

# Cyclodextrin-Cross-Linked Hydrogels for Adsorption and Photodegradation of Cationic Dyes in Aqueous Solution

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Abstract: Possessing three-dimensional porous structures and tunable mechanical strengths, cyclodextrin-containing polymeric hydrogels are one of the most promising waterbased adsorbent materials due to their easy availability, simple chemical modification and environmental friendliness. In this work, two kinds of hydrogels were prepared via the copolymerization with acrylic acid and vinyl-derivatized  $\beta$ cyclodextrins in water. These two gels have showed good adsorption performance towards cationic dyes through the noncovalent interactions with their anionic backbones and

### Introduction

Hydrogels, a kind of soft materials, have valuable practical applications in miscellaneous fields, such as drug delivery, water treatment, biosensing, catalysis, information encryption, and luminescent materials.<sup>[1-6]</sup> Structurally, hydrogels possess multidimensional porous networks and good swelling behaviors in water without dissolution or dispersion. The fabrication of hydrogels with extraordinary mechanical properties mostly relies on the extensive cross-linkage of subunits via the covalent and noncovalent methods.<sup>[7]</sup> In the covalent-type hydrogels, the backbone of porous network is mostly built through chemically cross-linked polymerization of small-molecular monomers. Comparatively, as for the noncovalent-type hydrogels, intermolecular cross-linkage can be achieved via multiple synergistic noncovalent interactions, including hydrogen-bonding connection,  $\pi$ -stacking, electrostatic attraction, metal-ligand coordination, and host-quest inclusion complexation.<sup>[8]</sup> Particularly, macrocycle-based inclusion complexation can not only entrap various substrates to enhance physicochemical properties of hydrogels but also endow these hydrogels with desirable multistimuli-responsiveness through dynamically reversible host-guest interactions.

Cyclodextrins (CDs), a family of macrocyclic receptors, are composed by D-glucose units via  $\alpha$ -1,4-glucosidic bonds to form cyclic oligosaccharides. Owing to the exposed reactive hydroxyl groups, CDs can be chemically modified at their upper porous network. Meanwhile, pseudo-second-order model was selected to clarify the adsorption kinetics process. Moreover, nano-scaled  $TiO_2$  was doped into these resultant cyclodextrins-based hydrogels to achieve efficient degradation of dyes upon light irradiation. The obtained  $TiO_2$ -loaded hydrogels could exhibit improved adsorption performance and make the adsorbed dyes photo-degraded with the decolorization rates above 95%. It can be envisioned that such cyclodextrin-based soft materials may find applications in dye clearance and water treatment.

and lower rims, which can be utilized to enhance water solubility and inclusion efficiency and further to construct a variety of photodegradable supramolecular assemblies and other functional materials.<sup>[9-11]</sup> Along with the rapid development of CD science in the past few decades, an impressive progress in this area is the emergence of CD-based supramolecular hydrogels, which can combine the inherent advantages of supramolecular chemistry and water-based materials. In general, CD units can be conveniently grafted onto the main chains of many polymers, including cellulose,<sup>[12]</sup> chitosan<sup>[13]</sup> and polyacrylic acid,<sup>[14]</sup> thus conferring host-guest binding characteristics to these environmentally friendly and biocompatible hydrogels. In this context, due to the facile and controllable preparation, in-situ copolymerization with vinylcontaining monomers is believed as one of the most reliable and effective methods for attaining functional hydrogels.<sup>[15]</sup> For example, by leveraging the covalent and noncovalent crosslinkage, Shi and Mao et al. fabricated a supramolecular hydrogel using vinyl-terminated  $\beta\text{-CD}$  and adamantane derivatives, which showed rapid self-recovery ability, high mechanical strength and good cell biocompatibility.<sup>[16]</sup> Moreover, when vinyl-containing  $\beta$ -CD and dextran were copolymerized with acrylic acid in water, a supramolecular hydrogel was constructed with the two polymeric chains, thus showing efficient adsorption of different organic pollutants through the synergistic electrostatic and host-quest interactions.<sup>[17]</sup> By utilizing the facile UV-initiated free-radical copolymerization with vinyl-containing monomers, our group also constructed a series of CD-based supramolecular hydrogels, which could be widely applied as tunable photoluminescent self-sorting materials<sup>[18]</sup> and polyrotaxane-based stretchable supercapacitors.[19]

