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1. Introduction

The increasing contamination of our environment with antibiotics is certainly one of the greatest problems for the future of humanity. Antibiotics are widely used for human and animal therapies, as well as in agricultural antimicrobials. However, the overuse and misuse of antibiotics has caused a serious environmental problem,¹ since such compounds can be found in municipal and industrial wastewater, wastewater sludge and agricultural runoff.² Thus, the way to effectively treat the antibiotics residues in the environment is urgent. The treatment methods have been investigated using microbial, chemical, and photochemical processes with varying success. Recent studies indicate that photocatalytic technology is a green technology which uses the solar energy and degrades pollutant to non-toxic.^{3,4}

Cadmium sulfide (CdS) is an important II–VI semiconductor and has received much attention due to its potential applications in electronics, optics, catalysis, and ceramics. CdS also has good photocatalytic activity due to its suitable band gap (2.4 eV)

and fine optical transmittance.5 Yet, it is well-known that pure CdS is unstable upon light illumination, and photocorrosion may occur in photocatalytic reaction.^{6,7} In addition, the photocatalytic activity is not high enough for application. Several ways have been used to modify CdS to overcome its drawbacks, such as coupling CdS with other semiconductors⁸ or polymer,⁹ doping with metal ion,10 depositing CdS onto the materials with high surface area,11 and so on. In our previous study, CdS/HNTs photocatalyst was synthesized,12 which have better photocatalytic activity. Halloysite nanotubes (HNTs) are a two-layered aluminosilicate clay mineral, possessing a naturally occur-ring unique tubular structure on the nano-scale which has the similar geometry to carbon nanotubes. Compared with carbon nanotubes, HNTs are readily obtainable, much cheaper and possessing of large reserves in China. On the other hand, HNTs possess advantages of high stabile property, resistible against organic solvents and ease of disposal or reusability.13-15 Therefore, the combination of CdS and HNTs effectively increase the using rate of light and enhance the photocatalytic activity. However, the modified photocatalysts have very poor selectivity and cannot differentiate these polluted targets. As we all know, the waste water usually includes different pollutants, it is important that some high risk pollutant is removed specially. Thus, it is very urgent to improve the selectivity of photocatalyst.

Molecular imprinting is a useful technique for the preparation of polymeric materials which provides artificial

Synthesis of thermal-responsive photocatalysts by surface molecular imprinting for selective degradation of tetracycline

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A novel thermal-responsive surface molecular imprinted photocatalyst of poly(*N*-isopropylacrylamide) (PNIPAm) modified CdS/halloysite nanotubes (HNTs) was prepared using surface molecular imprinting technology and evaluated as a potential effective photocatalyst for selectively remove tetracycline (TC) existing in aquatic environments. Free radical polymerization of TC, NIPAm, *N*,*N'*-methylenebisacrylamide (MBA) and 2,2'-azobisisobutyronitrile (AIBN) was used as a molecular template, functional monomer, cross-linking agent and initiator, respectively. The imprinted photocatalysts were further characterized by SEM, EDS, TEM, UV-vis DRS, FT-IR, BET and TG, which showed that the CdS/HNTs were successfully imprinted with PNIPAm. In addition, benefiting from the common effect of the specific binding of imprinted polymers, thermo-responsiveness of PNIPAm shells, and high photocatalytic activity of CdS/HNTs cores, the obtained material showed high photocatalytic activity and excellent selectivity to remove molecular template TC and the photocatalytic activity could be tuned by changing the environmental temperature. According to our experimental and characterized results, the mechanism of the preparation of imprinted photocatalyst and its use in photocatalytic degradation was further discussed, respectively.

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receptor-like binding sites for template molecules. These potential binding sites are generated by copolymerization of a cross-linking agent with the complex formed from a template and polymerizable monomers that have functional groups specifically interacting with the template through covalent or non-covalent bonds.¹⁶ Subsequently, the imprinted templates are removed from the polymer network and leaved binding sites with stereochemical complementarity to the template molecules.17,18 However, there are some defects for molecular imprinted photocatalyst, such as incomplete template removal, slow mass transfer and low binding ability. The introduce of surface molecular imprinting technology can reduce these drawbacks, which the functional monomers and template molecules are pre-grafted on the surface of supported materials and the template molecules are easily removed from the surface imprinted layer.¹⁹⁻²¹ Thus, it is possible to use surface imprinting technology to modify the surface of photocatalyst and improve the selectivity photo-degradation of template molecules.

