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This work revealed that  $\beta$ -cyclodextrin was attached onto the surface of TiO<sub>2</sub> predominately by its secondary ring side, which caused paradoxical functions of  $\beta$ -cyclodextrin in the photodegradation of the four bisphenols. The equilibrium between the guest adsorbed through  $\beta$ -cyclodextrin onto TiO<sub>2</sub> and the one locked in  $\beta$ -CD in water could also change the role of  $\beta$ -cyclodextrin in the degradation of a certain guest.

Cyclodextrin (CD) modified nanomaterial, a typical type of hostmodified nanomaterial, has attracted considerable interest because of its unique properties.1-6 As one of the most common host molecules, cyclodextrin does not only alter the external morphology of the nanomaterial,<sup>7–11</sup> but also the intrinsic properties including photoactivity, photoelectric activity, energy transfer, etc.2,4,12-15 More importantly, nanomaterial can be endowed with the recognition ability for certain guest molecules after the modification with cyclodextrin,<sup>1,3,16,17</sup> which can lead to more guest-targeting and efficient functions of the nanomaterial for cyclodextrin can play a role as a "channel" or "bridge" between the guest molecules and the surface of the nanomaterial. The size/shape-fit relationship between cyclodextrin and the guest molecule, a general rule to predict the possibility of forming a complex in aqueous solution, is usually adopted in the design of cyclodextrin modified nanomaterial.<sup>13,18,19</sup> On the other hand, once cyclodextrin, whose primary ring side has smaller dimensions than its secondary ring side, is attached onto the surface of the nanomaterial, the relationship between its orientation onto the nanomaterial (through which side cyclodextrin attaches) and its inclusion routes of the guest (from which side the guest can enter the cavity of cyclodextrin) can

# $\beta$ -Cyclodextrin's orientation onto TiO<sub>2</sub> and its paradoxical role in guest's photodegradation<sup>+</sup>

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be a potential factor affecting the approach of the guest to the nanomaterial.

Cyclodextrins/TiO<sub>2</sub> (CDs/TiO<sub>2</sub>) nanomaterial is generally found to show more effective activity in the degradation of pollutants compared to TiO2.<sup>13,18,20</sup> In addition to facilitating photogenerated electron-hole separation,<sup>1,2,21</sup> the cyclodextrins are hypothesized to recognize and transfer the size/shape-fitted pollutants to TiO<sub>2</sub>.<sup>18,22</sup> The  $\beta$ -CD/TiO<sub>2</sub> nanomaterial can be easily obtained by the direct adsorption or photo-induced self-assembly of  $\beta$ -CD onto TiO<sub>2</sub>,<sup>23</sup> which is considered to be achieved by the physisorption and/or H-bonding interactions between β-CD and TiO<sub>2</sub>.<sup>6,23</sup> However, the orientation of cyclodextrin onto TiO<sub>2</sub> is not clear and has not attracted enough attention in the photodegradation of certain pollutants by CD/TiO2. Our adsorption experiments of  $\beta$ -CD and its derivatives (Fig. S1, ESI<sup>+</sup>) onto TiO<sub>2</sub> showed that their adsorption isotherms followed the Langmuir model (Fig. S2, ESI<sup>+</sup>) and the maximum adsorption capacities  $(q_{max})$ onto TiO<sub>2</sub> followed the order of  $\beta$ -CD (33 µmol g<sup>-1</sup>) > 2-O-methyl- $\beta$ -CD (15.2  $\mu$ mol g<sup>-1</sup>; DS is around 4) > 2,6-di-O-methyl- $\beta$ -CD (0  $\mu$ mol g<sup>-1</sup>; DS is 14). Those results confirmed that the hydroxyl group at ring sides of β-CD played a dominant role in its adsorption onto TiO<sub>2</sub>, though the results could not reveal the orientation of  $\beta$ -CD onto TiO<sub>2</sub>. Knowing that the specific surface area of  $TiO_2$  is approximately 250 m<sup>2</sup> g<sup>-1</sup> and the calculated surface area of the 33  $\mu$ mol  $\beta$ -CD molecule is 36.5 m<sup>2</sup>, it is also worth noting that the maximum coverage of TiO<sub>2</sub>'s surface by attached  $\beta$ -CD is calculated to be 14.6%, so the space between two attached  $\beta$ -CD molecules is still large enough for the adsorption of other guest molecules.