In the wake of these fascinating results and inspired by our ongoing interest in the CD-based supramolecular hydrogels, we herein reported two kinds of hydrogels prepared by the in-situ copolymerization of acrylic acid with 2-isocyanatoethylacrylate-modified  $\beta$ -CD (CD-AOI) in water. The mechanical strengths and rheological properties of the obtained supramolecular hydro-

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gels could be conveniently adjusted by the substitution degrees of AOI groups on the  $\beta$ -CD's skeleton. Moreover, benefitting from the abundant carboxyl groups and the high porosity in the obtained hydrogels, positively charged dye molecules could be efficiently adsorbed via the electrostatic interaction in aqueous solution. Significantly, NH<sub>2</sub>-capped nano-scaled titanium dioxide (TiO<sub>2</sub>) could be further loaded in the gel matrix without sedimentation. Thus, by virtue of the TiO<sub>2</sub> nanoparticles as photocatalyst, the trapped organic dyes could be efficiently degraded upon light irradiation at 365 nm. Our work demonstrates the superiority of cross-linked supramolecular hydrogels possessing desirable mechanical properties and degradation ability toward organic pollutants, which may have great potentials as powerful adsorbents for removal of pollutants in water.

## **Results and Discussion**

The synthetic routes of two kinds of supramolecular hydrogels (**Gel**<sub>1,3</sub> and **Gel**<sub>2,9</sub>) were depicted in Scheme 1. The AOI groups could be simply decorated onto the upper rims of  $\beta$ -CDs through a one-step modification at different molar ratios between  $\beta$ -CD and AOI (Figure S1, Supporting Information). Accordingly, the degrees of substitution could be determined by mass spectrometry and the integral ratios of proton peaks between  $\beta$ -CD and AOI. In our case, **CD-AOI**<sub>1,3</sub> and **CD-AOI**<sub>2,9</sub> were obtained with 1.3 and 2.9 units of AOI groups on average, respectively, in each  $\beta$ -CD. Moreover, compared to the native  $\beta$ -CD, two new bands appeared at 1704.53 and 1533.27 cm<sup>-1</sup> in the FT-IR spectra, corresponding to the characteristic stretching vibrations of carbonyl group and C=C chemical bond, respectively, in **CD-AOI**<sub>1,3</sub> and **CD-AOI**<sub>2,9</sub> (Figures S2 and S3, Supporting Information). Subsequently, hydrogel network was formed via



**Scheme 1.** Synthetic routes and schematic illustration of dye removal and photodegradation by **Gel**<sub>1.3</sub> and **Gel**<sub>2.9</sub> in water.

the in-situ copolymerization with acrylic acid in the presence of potassium peroxydisulfate as initiators in aqueous solution. The optimal condition for hydrogel formation was also examined using different concentrations of acrylic acids, revealing that the hydrogel could be obtained when the concentration of acrylic acid reached up to 72 mg L<sup>-1</sup> (Table S1, Supporting Information). Otherwise, only fragile white solid was formed after freeze-drying the samples when the concentration of acrylic acid was used lower than 72 mg L<sup>-1</sup>. Meanwhile, different mass ratios of **CD-AOI**<sub>1.3</sub> were also checked and it was found that 5% mass ratio was the critical value for the formation of hydrogels (Table S2, Supporting Information). These results jointly demonstrated that the existence of vinyl-substituted  $\beta$ -CDs played a crucial role in cross-linking the linear polyacrylic acids.