Recently, the development of smart imprinting systems has attracted interests due to their remarkable responsive to specific external stimuli such as light,²² temperature²³ and pH value.24 Among them, temperature has attracted much more attention because of its easily operability and widely applicability. Zhao's group²⁵ described a thermo-sensitive and salt-sensitive molecularly imprinted hydrogel based on N-[3-(dimethylamino) propyl] methacrylamide (DMAPMA) and N-isopropylacrylamide (NIPAm), and the imprinted polymer exhibited positively thermo-sensitive molecular recognition of bovine serum albumin. A novel thermal-responsive magnetic molecularly imprinted polymer for selectively remove sulfamethazine (SMZ) existed in aquatic environments has been reported, and NIPAm and acrylamide (AAm) were selected as functional monomers.26 PNIPAM is a well-known thermosensitive polymer, exhibiting a lower critical solution temperature (LCST) at about 32 °C in water solution. The hydrophilicity of PNIPAm increases along with the decreasing temperatures, which makes PNIPAm swell in water, and vice versa. Thus, the selective molecule recognition ability of the thermo-sensitive molecularly imprinted polymer varies when environmental temperature changed. Thus, the preparation of stimuliresponsive imprinted polymers based on nanosized materials is of great scientific importance for the development of smart surface molecular imprinted polymers.

It should be noted that, if three promising concepts (a nanosized surface imprinting technique, high photocatalytic activity CdS/HNTs and PNIPAm) were combined, the novel thermal-responsive surface molecular imprinting photocatalysts could be fabricated and exhibited intelligent sensitivity and excellent selectivity remove antibiotics from waste water. In this study, CdS/HNTs were prepared by hydrothermal synthesis method. The photocatalysts were further modified with thermo-responsive polymer PNIPAm. Free radical polymerization of TC, NIPAm, N,N'-methylenebisacrylamide (MBA) and 2,2'-azobisisobutyronitrile (AIBN) was used as molecular template, functional monomer, cross-linking agent and initiator, respectively. The characterization, photocatalytic activity,

selectivity and regeneration of photocatalyst were investigated. The results demonstrated the photocatalyst which we prepared could efficiently and selectively photo-degradation of TC. The more worth noting is the tunable photocatalytic property of temperature responsive imprinted polymers by switch temperature. At last, the mechanism of preparation and recognition were proposed.

2. Experiment section

2.1 Materials

HNTs were purchased from Zhengzhou Jinyang guang Chinaware Co. Ltd., Henan, China. Polyvinylpyrrolidone (PVP), 3-(methacryloyloxy) propyl trimethoxysilane (MPS), cadmium chloride, thiourea, and salicylic acid (SA) were all purchased from Shanghai Chemical Reagent Co., Ltd. and used as received. *N*-Isopropylacrylamide (NIPAm), 2,2'-azobisisobutyronitrile (AIBN), *N*,*N*'-methylenebisacrylamide (MBA), were purchased from Aladdin Reagent Co., Ltd. Tetracycline (TC), oxytetracycline HCl (OTC-HCl) and Ciprofloxacin (CIP) were purchased by Shanghai Shunbo Biological Engineering Co., Ltd. Ethanol, methanol were purchased from Sinopharm Reagent Co., Ltd. Deionized and doubly distilled water were used throughout this work.

2.2 Sample preparation

2.2.1 Attaching CdS nanoparticles onto HNTs. CdS/HNTs were fabricated according to our previously reported method.¹² Briefly, 1.0 g HNTs were ultrasonically dispersed in 25.0 mL NaOH solution. Then 20.0 mL CdCl₂ solution was dropped in 25.0 mL of HNTs suspension while stirring. After 2 h stirring, added into thiourea solution dropping under stirring. Then, the solution was transferred to a teflon-lined stainless-steel autoclave (100 mL capacity). The autoclave was heated at 160 °C for 12 h. After cooling to room temperature, the precipitates were rinsed several times with ethanol and deionized water and dried at 60 °C for 12 h.

2.2.2 Preparation of 3-(methacryloyloxy) propyl trimethoxysilane (MPS) modified CdS/HNTs. A total of 2.0 g CdS/HNTs were dispersed in a mixture of 10.0 mL MPS and 100.0 mL of ethanol. The mixture was stirred at 40 °C for 12 h. The MPS-modified CdS/ HNTs (MPS-CdS/HNTs) were then washed repeatedly with ethanol and water, dried at 50 °C for 12 h in vacuum.

