CdS/TiO₂ composite gel was obtained. The gel was aged at room temperature for 12 h. The aged gel was dried in at 100 °C for 12 h. The resulting sample was ground and calcined at 350 °C for 2 h. The MIP-CdS/TiO₂ was obtained. CdS/TiO₂ was prepared in the same way except that no template was added in preparation.

Characterization

The morphological characteristics of MIP-CdS/TiO₂ were observed on field emission scanning electron microscope (SEM) (Hitachi, Japan). The Xray diffraction (XRD) patterns were obtained on D8 Advance X-ray diffraction spectrometer (Bruker AXS Company, Germany). The infrared spectra were obtained from FT-IR650 Fourier transform infrared spectrometer (Shimadzu, Japan). UV-vis diffused reflectance spectra of the samples were collected on a UV-vis spectrophotometer (UV2550, Shimadzu, Japan). BaSO₄ was used as a reflectance standard. Xray photoelectron spectra (XPS) were obtained on AXIS UTLTRADLD X-ray photoelectron spectrometer (Shimadzu, Japan) to identify elemental state of the samples. The Photoluminescence spectra (PL) were measured by F4500 fluorescence spectrometer (HITACHI, Japan).

Adsorption test

A given amount of photocatalyst was added into 30 mL of DEHP/methanol solution in a conical flask with initial concentration of 5 mg/L and stirred at 25 $^{\circ}$ C in dark. After the adsorption was finished, the concentration of DEHP in flask was determined by HPLC, and a parallel was measured three times and averaged. The adsorption amount was calculated according to eq. (1).

$$Q = \frac{V(C_0 - C)}{M}$$
(1)

Where, Q (mg/g) is the adsorption amount at time t, C_0 (mg/L) is the initial concentration of DEHP. C_e (mg/L) is the concentration of DEHP at equilibrium, V (mL) is the volume of DEHP/methanol, M (g) is the weight of the photocatalyst.

Photocatalytic degradation of RhB

The activity of the samples for photocatalytic degradation of RhB was evaluated using 300 W xenon lamp as simulative solar light irradiation. MIP-CdS/TiO₂ (18 mg) was dispersed in 30 mL of DEHP/methanol solution with the initial concentration of 5 mg/L and pH of 7. The mixed suspensions were stirred in the dark for 30 min to achieve adsorption-desorption equilibrium, and then exposed to irradiation of simulative solar light produced by a 300 W xenon lamp which was located with a distance of 8 cm at one side of the DEHP solution. At a certain time interval, 2 mL of suspensions were extracted and centrifuged. The concentration of DEHP in supernatant was determined by HPLC. The degradation efficiency was obtained by equation (2).

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$
 (2)

Where, η (%) is degradation efficiency of DEHP, C_0 (mg/L) is the initial concentration of DEHP. C_t (mg/L) is the concentration of DEHP at time t.

Determination of DEHP, DBP and DMP

DEHP, DBP and DMP were determined by HLPC (Shimadzu, Japan) with Inertsil ODS-SP C_{18} column and UV detector. The mobile phase was methanol/water (95/5, V/V), the flow rate was 0.5 mL/min. The column temperature was 35 °C and the wavelength for determination was 254 nm.

Results and Discussion

Characterization of the catalyst

FI-IR spectra

To investigate whether template DEHP had been imprinted in the prepared catalyst, FT-IR spectra of the prepared samples were collected and shown in Fig.1. As seen in the spectrum of TiO_2 (Fig.1a), the strong absorption band at 500-750 cm⁻¹ corresponds to the vibrations of Ti-O in Titania molecule. The absorption peaks at 1537 cm⁻¹ and 3407 cm⁻¹ respectively belong to the bending vibration and the stretching vibration of the hydroxyl which originates from water molecular adsorbed on the surface of TiO₂ sample [34-36]. Compared to TiO₂, a few of new absorption peaks are observed at 1414 cm⁻¹, 2938 cm⁻¹ ¹, 1726 Cm⁻¹ and 1277 cm⁻¹ in the spectrum of uncalcined MIP-CdS/TiO₂ (Fig.1c). The absorption bands at 1414 cm⁻¹ and 2938 cm⁻¹ are attributed to the bending and stretching vibration of methylene in DEHP, respectively. The absorption peaks at 1726 cm⁻¹ and 1277 cm⁻¹ are assigned to stretching vibration of ester carbonyl in DEHP. It is concluded that DEHP molecule has been successfully imprinted on the uncalcined catalyst. It can be seen in the spectrum of MIP-CdS/TiO₂ (Fig. 1b) that the peaks at 1414 cm⁻¹, 2938 cm⁻¹, 1726 cm⁻¹ and 1277 cm⁻¹ have all disappeared, indicating that the template molecule DEHP has been completely removed after calcination, but leaving behind the binding sites that can specifically recognize DEHP. The absorption peak at 1043 cm⁻¹ in the spectra of MIP-CdS/TiO₂ is due to Cd-S bond [37], indicating the formation of composite of CdS and TiO₂.