Subsequently, the mechanical properties of supramolecular hydrogels were investigated by the rheology measurements. Taking **Gel**<sub>1,3</sub> as an example, as discerned from Figure 1a, the storage modulus (G') showed an upward trend with increase of mass ratios of CD-AOI1.3 in the frequency sweep tests. The viscosity of obtained hydrogels could be accordingly enhanced at the same oscillation frequencies when more CD-AOI<sub>1.3</sub> were presented in the hydrogels (Figure 1b). Thus, in the following cases, the mass ratio of CD-AOI was used as 5% for the construction of Gel<sub>1.3</sub>, and Gel<sub>2.9</sub>. Upon fixing  $\omega = 6.28$  rad/s in the rheological experiments, no gel-to-sol state transition was observed at a wide strain region ( $\gamma < 1000\%$ , Figure 2a and 2c). Moreover, according to frequency ( $\omega$ ) sweep test results at a fixed strain ( $\gamma$ ) of 10%, both **Gel**<sub>1.3</sub>, and **Gel**<sub>2.9</sub> showed higher storage modulus (G') than loss modulus (G"), implying that the gel-phase materials were stable enough and the gel structure could not be destroyed at the tested frequency range of  $\omega =$ 0.01-100 rad/s (Figure 2b and 2d). In addition, it was noteworthy that the value of G' for Gel2.9 was relatively larger than that of Gel<sub>1.3</sub>, which was attributed to more cross-linking sites in CD-AOI<sub>2.9</sub> for reacting with acrylic acids. Typically, the porous morphology was observed after lyophilisation in the scanning electronic microscopic (SEM) images, and the Brunauer-Emmett-Teller (BET) surface areas of two hydrogels were also analyzed through N<sub>2</sub> adsorption isotherms (Figure 3). Apparently, the extensive porous network in Gel1.3, and Gel2.9 would facilitate the dye adsorption and concomitant photo-degradation, as described below.



**Figure 1.** (a) Frequency sweep tests of  $Gel_{1,3}$  at  $\omega = 0.01-100$  rad/s and  $\gamma = 10\%$  with different mass ratios of CD-AOI<sub>1,3</sub> and (b) viscosity tests of Gel<sub>1,3</sub> with different mass ratios of CD-AOI<sub>1,3</sub> as a function of frequency.



**Figure 2.** (a) Strain sweep tests of **Gel**<sub>1.3</sub> at  $\gamma = 0.01-3500\%$  and  $\omega = 6.28$  rad/s; (b) Frequency sweep tests of **Gel**<sub>1.3</sub> at  $\omega = 0.01-100$  rad/s and  $\gamma = 10\%$ ; (c) Strain sweep tests of **Gel**<sub>2.9</sub> at  $\gamma = 0.01-3500\%$  and  $\omega = 6.28$  rad/s; (d) Frequency sweep tests of **Gel**<sub>2.9</sub> at  $\omega = 0.01-100$  rad/s and  $\gamma = 10\%$ .



**Figure 3.** SEM image of (a)  $\text{Gel}_{1,3}$  and (b)  $\text{Gel}_{2,9}$  (Inset: photograph after gelation). N<sub>2</sub> adsorption-desorption isotherms of (c)  $\text{Gel}_{1,3}$  and (d)  $\text{Gel}_{2,9}$ . Note that the mass ratios of **CD-AOI** in  $\text{Gel}_{1,3}$  and  $\text{Gel}_{2,9}$  were fixed at 5%.

In our case, the high porosity and abundant exposed carboxyl groups (--COOH) in the obtained hydrogels enabled efficient adsorption of cationic dyes, such as methylene blue (MB) and rhodamine B (RhB). The derived parameters of the obtained hydrogels for dye adsorption were shown in Table 1. The standard curves of two examined dyes were presented in Figures S4 and S5 (Supporting Information). The UV-vis absorbance of MB and RhB gradually decreased over time in the presence of supramolecular hydrogels (Figures 4a-4b and S6a-6b, Supporting Information). Eventually, more than 95% of these two dyes were adsorbed by Gel<sub>1.3</sub> and Gel<sub>2.9</sub> at the equilibrium state in 60 min (Figures 4c and S6c, Supporting Information). After adsorbing these organic dyes, particulate aggregates were gathered onto the surface of hydrogels (Inset photos in Figures 4c and S6c, Supporting Information). Meanwhile, after adopting the pseudo-second-order model, the adsorption kinetics could be clarified in the dye removal process. It was noteworthy that high correlation coefficients  $(R^2 > 0.99)$  after fitting adsorption experimental data were presented to feedback precisely the pseudo-second-order model as adsorption equations according to results of adsorption studies (Figures 4d and S6d, Supporting Information). Thus, it was found that the adsorbing capacities at equilibrium  $(q_e)$  of  $Gel_{1.3}$  and  $Gel_{2.9}$  were higher toward RhB (308.74 mg g<sup>-1</sup> for  $\mathbf{Gel}_{1,3}$  and 234.25 mg g<sup>-1</sup> for  $\mathbf{Gel}_{2,9}$ ) than MB (228.96 mg g<sup>-1</sup> for  $Gel_{1,3}$  and 224.69 mg g<sup>-1</sup> for  $Gel_{2,9}$ ). This was probably due to the stronger binding strength of  $\beta$ -CD with RhB than MB.<sup>[9,20]</sup> Moreover, the apparent rate constants  $(k_A)$  calculated from adsorption equations demonstrated that Gel<sub>1.3</sub> possessed relatively largest value against RhB up to 4.61×  $10^{-3}$  g mg<sup>-1</sup> min<sup>-1</sup> (Table 1). It is known that  $k_A$  reflects the comprehensive outcomes of the different adsorption performance of outer surfaces (referred to readily accessible contacting sites) and interior surfaces (referred to less accessible binding sites) of adsorbent.<sup>[21]</sup> Therefore, the CD-containing hydrogels/ adsorbents may possess different adsorption performance towards dye molecules, thus giving quite distinctive kinetics parameters.<sup>[12,14,17,22,23]</sup>