2.2.3 Preparation of surface imprinted photocatalysts. The imprinted photocatalysts were prepared *via* surface molecular imprinted technology. The basic synthesis process as follows: in a three neck flask equipped with a magnetic stirring bar, 0.5 mmol molecular template of TC were completely dissolved into 100 mL solvent (v/v: methanol-H₂O = 75/25). Then, 4.0 mmol NIPAm, 4.0 mmol MBA, 0.5 g MPS-CdS/HNTs and 0.2 g PVP were added into the mixed solution by ultrasonication for 10 minutes. After purging oxygen with nitrogen gas, 0.05 g of AIBN was added to the three-necked flask while the temperature was increased to 60 °C for 12 h under nitrogen protection. After the polymerization, the samples were filtered and washed with distilled water and dried at 50 °C for 12 h.

The template molecules were removed by washing with a mixture of methanol-acetic acid (95:5, v/v) using Soxhlet extraction. When no template was detected in the extraction solution, the composites were further washed with distilled water and ethanol. For comparison, the non-imprinted photocatalyst was also prepared using the same procedure, but without the addition of TC template.

2.3 Material characterization

The morphology of photocatalysts was observed via the transmission electron microscopy (TEM) on a JEOL IEM-200CX TEM. The SEM image was examined with XL30-ESEM scanning electron microscopy (Philips-FEI Co., Netherlands). XRD patterns were obtained with a D/max-RA X-ray diffractometer (Rigaku, Japan) equipped with Ni-filtrated Cu Ka radiation (40 kV, 200 mA). The 2θ scanning angle range was 10–80° at a scanning rate of 0.02°/0.2 s. The UV-vis diffuse reflectance spectra (DRS) were obtained with a Shimadzu 2450 UV-vis spectrophotometer (Shimazu, Japan) equipped with an integrating sphere at tachment ISR 240A and BaSO₄ powder as the internal standard. The Fourier transform infrared (FT-IR) absorption spectra were studied with a Nicolet Nexus 470 FT-IR (America thermo-electricity Company), using KBr pellets. The specific surface area (BET) was estimated from the N₂ adsorption-desorption isotherms, measured by a Quantachrome NOVA4000 surface area apparatus. TGA was performed for powder samples using a Diamond TG/DTA Instruments (Perkin-Elmer, USA) under a nitrogen atmosphere up to 800 °C with a heating rate of 5.0 °C min⁻¹.

2.4 Measurement of photocatalytic activity

To test photocatalytic behavior of the as-synthesized samples, photo-degradation of TC in water was chosen as a probe reaction. A 500 W Xe lamp with cutoff filter were used as the light source to provide visible light irradiation. Briefly, photocatalyst (0.05 g) was added into 50 mL of TC solution. The mixed suspension was stirred for 20 min in the dark in order to reach the adsorption-desorption equilibrium between the catalyst and the TC. Then, the suspensions were exposed to visible-light irradiation. The temperature of the reactant solution was maintained below 298 K by a flow of cooling water during the reaction. The reaction continued for 1 h and conducted in 10 min interval. The reaction mixture was analyzed by UV-vis spectrometer at wavelength of 357 nm. The photocatalytic degradation rate (DR) was calculated by this equation: DR = $[(1 - A_i/A_0)] \times 100\%$. Where A_0 is the initial absorbency of TC solution which reached absorption equilibrium and A_i is the absorbency of reaction solution.

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3. Results and discussion

3.1 TEM, SEM and EDS analysis

The morphology and structure of the as-prepared photocatalysts were investigated by TEM SEM and EDS. As shown in Fig. 1a, the majority of the samples were consisted of cylindrical tubes, and the nanotubes were open-ended. HNTs were rather polydisperse in length. The empty lumen of HNTs is 15-25 nm in diameter (see the inset of Fig. 1a at a higher magnification). As shown in Fig. 1b, large amounts of nanoparticles were deposited on the surface of HNTs. The surface of CdS/HNTs-MPS was coated with a non-uniform laver compared with Fig. 1b, which may be the formation of imprinting layer (Fig. 1(c)). From the SEM and EDS images in Fig. 1d and e, which illustrated that C, N, O, Si, Al, Cd, S were existed in the molecular imprinted photocatalyst. The peaks of Al, Si and O were mainly generated by HNTs and the peaks of Cd and S were generated by CdS nanoparticles. Above all, the CdS/HNTs was perfectly imprinted in the process of surface imprinting.