Fig. 1: FT-IR spectra of MIP-CdS/TiO₂ (a), TiO₂ (b) and uncalcined MIP-CdS/TiO₂ (c).

SEM and EDS

Fig. 2 shows the SEM images and EDS of MIP-CdS/TiO₂. As shown in Fig. 2, MIP-CdS/TiO₂ exists in slightly agglomerated and rough nanoparticles with diameters ranging from 50 to 100nm. EDS result reveals the presence of Ti, O, S and Cd, indicating the formation of composite CdS/TiO₂. Furthermore, no existence of C and H indicates the thorough removal of template DEHP from the as-prepared MIP-CdS/TiO₂, which is in agreement with FT-IR results.

XRD analysis

The XRD patterns of MIP-CdS/TiO₂, CdS/TiO₂ and TiO₂ are given in Fig. 3. As shown in Fig.3, the XRD pattern of MIP-CdS/TiO₂ is nearly in accordance with that of TiO₂ and CdS/TiO₂. The diffraction peaks at 25.31°, 37.90°, 48.02°, 54.64° and 62.83° correspond to the (101), (101), (200), (105) and (204) plane of anatase TiO₂ (JCPDS 21-1272), illustrating that MIP-CdS/TiO₂ remains well anatase structure. Meanwhile, the diffraction peaks of the asprepared MIP-CdS/TiO₂ are more intensive and sharp than that of TiO₂ and CdS/TiO₂, It is suggested that MIP-CdS/TiO₂ is well-crystallized. Nevertheless, no presence of typical diffraction peaks of CdS are observed in the XRD patterns of MIP-CdS/TiO₂, CdS/TiO₂. It might be due to low amount of CdS.





Fig. 2: SEM images (a) and EDS spectrum (b) of MIP-CdS/TiO₂



Fig. 3: XRD patterns of MIP-CdS/TiO₂ (a), and CdS/TiO₂ (b) and TiO₂ (c)

XPS analysis

To investigate the elemental composition and chemical states of the as-prepared MIP-CdS/TiO₂, XPS measurement was carried out and the results are depicted in Fig. 4. The peaks of Ti, O, Cd, S and C are found in the overall spectra (Fig.4a). In Fig.4b, peaks at binding energy of 458.9 eV and 464.7 eV are due to Ti 2p3/2 and Ti 2p1/2, respectively, suggesting that the existence of Ti⁴⁺ [38]. The peak appearing at 530.2 ev (Fig.4c) is due to the lattice oxygen in TiO2. In Fig.4d, the band locating at the binding energy of 405.1 ev and 411.9 ev are attributed to Cd 3d5/2 and Cd 3d3/2, respectively, indicating the presence of Cd⁺². Moreover, the peak at 161.9 ev in Fig.4e corresponds to S 2p, illustrating the existence of CdS in the asprepared MIP-CdS/TiO2. The peak of C 1s at 284.56 ev is attributed to the adventitious hydrocarbon from XPS instrument itself [39].





Fig. 4: XPS spectra of MIP-CdS/TiO₂.

UV-vis diffuse reflectance spectra

Fig. 5 shows the UV-vis spectra of TiO₂, CdS/TiO₂ and MIP-CdS/TiO₂. As given in Fig. 5, TiO₂ only absorbs UV light with the wavelength less than 400nm. Nevertheless, CdS/TiO₂ and MIP-CdS/TiO₂ perform absorption in a wide wavelength range from UV to visible light with the band-edge of 550 nm and 800 nm, respectively. This is because CdS with narrow band-gap can be excited by visible light irradiation, and the migration of photo-induced electron from conduction band of CdS to conduction band of TiO₂ resulted in enhanced visible light adsorption of CdS/TiO₂ and MIP-CdS/TiO₂ [40]. Furthermore, MIP-CdS/TiO₂ exhibits more intensive and broad absorption of visible light than CdS/TiO₂, indicating that molecular imprinting is favor of improvement of light absorption of CdS/TiO2. The enhanced capacity of MIP-CdS/TiO₂ to absorb visible light suggests their highly photocatalytic activity under solar-driven application.