It is known that TiO<sub>2</sub> nanoparticles (NPs) have been studied extensively as photocatalyst in the field of environmental protection because of its excellent photocatalytic performance, high chemical stability, and commercial availability.<sup>[24]</sup> Therefore, TiO<sub>2</sub> NPs were further introduced into the three-dimensional networks of hydrogels to achieve the desirable photocatalytic

Table 1. Derived parameters of the obtained hydrogels for MB and RhB adsorption.						
Gel	MB Removal Efficiency [%]	$q_{ m e}$ [mg g <sup>-1</sup> ]	<i>k</i> <sub>A</sub> [g mg <sup>-1</sup> min <sup>-1</sup> ]	RhB Removal Efficiency [%]	$q_{ m e}$ [mg g <sup>-1</sup> ]	k <sub>A</sub> [g mg <sup>−1</sup> ∙min <sup>−1</sup> ]
Gel <sub>1,3</sub> Gel <sub>2,9</sub> TiO <sub>2</sub> -loaded Gel <sub>1,3</sub> TiO <sub>2</sub> -loaded Gel <sub>2,9</sub> Gel <sub>1,3</sub> / TiO <sub>2</sub> -NH <sub>2</sub> Gel <sub>2,9</sub> / TiO <sub>2</sub> -NH <sub>2</sub>	95.97 97.56 96.32 97.16 98.74 97.80	228.96 224.69 228.96 231.24 239.79 237.51	$\begin{array}{c} 1.94 \times 10^{-3} \\ 2.68 \times 10^{-3} \\ 7.61 \times 10^{-3} \\ 9.01 \times 10^{-3} \\ 1.15 \times 10^{-3} \\ 1.74 \times 10^{-4} \end{array}$	95.50 94.90 94.58 96.15 96.73 96.62	308.74 234.25 236.86 240.78 284.89 284.56	$\begin{array}{c} 4.61 \times 10^{-3} \\ 1.47 \times 10^{-3} \\ 2.98 \times 10^{-3} \\ 2.16 \times 10^{-3} \\ 1.42 \times 10^{-3} \\ 1.15 \times 10^{-3} \end{array}$

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**Figure 4.** UV-vis spectra of (a) MB (4 mg L<sup>-1</sup>) and (b) RhB (5 mg L<sup>-1</sup>) aqueous solution in the presence of **Gel**<sub>1,3</sub> (2 mg mL<sup>-1</sup>) at different contacting times at 25 °C (Inset: Photographs of MB and RhB aqueous solution before and after adsorption); (c) Time-dependent percentage removal efficiency of MB and RhB by **Gel**<sub>1,3</sub> (Inset: SEM images of **Gel**<sub>1,3</sub> after adsorption for (I) MB and (II) RhB); (d) Pseudo-second-order plots for **Gel**<sub>1,3</sub> towards MB and RhB (Note: The 'x' and 'y' in the fitting equations were denoted as 't' and 't/q'<sub>t</sub>', respectively).