Fig. 1 TEM images of (a) HNTs (b) CdS/HNTs-MPS (c) molecular imprinted, SEM (d) and EDS (e) image of molecular imprinted.



Fig. 2 XRD pattern of (a) CdS/HNTs (b) non-imprinted (c) molecular imprinted.

3.2 XRD analysis

The crystal structure of the imprinted photocatalyst was determined by XRD. Fig. 2 presented the XRD pattern of both types of particles (non-imprinted and molecular imprinted) revealing the similar XRD pattern as CdS/HNTs, indexed as belonging to a hexagonal phase. After surface imprinting, the peak intensity was weaker than those of CdS/HNTs, indicating that a layer of the organic molecular layer was formed on the surface of CdS/HNTs. The result was consistent with the corresponding TEM image.

3.3 UV-vis DRS analysis

The optical absorption property and the band structure of photocatalysts were determined by UV-vis DRS. As shown in Fig. 3, the absorption boundary of surface molecular imprinted photocatalyst red shifted was seen obviously compared with CdS/HNTs and non-imprinted. And their absorption intensity of



Fig. 3 UV-vis diffuse reflectance spectra (DRS) of (a) CdS/HNTs (b) non-imprinted (c) molecular imprinted.

CdS/HNTs, non-imprinted and molecular imprinted were also increased. The reason may be caused from the imprinted process which could introduce some organic parts, and the organic parts can effectively enhance the absorbency of light. According to the formula: $E_g = 1240/\lambda$ (which E_g is the band gap energy and λ is the wavelength of the absorption edge.) it was estimated that the band gap of molecular imprinted photocatalyst was lower than CdS/HNTs. Therefore, there may be an improved TC activity of molecular imprinted photocatalyst under solar light irradiation. The main reason may be that the molecular imprinted photocatalyst could produce more electronic-hole in visible light with a narrow band gap.27 Meanwhile the surface defect was introduced after the process of surface imprinting and the elution. The surface defect can serve as charge traps retarding electron-hole combination rate, enhancing the interfacial charge transfer.

3.4 FT-IR spectra analysis

In order to verify the expected products were obtained in different steps of molecular imprinted fabrication, the FT-IR spectra for HNTs, CdS/HNTs, CdS/HNTs-MPS and molecular imprinted were recorded and showed in Fig. 4a-d, respectively. As shown in Fig. 4a, The characteristic bands in 3695 and 3627 cm⁻¹ were due to the stretching vibrations of inner-surface hydroxyl groups and the peak at 1635 cm⁻¹ was due to the deformation vibration of interlayer water.28 The deformations of Al-O-Si, Si-O-Si and O-H groups of the inner hydroxyl groups were at 536 cm⁻¹, 1031 cm⁻¹ and 909 cm⁻¹, respectively. In Fig. 2c, the peaks at 1713 cm^{-1} (C=C bond stretching vibration) indicated that CdS/HNTs were successfully modified by MPS. In Fig. 2d, the peaks at 1650 cm^{-1} , 1528 cm^{-1} (secondary amide C=O stretching), and 1390 cm^{-1} (deformation of methyl groups on $-C(CH_3)_2$ could be attributed to the characteristic peaks of PNIPAm,26 which implied that the fabrication of molecular imprinted photocatalyst had been successfully performed.



Fig. 4 FT-IR spectra of (a) HNTs (b) CdS/HNTs (c) CdS/HNTs-MPS (d) molecular imprinted.



Fig. 5 TGA profiles of (a) CdS/HNTs (b) non-imprinted (c) molecular imprinted.

3.5 TG analysis

Fig. 5 showed the TGA curves of CdS/HNTs, non-imprinted and molecular imprinted photocatalyst. As shown in Fig. 5a, the weight loss processes at two periods, the loss of absorbed water from 25 to 100 °C, the dehydroxylation of structural aluminol groups present in HNTs from 400 to 600 °C. Compared with CdS/HNTs, the significantly different about weight losses of non-imprinted and molecular imprinted photocatalysts were assigned to the decomposition of the imprinted layer. According to the weight loss obtained from TGA analysis, the slight difference of weight losses (non-imprinted and molecular imprinted photocatalysts) may be due to the template molecules, which made the grafting density of polymer different in polymerization.²⁶ The remaining mass for non-imprinted and molecular imprinted photocatalysts was assigned to the thermal resistance of CdS/HNTs nanoparticles, and the quantity of CdS/HNTs nanoparticles in the non-imprinted and molecular imprinted photocatalysts were 84.77% and 86.14%, respectively, indicating that the non-imprinted and molecular imprinted possessed of similar morphological structure and size distribution.