Fig. 5: UV-Vis spectra of MIP-CdS/TiO₂, CdS/TiO₂ and TiO₂

Photoluminescence (PL) spectra

PL emission primarily results from recombination of photo-induced carries. As a result, PL spectroscopy is commonly used to investigate the migration and recombination of photo-generated electron and hole of the semiconductor. The low fluorescence intensity means the low recombination rate of the photo-induced electron and hole [41]. The PL spectra of MIP-CdS/TiO₂ and CdS/TiO₂ were recorded and depicted in Fig. 6. It is observed in Fig. 6 that MIP-CdS/TiO₂ exhibits similar PL spectrum with CdS/TiO₂, and no any new emission bands is observed in PL spectrum of MIP-CdS/TiO₂. However, emission intensity of MIP-CdS/TiO₂ is distinctly weakened compared with that of CdS/TiO₂. It is suggested that molecular imprinting on the surface of CdS/TiO₂ can inhibit the recombination of photo-induced electron-hole pairs and would be propitious to enhancement of photocatalytic activity.



Fig. 6: photoluminescence spectra of CdS/TiO_2 and MIP-CdS/TiO₂.

Binding capacity of MIP-CdS/TiO₂

The binding capacity of photocatalysts is an important factor to influence photocatalytic activity. In order to investigate the binding properties of MIP-CdS/TiO₂ with DEHP, the adsorption rate and selective recognition of MIP-CdS/TiO₂ to DEHP were determined.

Adsorption rate curves

Fig. 7 shows the adsorption rate curves of DEHP by the as-prepared catalysts. As seen from Fig. 7, the adsorption amount of DEHP on the three photocatalysts increases with time and reach equilibrium at 30min. While, since from 10 min, the adsorption amount of MIP-CdS/TiO₂ for DEHP is evidently higher than that of CdS/TiO₂ and TiO₂, indicating that MIP-CdS/TiO₂ has more fast binding rate than the other two photocatalysts. Meanwhile, compared with CdS/TiO₂ and TiO₂, MIP-CdS/TiO₂ had obviously higher equilibrium adsorption amount. The excellent binding properties of MIP-CdS/TiO₂ are due to the existence of specific recognition site for DEHP, which would be in favor of selective degradation of DEHP.



Fig. 7: Curves of adsorption rate for MIP-CdS/TiO₂, CdS/TiO₂ and TiO₂

Selective recognition of MIP-CdS/TiO₂ to DEHP

DMP, DBP and DEHP were selected as analogues to investigate the selective recognition ability of MIP-CdS/TiO2. 5 mg/L of solutions of DMP, DBP and DEHP was individually prepared for testing the binding characteristic of MIP-CdS/TiO2 and CdS/TiO₂. Fig. 8 shows the equilibrium adsorption amount of DMP, DBP and DEHP on asprepared MIP-CdS/TiO₂ and CdS/TiO₂. As given in Fig. 8, CdS/TiO₂ exhibits not only low but also similar adsorption amount for the three analogues, indicating that there is no presence of selective recognition site in CdS/TiO₂ due to the absence of preparation template during the process. Nevertheless, the adsorption amount of MIP-CdS/TiO₂ for DEHP was much higher than that for DMP and DBP, suggesting that MIP-CdS/TiO₂ can selectively bind DEHP. This is because that in the process of fabrication of MIP-CdS/TiO₂, template DEHP has bound with monomer tetrabutyl titanate via hydrogen bond, so that DEHP has been fixed in MIP-CdS/TiO₂. After the template DEHP has been removed away via incineration, imprinting cavities and binding sites matching with the molecular size and chemical structure is remained in the as-prepared MIP-CdS/TiO₂. The specific recognition suggests the enhancement in photocatalytic efficiencies and selectivity of DEHP.



Fig. 8: Selective adsorption of MIP-CdS/TiO₂ and CdS/TiO₂.

The selective binding ability of MIP-CdS/TiO₂ and CdS/TiO₂ can be evaluated by the imprinting factor (\hat{a}) and selectivity coefficient (\hat{a}) which is calculated by equation (3) and (4), respectively.

$$\acute{a} = K_{\rm i}/K_{\rm c} \tag{3}$$

 $\hat{a} = \hat{a}_{\text{DEHP}} / \hat{a}_{\text{i}}$

Where, \dot{a}_{DEHP} and \dot{a}_{i} is the imprinting factors for DEHP and the two analogues, respectively. K_{i} and K_{c} represent the partition coefficients of the analyte on MIP-CdS/TiO₂ and CdS/TiO₂, respectively, which can be determined according to equation (5).