degradation property.<sup>[25]</sup> The TiO<sub>2</sub>-loaded Gel<sub>1,3</sub> and Gel<sub>2,9</sub> were prepared and similar rheological properties were obtained after doping TiO<sub>2</sub> NPs (Figure S7, Supporting Information). The agglomerate TiO<sub>2</sub> NPs were also found in the SEM images after lyophilization (Figure S8, Supporting Information). As shown in Figures S9–S10 (Supporting Information), two TiO<sub>2</sub>-loaded hydrogels showed excellent adsorption performance, including similar removal efficiency,  $k_{\rm A}$  values and morphological changes after dye adsorption. However, these two gels could not efficiently degrade the cationic dyes after light irradiation. For example, as discerned from Figure S11 (Supporting Information), 79.8% of UV-vis absorbance of MB was still observed in the presence of TiO<sub>2</sub>-loaded Gel<sub>1.3</sub> even after light irradiation. No obvious decolorization was found in the TiO2-loaded samples. The decolorization rate of RhB was only 7.6% by TiO<sub>2</sub>loaded Gel<sub>1.3</sub>. These unsatisfactory photo-degradation results were mainly contributed to the low and nonuniform dispersion of pristine TiO<sub>2</sub> NPs into the hydrogels, thus leading to the less efficient contact between the catalytic centres and the trapped dye molecules (Inset photo in Figure S8, Supporting Information).

To overcome the above-mentioned disadvantages, the pristine  $TiO_2$  NPs were further modified with NH<sub>2</sub>-pendent silane coupling agent to improve their dispersion ability in water and to enhance the electrostatic interaction with the carboxyl-rich network in hydrogels. TEM images showed the NH<sub>2</sub>-capped  $TiO_2$  NPs could be dispersed with the diameter of *ca.* 20 nm (Figure S12b, Supporting Information). As shown in Figure S12 (Supporting Information), the bands at 2925.98 and 2864.33 cm<sup>-1</sup> in FT-IR spectra were assigned to the C–H stretching vibration and the characteristic band of Si–O–Si was observed at 1112.21 cm<sup>-1</sup>.<sup>[26]</sup> The surface analysis by X-ray

photoelectron spectroscopy (XPS) revealed the characteristic peaks of C1s (284.8 eV), N1s (399.2 eV), O1s (532.1 eV), Si2p (102.3 eV) and Ti2p (458.3 eV). Thermogravimetric analysis (TGA) also demonstrated that the mass loss (1.7%) above 223 °C was originated from the combustion of the capping agents on the surface.<sup>[27]</sup> All these results demonstrated the successful modification of NH<sub>2</sub> group onto TiO<sub>2</sub> NPs. More gratifyingly, compared to pristine TiO<sub>2</sub> NPs, the NH<sub>2</sub>-pendent ones could not precipitate in water within 12 h at least (Figure S13, Supporting Information).

Furthermore, the same procedure was implemented to construct Gel<sub>1.3</sub>/TiO<sub>2</sub>--NH<sub>2</sub> and Gel<sub>2.9</sub>/TiO<sub>2</sub>--NH<sub>2</sub> by mixing Gel<sub>1.3</sub> and Gel<sub>2.9</sub> with the chemically modified TiO<sub>2</sub> NPs. These NH<sub>2</sub>capped TiO<sub>2</sub> NPs could stand in hydrogel for a long time without sedimentation and the stable gel-phase was maintained as evidenced by the rheological experiments (Figure S14, Supporting Information). As shown in Figure 5, the TiO<sub>2</sub> NPs were well immobilized and adhered on the surface of hydrogel networks after gelation and the specific surface areas were not affected obviously after the introduction of TiO<sub>2</sub>. Subsequently, the adsorption performance of the two hydrogels was verified as adsorbents for removal of the two dyes. Taking Gel1.3/ TiO<sub>2</sub>-NH<sub>2</sub> as an example, the UV-vis absorbance of dye molecules rapidly decreased and the removal efficiency could reach nearly 100% in 60 min (Figure 6a-6c). Compared to the free hydrogels, the introduction of TiO<sub>2</sub> NPs could not make any negative impact on the removal efficiency. As for the adsorption kinetics, the  $q_e$  values of  $Gel_{1,3}/TiO_2-NH_2$  and  $Gel_{2,9}/TiO_2-NH_2$ were apparently higher than those of TiO<sub>2</sub>-loaded Gel<sub>1.3</sub> and **Gel**<sub>2.9</sub>, respectively. However, the relatively smaller  $k_A$  values were found in the  $Gel_{1,3}/TiO_2-NH_2$  (Figure 6d and Table 1). This is reasonable, because the introduction of bulky NH<sub>2</sub>-capped TiO<sub>2</sub> NPs may act as steric hindrance to prevent the dye molecules from efficient accessibility in the hydrogel matrix. Indeed, after adsorption of RhB, numerous nano-sized particles could be found for the Gel<sub>1.3</sub>/TiO<sub>2</sub>--NH<sub>2</sub>, corresponding to the



Figure 5. SEM images of (a) Gel<sub>1.3</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and (b) Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and their corresponding photographs after gelation (Inset photographs). N<sub>2</sub> adsorption-desorption isotherms of (c) Gel<sub>1.3</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and (d) Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub>.