In this communication, a selective photodegradation phenomenon of a series of size/shape-fitted bisphenols by  $\beta$ -CD/TiO<sub>2</sub> is reported, and selectivity to guests was found be related to the orientation of cyclodextrin onto TiO<sub>2</sub> through the adsorption of the bisphenols onto  $\beta$ -CD/TiO<sub>2</sub> and their complex structures with  $\beta$ -CD in aqueous solutions were investigated. Based on the type of orientation of cyclodextrin onto TiO<sub>2</sub>, an explanation was further proposed for the paradoxical role of  $\beta$ -CD in the  $\beta$ -CD/TiO<sub>2</sub> system under different conditions. Bisphenol is a typical kind of endocrine disrupting chemical.<sup>24</sup> As listed in Table 1, bisphenol A (BPA),

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Detailed experimental description, a table showing the inclusion constants of four bisphenols with cyclodextrins and the adsorption capacity of cyclodextrins onto TiO<sub>2</sub>, <sup>1</sup>H ROESY spectra of the  $\beta$ -CD–BPE and  $\beta$ -CD–BPF complexes. See DOI: 10.1039/c2cc37244d

**Table 1** Complex stability constant ( $K_s$ ) of bisphenols with  $\beta$ -CD, observed degradation constants ( $k_{obs}$ ) and maximum adsorption capacity ( $q_{max}$ ) for bisphenols onto 1.0 g L<sup>-1</sup> TiO<sub>2</sub> in the presence and the absence of 20  $\mu$ M  $\beta$ -CD, 25 °C

		$k_{ m obs}  imes 10^2/{ m min}^{-1}$		$q_{ m max}$ /µmol g $^{-1}$	
Guest	$\log K_{\rm s}/\log {\rm M}^{-1}$	Without β-CD	With 20 μM β-CD	Without β-CD	With 20 μM β-CD
BPA BPE BPF BPAF	$\begin{array}{c} 4.9 \pm 0.3 \\ 4.6 \pm 0.4 \\ 4.2 \pm 0.2 \\ 4.4 \pm 0.3 \end{array}$	$egin{array}{c} 2.1 \pm 0.1 \ 2.3 \pm 0.1 \ 1.7 \pm 0.1 \ 1.5 \pm 0.2 \end{array}$	$\begin{array}{c} 3.9 \pm 0.1 \\ 4.2 \pm 0.3 \\ 2.9 \pm 0.3 \\ 0.0 \pm 0.0 \end{array}$	$\begin{array}{c} 5.8 \pm 0.5 \\ 4.3 \pm 0.6 \\ 5.0 \pm 2.0 \\ 7.8 \pm 1.0 \end{array}$	$\begin{array}{c} 15.7 \pm 1.6 \\ 21.8 \pm 2.2 \\ 22.2 \pm 2.0 \\ 7.0 \pm 1.2 \end{array}$

bisphenol E (BPE), bisphenol F (BPF) and bisphenol AF (BPAF) were decomposed in TiO<sub>2</sub> dispersion with similar degradation kinetic constants ( $k_{obs}$ ). Stability constants ( $K_s$ ) for 1 : 1 complexes of  $\beta$ -CD with all these four bisphenols were very high (more than  $10^4 \text{ M}^{-1}$ ), which suggested that β-CD strongly included all these bisphenols in aqueous solutions. However, it is interesting to find that  $\beta$ -CD showed distinguishable effects on the degradation of these bisphenols by TiO2. The photodegradation of 5 µM BPA, BPE or BPF in 1.0 g  $L^{-1}$  TiO<sub>2</sub> dispersion was highly promoted in the presence of 20  $\mu$ M  $\beta$ -CD, while the photodegradation of 5  $\mu$ M BPAF was selectively totally inhibited in the presence of 20  $\mu$ M  $\beta$ -CD (Fig. 1). Since cyclodextrin is considered as a "channel" to recognize and transfer the guest to TiO<sub>2</sub>, the adsorption of the bisphenols onto β-CD/TiO2 could provide some useful information to reveal the difference between BPAF and the other three bisphenols in the degradation by  $\beta$ -CD/TiO<sub>2</sub>. As listed in Table 1, the adsorption of BPAF on TiO<sub>2</sub> shows no change in the presence and the absence of 20  $\mu$ M  $\beta$ -CD, while the adsorption of other three bisphenols considerably increased in the presence of 20  $\mu$ M  $\beta$ -CD. The distinct results of BPAF against the other bisphenols suggest that β-CD cannot effectively transfer BPAF to TiO<sub>2</sub>, in other words, BPAF actually cannot access the attached  $\beta$ -CD, even though it can be easily included into  $\beta$ -CD in aqueous solution.