3.6 BET analysis

The specific surface area values were calculated using data of liquid nitrogen physisorption experiments BET method. The BET analysis of the surface area, pore volume and pore size of molecular imprinted photocatalyst were shown in Table 1. From the table, we can see clearly that the surface areas changing with different synthetic conditions, the reason mainly caused by the imprinted process which can cover the surface holes and/or increase the particle size.

3.7. Photocatalytic experiments

The photocatalysis experiments were conducted to research the relationship between the photocatalytic efficiency and the molar ratio of functional monomer, molecular template and cross linking agent, the amount of imprinted molecular template and polymerized time. Bearing this in mind, the effect of the three factors was studied.

3.7.1 The impact of different molar ratio of molecular template, functional monomer and cross linking agent on the photocatalytic activity. As described previously, the interaction among molecular template, functional monomer and cross linking to polymerized extent on the surface of photocatalyst were important. Fig. 6A showed photocatalytic effect on TC using the as-prepared photocatalysts which prepared with the different proportion of molecular template, functional monomer and cross linking agent. It was clearly seen that the molar rate of 1:8:8 showed the highest photocatalytic activity. The reason may be as follows: when the functional monomer was too little (1:4:8), template molecular may not be completely bonding, which may affect the photocatalytic activity. However, the high proportion of cross linking may produce the imprinted photocatalyst with high cross-linking degree, which reduced the photocatalytic activity. It indicated that appropriately prepared proportion can effectively enhance the photocatalytic activity. While the appropriately proportion may induced polymerized the appropriately polymer layer which was exerted positive on the photo-generated electrons transfers, and lead to the high photocatalytic activity.

In order to study the influence of temperature responsiveness on the photocatalytic activity, the other representative temperature, *i.e.*, 45 °C (higher than LCST of polymers) was selected as contrastive studies. As shown in Fig. 6B, the photocatalyst with different molar ratio performed a poor photocatalytic activity at 45 °C. The results may be caused by the thermo-sensitive dependence behaviors, the shrinking of the polymer layer and the decreasing of hydrophilic properties which can affect the access of template TC to polymers at high temperatures. There was an unusual phenomenon in the later stages of photocatalytic degradation, the DR of the photocatalyst reduced with the increasing time. The main reason may due to the instability of TC at illumination and high

Table 1 BET and pore and	nalysis											
Different molar ratio of molecular template, functional monomer, cross linking agent				Different amount imprinted molecular template (mmol)					Different polymerized time			
Photocatalyst	1:4:8	1:8:8	1:8:12	0.5	0.25	0.1	0.05	0.01	3 h	6 h	12 h	24 h
Surface area $(m^2 g^{-1})$	16.23	14.97	13.41	14.97	15.23	20.26	22.23	24.72	27.98	23.54	24.72	26.04
Pore size (nm)	9.59	10.73	10.18	10.73	10.22	10.77	10.68	11.29	10.19	10.78	11.29	11.49
Pore volume (cm ³ g ^{-1})	0.04	0.04	0.03	0.04	0.05	0.04	0.07	0.07	0.07	0.06	0.07	0.07



Fig. 6 (A) The influence of different molar ratio of molecular template, functional monomer and cross linking agent (a) 1 : 4 : 8 (b) 1 : 8 : 8 (c) 1 : 8 : 12 at 25 °C. (B) The influence of different molar ratio of molecular template, functional monomer and cross linking agent (a) 1 : 4 : 8 (b) 1 : 8 : 8 (c) 1 : 8 : 12 at 45 °C.

temperatures, which the dimer of TC maybe formed, and lead to the change of DR.

3.7.2 The impact of different amounts of molecular template (TC) on the photocatalytic activity. In order to investigate the effect of different amounts of molecular template on the photocatalytic activity, the various amounts of TC template were used to prepare the surface imprinted photocatalyst. As shown in Fig. 7, the amount of surface molecular imprinted photocatalyst with 0.01 mmol showed the highest photocatalytic activity, while excessive molecular templates reduced the photocatalytic activity. The reasons may be due to that the more molecular templates could process more area of the photocatalysts surface which resulted incomplete imprinted polymerized layer and influenced the formation of the effective heterojunction for transfer of photoelectrons, and lead to low photocatalytic activity.