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**Figure 6.** UV-vis spectra of (a) MB (4 mg L<sup>-1</sup>) and (b) RhB (5 mg L<sup>-1</sup>) aqueous solution in the presence of Gel<sub>1.3</sub>/TiO<sub>2</sub>–NH<sub>2</sub> (2 mg mL<sup>-1</sup>) at different contacting time at 25 °C (Inset: Photographs of MB and RhB before and after adsorption); (c) Time-dependent percentage removal efficiency of MB and RhB by Gel<sub>1.3</sub>/TiO<sub>2</sub>–NH<sub>2</sub> (Inset: SEM images of Gel<sub>1.3</sub>/TiO<sub>2</sub>–NH<sub>2</sub> after adsorption for (I) MB and (II) RhB); (d) Pseudo-second-order plots for Gel<sub>1.3</sub>/TiO<sub>2</sub>–NH<sub>2</sub> towards MB and RhB (The 'x' and 'y' in the fitting equations were denoted as 't' and 't/q'<sub>t</sub>', respectively).

co-existence of aggregated TiO<sub>2</sub> NPs and dye molecules on the surface of hydrogels (Figure 6c(II), inset photos). The similar adsorption performance was also found in the group of  $Gel_{2.9}$ /TiO<sub>2</sub>-NH<sub>2</sub> (Figure S15, Supporting Information).

More gratifyingly, as expected, benefitting from the welldispersed NH<sub>2</sub>-capped TiO<sub>2</sub> NPs as photocatalysts, both Gel<sub>1.3</sub>/  $\text{TiO}_2\text{--}\text{NH}_2$  and  $\text{Gel}_{2.9}\text{/}\text{TiO}_2\text{--}\text{NH}_2$  exhibited much better photodegradability toward the adsorbed dyes than the pristine TiO<sub>2</sub>loaded hydrogels upon the UV light irradiation at under the same experimental conditions (Figure S11, Supporting Information). As shown in Figure 7, the dyes in coloured solution turned nearly colourless after adsorption followed by the light irradiation at 365 nm (Figure 7a and 7b). In addition, the photodegradation of dye molecules could be also directly realized in the hydrogels; that is, the dyes could be efficiently degraded once they were trapped by the hydrogels (Figure 7c). Accordingly, the decolorization rates for the two CD-based hydrogels could reach > 95% (Figure 7d).<sup>[28]</sup> Finally, the total organic carbon (TOC) values of the supernatants in the presence of hydrogels were compared before and after light irradiation. As shown in Table S3 (Supporting Information), the TOC values could decrease to some extent after light irradiation, suggesting that the adsorbed dyes were partially converted into fractional intermediates at the photocatalytic centres. However, it should be noted that the insufficient decomposition of adsorbed organic dyes may have potential environmental risks.<sup>[29]</sup>

# Conclusion

In conclusion, two kinds of CD-based hydrogels,  $Gel_{1,3}$  and  $Gel_{2,9}$ , were prepared via the free-radical copolymerization



Figure 7. Photodegradation performance of hydrogels. UV-vis spectra of (a) MB and (b) RhB aqueous solution in the presence of Gel<sub>1.3</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub> before and after light irradiation at 25 °C (Inset: Photographs of samples using (I) Gel<sub>1.3</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and (II) Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub>). (c) Photographs of Gel<sub>1.3</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub> with the adsorption of dyes before and after light irradiation. (d) Decolorization rates of Gel<sub>1.3</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub> with the adsorption of dyes before and after light irradiation. (d) Decolorization rates of Gel<sub>1.3</sub>/TiO<sub>2</sub>–NH<sub>2</sub> and Gel<sub>2.9</sub>/TiO<sub>2</sub>–NH<sub>2</sub> for MB and RhB.