(4)

$$K = Q_{\rm e}/C_{\rm e} \tag{5}$$

Where, Q_e is the equilibrium adsorption amount, and C_e is the equilibrium concentration.

The imprinting factor of DEHP, DBP and DMP and the selectivity coefficients of DEHP to DBP and DMP have been calculated and listed in Table-1. As presented in Table-1, the imprinting factor of MIP-CdS / TiO₂ to DEHP is significantly higher than that to DBP and DMP, The selectivity coefficients of MIP-CdS/TiO₂ to DBP and DMP are 2.78 and 2.60 respectively, which further indicates that MIP-CdS/TiO₂ has a remarkably selective recognition to DEHP.

Table-1: Selective adsorption parameter of the MIP-CdS/TiO₂ to DEHP

Analytes	K _{MIP-CdS/TiO2} (L/g)	$K_{CdS/TiO2}(L/g)$	á	â
DBP	0.101	0.105	0.97	2.78
DMP	0.105	0.102	1.03	2.60
DEHP	0.311	0.116	2.69	-

Photocatalytic activity for DEHP

Fig. 9 shows the photocatalytic degradation efficiencies of DEHP in individual system by MIP-CdS/TiO₂ and CdS/TiO₂. It can be seen from Fig. 9 that the photocatalytic degradation rate of DEHP is fast in the first 2 h of the reaction. After 2 h, the degradation rate of MIP-CdS/TiO₂ decreases. After 5 h, the degradation efficiency of DEHP catalyzed by CdS/TiO₂ is only 46.4%, while the degradation efficiency of DEHP catalyzed by MIP-CdS/TiO₂ is up to 75.5% which is much higher than that by CdS/TiO₂. The degradation process of DEHP can be simulated by the first-order kinetics as equation (6).

$$\ln \frac{C_0}{C} = kt \tag{6}$$

Where, C_0 (mg/L) is the initial concentration of DEHP, C (mg/L) is the concentration of DEHP at time t, t (min) is reaction time, k (min⁻¹) is degradation rate constant.



Fig. 9: Degradation curves of DEHP photocatalyzed by MIP-CdS/TiO₂ and CdS/TiO₂

The *k* values of DEHP over MIP-CdS/TiO₂ and CdS/TiO₂, obtained from the slope of the curve of ln (C₀/C)~t, are 0.275 min⁻¹ (correlation coefficient R² of 0.9898) and 0.113 min⁻¹ (correlation coefficient R² of 0.9546), respectively. The degradation rate of DEHP over MIP-CdS/TiO₂ is 2.4 times as high as that over CdS/TiO₂. It is evident that molecularly

imprinting plays a vital role in improving photocatalytic activity of MIP-CdS/TiO₂. The enhanced photocatalytic activity is due to the fact that the presence of the binding site matching the structure of DEHP on MIP-CdS/TiO₂ surface results in selective recognition of DEHP and consequently preferential degradation. Moreover, molecularly imprinting inhibits the recombination of photoinduced electron-hole pairs to improve photocatalytic activity.

The photocatalytic mechanism of MIP-CdS/TiO₂ for DEHP is schematically shown in Fig. 10. Firstly, DEHP molecules are adsorbed onto the surface of MIP-CdS/TiO2 due to the selective recognition of MIP-CdS/TiO2 toward DEHP. Then MIP-CdS/TiO₂ is illuminated with simulative sunlight produced by a xenon lamp, and the electronhole pairs are produced. The photo-generated electrons (e⁻) migrate from the conduction band (CB) of CdS to the CB of TiO₂. Photo-generated holes (h⁺) transfer from the valence band (VB) of TiO₂ to the VB of CdS. As a result, the photo-generated electronhole pairs of CdS and TiO₂ can be rapidly separated. Furthermore, the presence of DEHP-imprinted site on MIP-TiO₂ can also promote electron-hole separation. The conduction potential of CdS and TiO₂ is more negative than the standard reduction potential of O_2/O_2^- . Therefore, photo-generated electrons can be trapped by oxygen to generate superoxide radical •O²⁻

. The photo-induced holes of CdS and TiO₂ can oxidize H₂O to hydroxyl radicals •OH. The produced \cdot O²⁻ and •OH oxidize DEHP adsorbed on the surface of MIP-CdS/TiO₂. In addition, Due to more positive valence band potential of CdS and TiO₂, holes in the valence band can directly oxidize DEHP.