3.7.3 The impact of different polymerized time on the photocatalytic activity. The thin and/or thick layer of imprinted polymer was an important factor for the photocatalytic activity of surface imprinted photocatalyst. Thus, surface imprinted



Fig. 7 The influence of different amount imprinted molecular template (TC) (a) 0.5 mmol (b) 0.25 mmol (c) 0.1 mmol (d) 0.05 mmol (e) 0.01 mmol.



Fig. 8 The influence of different polymerized time (a) 24 h (b) 12 h (c) 6 h (d) 3 h.

photocatalysts with different polymerized time were studied. As shown in Fig. 8, 6 h was the best polymerized time for the photocatalytic activity. The cavity of template molecular could not be effectively formed for incomplete polymerization of imprinted layer of short polymerized time, which lead to lower photocatalytic activity. While the long polymerized time may induce the thick imprinted layer and lead to the coverage of active sites or the difficulty in transferring of electronic and hole, which reduced the activity of photocatalytic materials. Therefore, the imprinted thickness for the photocatalyst degradation was important, the most suitable thin layer exhibited better photocatalytic activity.

At last, two control experiments were performed under different conditions: (a) in the presence of the photocatalysts but in the dark (b) with visible light irradiation but in the absence of the photocatalysts. It was clearly seen that (Fig. 9) TC molecules contacting with molecular imprinted photocatalyst did not cause a sharp decline of the TC degradation rate in the



Fig. 9 The degradation rate of TC in the presence of the photocatalysts but in the dark (a) and with visible light irradiation but in the absence of the photocatalysts. (b) Degradation rate of TC over the samples: (c) CdS/HNTs (d) molecular imprinted photocatalyst.

dark reaction condition. And, there was no appreciable degradation of TC after 60 min in the absence of photocatalysts. Fig. 9c and d showed the degradation curves of TC on the CdS/HNTs and molecular imprinted photocatalyst. It could be seen that the two photocatalysts showed higher photocatalytic activities. But, the DR of molecular imprinted photocatalyst was decreased slightly compared with CdS/HNTs. The reason may be that the active site of CdS was covered by polymer layer.

3.7.4 Stability and reusability of molecular imprinted photocatalyts. The most important factor for the practical utility of a photocatalyst is its reusability and stability during the course of illumination. As shown in Fig. 10, a slight decrease of DR was found after they were repeatedly performed and recycled in TC photo-degradation for three times, indicating that molecular imprinted photocatalyts had excellent photochemical stability and reusability. The good recycling performance

and longevity maintained on the photocatalyst make it promising candidate in practical applications.

3.7.5 The selective degradation of molecular imprinted photocatalyts. To study the selectivity of prepared surface molecular imprinted photocatalyts on different targets, a series of photo-degradation experiments with the same conditions were conducted, and the result was obtained in Fig. 11. It was clearly seen that the photo-degradation rate of non-target molecular template were much lower than the photocatalyst of target molecular template. It may be due to the specially sizes, structures and functional groups of the template, different binding forces could form between the TC and PNIPAm, resulting in a different recognition effect. Moreover, OTC-HCl has nearly the same structure as TC except the lack of hydroxyl and chlorine functional group, but the photo-degradation capacity was still lower than that for TC, suggesting that the memory of specific functional groups also played an important role in the preparation of molecular imprinted photocatalyts.

In the experiment, the measured apparent rate constants (k)were used to evaluate the influence of the molecular imprinted photocatalysts on the photo-degradation rate of pollutants and the selectivity of various photocatalysts, the results were shown in Table 2. As anticipated, the rate constants for the target's degradation over the surface molecular imprinted photocatalysts were larger than others. Especially, the apparent rate constant (k) of degradation of TC was 0.02809 min⁻¹, which was much higher than that of SA (0.00439 min^{-1}). This may due to the maximum differentiation in structure between SA and TC. Nevertheless, the structure of TC and OTC-HCl were very similar, while the apparent rate constant (k) of degradation of OTC-HCl (0.01199 min⁻¹) was still different from that of TC $(0.02809 \text{ min}^{-1})$. It suggested that the as-prepared molecular imprinted photocatalyts had the strong ability to selective recognition and photo-degradation of TC.