between acrylic acid and CD-AOI with different substitution degrees. As investigated by the rheological experiments, the mechanical properties of obtained hydrogels could be easily controlled by the mass ratios and numbers of substituent groups of  $\beta$ -CD derivatives. By virtue of the high porosity of hydrogels and the abundant carboxyl groups in the main chains of polymers, adsorption kinetic studies demonstrated that both Gel<sub>1.3</sub> and Gel<sub>2.9</sub> exhibited excellent adsorption performance by selecting the positively charged MB and RhB as dye model molecules and the removal efficiency could reach above 95%. Moreover, NH<sub>2</sub>-capped TiO<sub>2</sub> nanoparticles could be well dispersed in the hydrogel matrix through electrostatic interaction while the high removal efficiency was still maintained toward the cationic dyes. Significantly, colourless solution and white solid could be obtained after the selected dyes were adsorbed and photo-degraded by the nano-scaled TiO<sub>2</sub> as photocatalysts with more than 95% of decolorization rate. Possessing the unique three-dimensional cross-linked network structures and excellent adsorption performance, our work emphasizes the superiority of CD-based supramolecular hydrogels, which may be further developed as promising adsorbents and scavengers for dye and wastewater treatments.

#### **Experimental Section**

**Synthesis of CD-AOI. CD-AOI**<sub>1.3</sub> was synthesized according to reported literature with slight modification.<sup>[16]</sup> Briefly,  $\beta$ -CD (5 g, 4.4 mmol, 1 equiv) was fully dissolved in anhydrous *N*,*N*'-dimethylformamide (DMF, 20 mL) under argon atmosphere. Then the catalyst tin(II) 2-ethylhexanoate (10  $\mu$ L) was added. After complete dissolution, 2-isocyanatoethylacrylate (AOI, 1 g, 7.1 mmol, 1.6 equiv) was added dropwise. After vigorously stirring for 1 h at room temperature, the reaction was continued at 40 °C for 4 h. The



resultant mixture was poured into acetone (400 mL) to precipitate crude product, which could be purified by repeatedly dissolving in water and then pouring into acetone to precipitate. Finally, the obtained product was dried at 35 °C for 48 h in vacuum oven.

**CD-AOI**<sub>2.9</sub> was synthesized in a similar procedure with **CD-AOI**<sub>1.3</sub> by adjusting molar ratios between  $\beta$ -CD and AOI to 1: 4.

Synthesis of TiO<sub>2</sub>–NH<sub>2</sub>. TiO<sub>2</sub>–NH<sub>2</sub> was synthesized according to reported literature with a slight improvement.<sup>[27]</sup> Silane coupling agent 3-aminopropyltriethoxysilane (KH-550, 0.5 g) was added into 1 mL ultrapure water to take prehydrolysis conducted by ultrasonic apparatus. Nano-TiO<sub>2</sub> (1.0 g) in 20 mL ethanol was added, and turbid liquid was taken under stirring at 80 °C for 6 h. After centrifugation, white solid was obtained and thoroughly washed with ethanol and water to remove the residual KH-550. The final solid was dried in a vacuum oven at 60 °C, and white product was obtained.

**Preparation of Gel**<sub>1.3</sub> **and Gel**<sub>2.9</sub>. **Gel**<sub>1.3</sub> was prepared via free radical polymerization of acrylic acid and **CD-AOI**<sub>1.3</sub> in water in the presence of potassium peroxydisulfate (KPS). Briefly, acrylic acid (72 mg) and **CD-AOI**<sub>1.3</sub> (3.6 mg, 5% m/m) were dissolved in 1 mL ultrapure water in a glass tube. After initiator KPS (2.7 mg, 1% n/n) was added, ultrasound was conducted to form homogeneous and transparent solution. Finally, polymerization was carried out in the resultant solution at 60°C for 12 h to construct transparent hydrogel.

 $Gel_{2.9}$  was prepared similarly with  $Gel_{1.3}$  by employing CD-AOI<sub>2.9</sub> instead of CD-AOI<sub>1.3</sub>.