Further complex structure studies revealed the difference between BPAF and the other bisphenols in the interaction with  $\beta$ -CD in aqueous solution. 2D ROESY is a powerful technique for investigating the complex structures of  $\beta$ -CD. The NOE correlation between the protons of the guest and the inner protons of the  $\beta$ -CD cavity (H-3 at the secondary ring side and H-5 at the primary ring side) is determined from the ROESY spectrum when the guest is included in the  $\beta$ -CD cavity. As shown in Fig. 2, the ROESY



spectrum of the β-CD-BPAF complex displayed clear NOE crosspeaks between the Hb and the H-3/H-5 (peaks A and B) and between the Ha and the H-5 (peak C), which indicated that the phenyl ring of BPAF was deeply included in the hydrophobic cavity of  $\beta$ -CD. Much more important was the fact that no NOE cross-peak between Ha and H-3 was observed, which revealed that Ha was not close to the secondary ring side of  $\beta$ -CD in the structure of the complex, that is, the phenyl ring of BPAF predominately penetrated into the  $\beta$ -CD cavity from the secondary ring side (Scheme 1a). In contrast, besides the same NOE cross-peaks observed in the ROESY spectrum of B-CD-BPAF, the clear NOE cross-peaks between Ha and H-3 were also observed in the ROESY spectra of  $\beta$ -CD-BPA,<sup>25</sup>  $\beta$ -CD-BPE (Fig. S3, ESI<sup>†</sup>) or  $\beta$ -CD-BPF (Fig. S4, ESI<sup>†</sup>). They corresponded to two equilibrium structures of those three complexes in aqueous solution, where the phenyl ring of BPA, BPE or BPF could be included into the  $\beta$ -CD cavity from both the primary ring side and the secondary ring side (Scheme 1b).<sup>25</sup>

From the observation that BPAF can mainly access  $\beta$ -CD from the secondary ring side of  $\beta$ -CD and cannot access the attached  $\beta$ -CD on the surface of TiO<sub>2</sub>, it can be deduced that mostly the secondary ring side of  $\beta$ -CD should face the TiO<sub>2</sub> surface and consequently be blocked when  $\beta$ -CD is attached onto the TiO<sub>2</sub> surface (Scheme 2). So  $\beta$ -CD adsorbs onto TiO<sub>2</sub> mainly through its secondary ring side. Because of this orientation of  $\beta$ -CD onto TiO<sub>2</sub>, guest molecules, such as BPA, BPE or BPF, that are able to enter  $\beta$ -CD from the primary ring side can be "transferred" onto TiO<sub>2</sub> more efficiently through  $\beta$ -CD and degraded. The other important thing to note is that the photodegradation of BPAF by TiO<sub>2</sub> was



**Fig. 1** Effect of 20 μM β-CD on the photodegradation of bisphenols in 1.0 g L<sup>-1</sup> TiO<sub>2</sub> suspension at 25 °C.  $\Delta k_{obs} = k_{obs} - k_{obs0}$ ,  $k_{obs}$  and  $k_{obs0}$  are the degradation kinetic constants for bisphenols in the presence and in the absence of β-CD, respectively.