On the other hand, the R^* ($R^* = k_{target}/K_{non-target}$) was also used to measure the selection of degradation. As shown in Table 1, the calculated coefficients of selection R^* relative to



Fig. 10 Photostability of molecular imprinted photocatalyst.



Fig. 11 The degradation rate of different targets

 Table 2
 Apparent rate constants and coefficients of selectivity for photocatalytic degradation

	$TC(min^{-1})$	CIP (min ⁻¹)	$SA(min^{-1})$	OTC-HCl (min ⁻¹)	$MIP(min^{-1})$	NIP (min^{-1})
k _{target}	0.02809	_	_	_	0.02809	0.0217
K _{non-target}	—	0.0143	0.00439	0.01199	—	—
$R^*, R^* = k_{\text{target}}/k_{\text{non-target}}$		1.964336	6.398633	2.342786	1.29447	



Scheme 1 Schematic layout synthesis of (a) MPS-CdS/HNTs (b) imprinted photocatalyst and its use in photocatalytic degradation.

HCl-OTC, CIP and SA were 2.342786, 1.964336 and 6.398633, respectively. Suggesting that the coefficient of selectivity R^* mainly depended on the structure of target pollutant. In addition, the coefficient selection of surface imprinted photocatalysts relative to non-imprinted was 1.29447, further confirmed that the surface molecular imprinted photocatalysts enhanced the photocatalytic selectivity toward the target contaminant.

3.7.6 The mechanism of preparation and application in photo-degradation with imprinted photocatalysts. According to our experimental and characterized results, the possible route for preparation of surface molecular imprinted polymer modified photocatalyst and its use in photocatalytic degradation was shown in Scheme 1. MPS modified CdS/HNTs were prepared by hydrothermal synthesis method and the main steps were shown in Scheme 1(a). In the first step, the surface of HNTs was modified with Cd²⁺ by interacting with cadmium chloride. Generally, the surface of HNTs has negative charges under the alkaline condition.²⁹ Thus, Cd²⁺ was more likely tend to bind with HNTs. Then, hydrolysis of thiourea was promoted synchronously in alkaline conditions ((NH₂)₂CS + 2OH⁻ \rightarrow CH₂N₂ +H₂O + S²⁻). Finally, the CdS nanocrystallines were formed on the surface of HNTs. Due to the hydrothermal reaction system, the oriented self-aggregating process of CdS nanocrystallines was promoted the growth of nanocrystallines. The surface of CdS/HNTs modified with MPS was through chemical modification, which the vinyl groups were introduced. FT-IR studies showed that the CdS/HNTs were successful modified by MPS.

The possible route for preparation imprinted photocatalysts was shown in Scheme 1(b). In this procedure, NIPAm was used as a functional monomer and combined with template molecules TC. MBA as a cross-linking agent was chosen to participate in the polymerization reaction. After free radical solution polymerization, the surface of CdS/HNTs-MPS was coated with temperature responsive molecularly imprinted layer. At last, the template molecules were removed by extensive washing with a mixture of methanol/acetic acid (95:5, v/v) using soxhlet extraction. A large number of TC tailor-made vacancies were formed and these imprinted cavities had with stereo-chemical complementarity to the template molecules (TC). In the process of photocatalytic degradation, the TC molecules were rebound to the adsorption sites at these imprinted cavities. Then, the adsorbed TC molecules were oxidized by the photo-generated oxidizing species such as OH radicals. At last, the TC molecules could be further degraded to CO2, H2O and other small inorganic molecular material.30 As surface molecular imprinted polymers were thermoresponsive, the swelling/shrinking of the polymer layer could be tunable by changing the environmental temperature, which significantly affected the photocatalytic activity of imprinted photocatalysts.

4. Conclusions

In this work, new thermo-sensitive polymer used as shells and CdS/HNTs as cores to fabricate a novel thermal-responsive surface molecularly imprinted photocatalyst. The imprinted

polymer layer provides the photocatalyst molecular recognition ability to form the selective photo-degradation of the target pollutant. Such selectivity is dependent mainly on the difference in the molecular size and shape between the target and nontarget pollutants. Meanwhile, the photocatalytic activity of surface imprinted photocatalysts could be tunable by changing the environmental temperature. Furthermore, the novel thermal-responsive surface molecular imprinting photocatalysts retained comparable photocatalytic activity after repeated uses for three times. The excellent selective, photocatalytic activity and thermo-sensitivity will be more broad application prospects for the treatment and disposal the residues of TC from waste water.

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