**Preparation of TiO**<sub>2</sub>**-loaded GeI**<sub>1.3</sub> and GeI<sub>2.9</sub>. These materials were prepared by physically doping pristine TiO<sub>2</sub> nanoparticles into the solution prepared for GeI<sub>1.3</sub> and then conducting polymerization. Briefly, acrylic acid (72 mg) and CD-AOI<sub>1.3</sub> (3.6 mg, 5% *m/m*) were dissolved in 1 mL ultrapure water in a glass tube. After pristine TiO<sub>2</sub> nanoparticle (7.2 mg, 10% *m/m*) and initiator KPS (2.7 mg, 1% *n/n*) were added, ultrasound was conducted and then the resultant solution was carried out at 60 °C for 12 h to obtain hydrogel.

 $TiO_2$ -loaded  $Gel_{2.9}$  was prepared similarly by employing  $CD-AOI_{2.9}$  instead of  $CD-AOI_{1.3}$ .

Preparation of  $Gel_{1.3}/TiO_2-NH_2$  and  $Gel_{2.9}/TiO_2-NH_2$ .  $Gel_{1.3}/TiO_2-NH_2$  and  $Gel_{2.9}/TiO_2-NH_2$  were prepared similarly by employing  $NH_2$ -capped  $TiO_2$  nanoparticles instead of the pristine  $TiO_2$  nanoparticles.

Adsorption kinetic studies. All adsorption experiments were performed in 50 mL brown reagent bottle equipped with magnetic stir bars on a magnetic stirring hot plate providing 200 rpm stirring rate at ambient temperature. As for stock solution of two dyes, the concentration of MB was fixed to 400 mgL<sup>-1</sup>, and standard curve was obtained at maximum absorption wavelength ( $\lambda_{max}$ ) of 664 nm via UV-vis spectroscopy. Using the same technique, the standard curve of RhB was obtained at  $\lambda_{max}$ =554 nm, and the stock concentration was made into 500 mgL<sup>-1</sup> for the adsorption experiments.

In these studies, the adsorbent gel (20 mg) was firstly transferred to reagent bottle and then dye stock solution (10 mL) was added. After immediately mixing, 30  $\mu$ L aliquots of the supernate was taken into tubes at set intervals. The residual concentrations at different time were determined by UV-vis spectrophotometer after each sample was diluted 100 folds.

The efficiency of dye removal (%) by the gel was determined by the following equation (1):

Removal efficiency (%) = 
$$\frac{c_0 - c_t}{c_0} \times 100\%$$
 (1)

where  $c_0 \text{ (mgL}^{-1})$  was the initial concentration of dye solution,  $c_t \text{ (mgL}^{-1})$  was the residual concentration of dye solution in the presence of gel at any sample time *t*.

The amount of dyes adsorbed onto the gel  $(q_t)$  was determined by the following equation (2):

$$q_t = \frac{c_0 - c_t}{c_A} \tag{2}$$

where  $q_t (mgg^{-1})$  was the amount of dyes adsorbed per gram of gel at time *t*.  $c_0 (mgL^{-1})$  and  $c_t (mgL^{-1})$  were the initial and residual concentration of dye in stock and supernate solution.  $c_A (mgmL^{-1})$  was the concentration of adsorbent.

The adsorption kinetic process was described by pseudo-secondorder adsorption model, shown as the following equation (3):

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_A q_e^2} \tag{3}$$

where  $q_t$  (mgg<sup>-1</sup>) and  $q_e$  (mgg<sup>-1</sup>) were the amount of dyes adsorbed at time *t* and at equilibrium time.  $k_A$  (gmg<sup>-1</sup>min<sup>-1</sup>) was the apparent adsorption rate constant.

**Dye degradation studies.** Pristine  $TiO_2$  nanoparticles and  $NH_2$ capped  $TiO_2$  nanoparticles served as the candidate photocatalysts for dye degradation. The details for this experiment were carried out as follows. After the adsorption experiments finished, the obtained gels with adsorbed dye molecules by centrifugation were irradiated for 1 h at 365 nm (LED lamp, 6 W). Immersing 5 mg hydrogels with or without light illumination in 5 mL ethanol for abundant time, the concentrations of supernate were recorded on UV-vis spectrophotometer.

The decolorization rates were determined by the following equation (4):

Decolorization rate (%) = 
$$\frac{c_D - c_L}{c_D} \times 100\%$$
 (4)

where  $c_{\rm D}$  (mgL<sup>-1</sup>) and  $c_{\rm L}$  (mgL<sup>-1</sup>) were the concentrations of dye supernate solution of immersed gels without and with light illumination, respectively.

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# **Conflict of Interest**

The authors declare no conflict of interest.

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