**Scheme 1** Possible structure of the complexes BPAF– $\beta$ -CD (a) and BPA– $\beta$ -CD, BPE– $\beta$ -CD, BPF– $\beta$ -CD (b) in aqueous solution.



Scheme 2 Mechanism for the adsorption of BPE and BPAF in  $\beta\text{-CD/TiO}_2$  suspension.



Fig. 3 Effect of concentrations of cyclodextrins on the photodegradation of 5  $\mu$ M BPE or BPAF in 1.0 g L<sup>-1</sup> TiO<sub>2</sub> suspension.

totally inhibited in the presence of 20  $\mu$ M  $\beta$ -CD, though BPAF still has the same adsorption amount on  $\beta$ -CD/TiO<sub>2</sub> as the amount on TiO<sub>2</sub> without  $\beta$ -CD. A plausible explanation is that  $\beta$ -CD has higher reactivity with the photogenerated reactive species including the valence band hole, the hydroxyl radical, etc. than that of BPAF.<sup>2,8,13,26</sup> To further support the hypothesis of the orientation of β-CD onto TiO2, the effects of 2-O-methyl-β-CD and 2,6-di-Omethyl-\beta-CD, which have similar inclusion ability for BPAF in aqueous solution to  $\beta$ -CD (Table S1, ESI<sup>+</sup>), on the photodegradation of BPAF were also investigated. The results clearly showed that both  $\beta$ -CD derivatives retard the photodegradation of BPAF in TiO<sub>2</sub> dispersion (Fig. 3). The retardation extent followed the order of  $\beta$ -CD > 2-O-methyl- $\beta$ -CD > 2,6-di-O-methyl- $\beta$ -CD, which is the same trend as the amount of hydroxyl groups at the secondary ring side of cyclodextrins and as the adsorption amounts of  $\beta$ -CD and its derivatives onto TiO<sub>2</sub>. This showed that the more hydroxyl groups present at the second ring side of cyclodextrin, the more amount of cyclodextrin attached onto TiO2 through those hydroxyl groups, and the higher retardation effect on the degradation of BPAF occurred. In contrast, cyclodextrins (except 2,6-di-O-methyl-β-CD) showed promotion effects on the degradation of BPE, which also followed the order of the amount of hydroxyl groups at the secondary ring side. 2,6-Di-O-methyl-β-CD did not adsorb onto TiO<sub>2</sub>, but it had a retardation effect on the photodegradation of the guest by TiO<sub>2</sub>. It was probably because the inclusion of cyclodextrin and BPE in bulk solution reduced the diffusion of BPE onto the surface of TiO<sub>2</sub>. It was also interesting that the ratio of  $\Delta k_{\rm obs}/k_{\rm obs_0}$  for BPE first increased with the increase of  $\beta$ -CD concentration to 20  $\mu$ M

(Fig. 3). However, further increase of  $\beta$ -CD concentration led to the decrease of the promotion extent. It was probably because further increase of  $\beta$ -CD concentration could only result in the increase of the bulk phase  $\beta$ -CD amount ( $\beta$ -CD<sub>free</sub>) rather than the attached  $\beta$ -CD amount ( $\beta$ -CD<sub>attached</sub>) (Scheme 2).  $\beta$ -CD<sub>free</sub> is supposed to play the same role as 2,6-di-O-methyl- $\beta$ -CD does, which could retard the diffusion onto TiO<sub>2</sub> and subsequently slow down the degradation of BPE.

In conclusion, it was uncovered that  $\beta$ -CD was attached onto TiO<sub>2</sub> mainly through its secondary ring side from the studies of the adsorption and the complex structures of four bisphenols. The orientation of  $\beta$ -CD onto TiO<sub>2</sub> reveals that  $\beta$ -CD has a distinct influence on the degradation kinetic results of BPAF from BPA, BPE or BPF. On the other hand, the equilibrium between the guest adsorbed on the surface of TiO<sub>2</sub> through attached  $\beta$ -CD and the one locked in  $\beta$ -CD in bulk solution is another factor that affects the approach of the guest to TiO<sub>2</sub> and consequently changes the role of  $\beta$ -CD in the guest's photodegradation.

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