Fig. 10: Schematic illustration of the photocatalytic mechanism of MIP-CdS/TiO₂.

Photocatalytic selectivity of MIP-CdS/TiO2 to DEHP

The photocatalytic selectivity of molecularly imprinted photocatalyst toward the template molecule can be assessed by the selectivity factor (α) which is expressed as equation (7) [42].

$$\alpha = \frac{R_{MIP}}{R_{NIP}} \tag{7}$$

$$R = \frac{k_{template}}{k_{analogue}} \tag{8}$$

Where, R_{MIP} is the ratio of degradation rate constant of template molecule to that of analogue over imprinted photocatalyst MIP-CdS/TiO₂, calculated by formula (8). R_{NIP} is the ratio of degradation rate constant of template molecule to that of analogue over non-imprinted photocatalyst CdS/TiO₂, calculated by formula (8).

To evaluate the photocatalytic selectivity of photocatalytic MIP-CdS/TiO₂, degradation experiment in a ternary system was carried out. The target pollutant DEHP (5mg/L) was degraded, by MIP-CdS/TiO2 and CdS/TiO2, in the presence of analogues DBP and DMP (5mg/L). Based on equation (6) and (7), the degradation rate constant kvalues and selectivity factor were calculated and listed in Table-2. It is observed from Table-2 that the degradation rate of DEHP over CdS/TiO₂ is very low (only 0.0782 h⁻¹) and has no obvious difference from those of DMP and DBP, indicating that the photocatalytic selectivity of CdS/TiO₂ is very poor. The distinction in chemical structure of DEHP, DBP and DMP has not obvious impact on the photocatalytic activity of CdS/TiO₂. In comparison, the degradation rate of DEHP over MIP-CdS/TiO₂ is enhanced significantly to 0.2162 h⁻¹, while the degradation rate of the analogue DBP and DMP over MIP-CdS/TiO₂ are reduced. Furthermore, the rate constant ratio of DEHP to DBP and DMP over MIP-CdS/TiO₂ are much higher than that over CdS/TiO₂. The selectivity factor of DEHP toward DBP and DMP are 3.20 and 3.30, respectively. The high α value demonstrates that molecularly imprinting has promoted photocatalytic selectivity of MIP-CdS/TiO2 toward DEHP.

Table-2: Degradation rate constants and Selectivity coefficient of MIP-CdS/TiO₂.

Parameters	MIP-CdS/TiO ₂			CdS/TiO ₂			
	DEHP	DBP	DMP	DEHP	DBP	DMP	
K (h-1)	0.2162	0.0713	0.0698	0.0782	0.0824	0.0832	
$R (k_{\text{template}}/k_{\text{analogue}})$		3.032	3.097		0.949	0.940	
$\alpha \left(R_{\rm MIP} / R_{\rm NIP} \right)$		3.20	3.30				3

Conclusions

The inorganic-framework molecularly imprinted composite catalyst MIP-CdS/TiO₂ has been successfully fabricated by sol-gel method using DEHP as template molecule and butyl titanate as functional monomer and titanium source. Inorganicframework molecular imprinting on the surface of the CdS/TiO_2 does not change the crystal structure of CdS/TiO₂. Compared with CdS/TiO₂, the absorption edges of MIP-CdS/TiO₂ shifts from 550 nm to 800 nm and the visible-light absorption intensity of MIPenhanced. Inorganic-framework CdS/TiO₂ is molecular imprinting on the surface of the CdS/TiO₂ can inhibit the recombination of the photo-induced electron-holes. The prepared MIP-CdS/TiO₂ has a specific ability to recognize DEHP. Under the same conditions, the adsorption amount of DEHP over MIP-CdS/TiO₂ is 1.46 times as high as that of DEHP over CdS/TiO2. The imprinting factor of DEHP over MIP-CdS/TiO₂ is 2.69, and the selectivity coefficient of DEHP relative to DBP and DMP are 2.78 and 2.60, respectively. Compared with CdS/TiO₂, MIP-CdS/TiO₂ exhibits higher photocatalytic activity and selectivity for DEHP. Under simulated solar light irradiation, the photocatalytic degradation efficiency of DEHP over MIP-CdS/TiO₂ is 75.5%, which is 1.63 times as high as that of DEHP over CdS/TiO₂. Hence, MIP-CdS/TiO₂ will be a promising photocatalyst for solar-driven application.

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