

# Easily Recoverable, Micrometer-Sized TiO<sub>2</sub> Hierarchical Spheres Decorated with Cyclodextrin for Enhanced Photocatalytic **Degradation of Organic Micropollutants**

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Supporting Information

ABSTRACT: Micrometer-sized titanium dioxide hierarchical spheres (TiO<sub>2</sub>-HS) were assembled from nanosheets to address two common limitations of photocatalytic water treatment: (1) inefficiency associated with scavenging of oxidation capacity by nontarget water constituents and (2) energy-intensive separation and recovery of the photocatalyst slurry. These micrometer-sized spheres are amenable to low-energy separation, and over 99% were recaptured from both batch and continuous flow reactors using microfiltration. Using nanosheets as building blocks resulted in a large specific surface area-3 times larger than that of commercially available TiO<sub>2</sub> powder (Evonik P25). Anchoring foodgrade cyclodextrin onto TiO2-HS (i.e., CD-TiO2-HS) provided hydrophobic cavities to entrap organic contaminants for more effective utilization of photocatalytically generated reactive oxygen species. CD-TiO<sub>2</sub>-HS removed over 99% of various contaminants with dissimilar hydrophobicity (i.e., bisphenol A, bisphenol S, 2-naphthol, and 2,4dichlorophenol) within 2 h under a low-intensity UVA input (3.64  $\times$  10<sup>-6</sup> einstein/L/ s). As with other catalyst (including  $TiO_2$  slurry), periodic replacement or replenishment



would be needed to maintain high treatment efficiency (e.g., we demonstrate full reactivation through simple reanchoring of CD). Nevertheless, this task would be offset by significant savings in photocatalyst separation. Thus, CD-TiO2-HS is an attractive candidate for photocatalytic water and wastewater treatment of recalcitrant organic pollutants.

## INTRODUCTION

The need for technological innovation to efficiently remove contaminants of emerging concern (such as endocrine disruptors) during water treatment and wastewater reuse has stimulated extensive research on advanced oxidation processes (AOPs), including photocatalysis.<sup>1-3</sup> Among the various photocatalysts available, titanium dioxide (TiO<sub>2</sub>) offers the advantages of being physically robust, relatively inexpensive, environmentally benign, and highly photoactive.<sup>4-6</sup> Therefore, TiO<sub>2</sub> has been widely considered for use in photocatalytic AOPs.<sup>7–9</sup> Extensive research has been conducted to improve the photocatalytic properties of TiO<sub>2</sub>. Inspired by exfoliation of single-layer graphene,<sup>10</sup> several researchers have synthesized ultrathin two-dimensional (2D)  $TiO_2$  nanosheets<sup>11-13</sup> to achieve a large surface area, superior transparency, and strong quantum confinement of electrons.<sup>14,15</sup> Nanosheets also offer a precise control over facet growth to obtain high-energy surfaces (e.g., 90  $J/m^2$  for 001 facets)<sup>12</sup> for superior photoactivity activity.<sup>11,16</sup>

Although significant progress has been made in synthesizing a wide variety of photocatalysts, few of these nanomaterials have found practical applications.<sup>17</sup> One challenge is that photocatalysts are commonly used as a well-mixed slurry (to minimize mass transfer limitations), and their small size requires high-energy separation processes such as ultrafiltration or nanofiltration to prevent their release into treated water and enable recovery for reuse. Separation and recovery of TiO<sub>2</sub> slurry can require more energy than the UV lamps used for photoexcitation.<sup>17</sup> Another barrier is that the limited durability of TiO<sub>2</sub> heteroarchitectures, composed of TiO<sub>2</sub> hybridized with other functional elements, often prevents efficient reuse.<sup>18</sup> Finally, similar to other photocatalysts, TiO<sub>2</sub>-based materials suffer from inefficient oxidation of target priority pollutants due to scavenging of oxidizing species (e.g., reactive oxygen species (ROS) such as hydroxyl radicals ( $\cdot$ OH) and superoxide  $(O_2^{\bullet-})$  and photogenerated holes  $(h^+)$  by nontarget substrates and minerals.<sup>19,20</sup> This is compounded by the fact that the TiO<sub>2</sub> surface is hydrophilic<sup>21,22</sup> and has little affinity for hydrophobic organic pollutants of emerging concern, such

August 2, 2018 Received: **Revised:** September 28, 2018 Accepted: October 1, 2018 Published: October 1, 2018

as most pharmaceuticals, personal care products, and other endocrine disrupting chemicals.<sup>23,24</sup> These technical barriers underscore the need for novel  $TiO_2$  composites that are robust, more efficient at adsorbing priority nonpolar pollutants near active sites and catalyzing their photocatalytic destruction, and are amenable for easy (low-energy) separation and reuse.

Our approach to enhance the affinity of  $TiO_2$  for nonpolar priority pollutants (and bring them closer to ROS generation sites) is to anchor carboxymethyl- $\beta$ -cyclodextrin (CD) onto the photocatalyst surface.<sup>25</sup> CD is a promising adsorbent for separation and complexation of various water contaminants such as bisphenol A, DDT, and ethinyl estradiol.<sup>26–28</sup> Its peculiar molecular structure, exhibiting a hydrophobic cavity packed by two hydrophilic outer surfaces, endows it with outstanding capability to entrap hydrophobic molecules,<sup>29–32</sup> which would facilitate concentrating them near ROSgenerating sites for more efficient photocatalytic degradation. Food-grade cyclodextrin is widely used for drug delivery<sup>33</sup> and should be relatively benign for water treatment applications.<sup>34,35</sup>

Here we report a novel and facile method to synthesize micrometer-sized TiO<sub>2</sub> hierarchical spheres (TiO<sub>2</sub>-HS) that offer several advantages over existing TiO2-based photocatalysts. The relatively large size of TiO<sub>2</sub>-HS (3-5  $\mu$ m, compared to previously reported TiO<sub>2</sub> spheres with hierarchical structures of 10 nm to submicrometer sizes<sup>36–39</sup>) offers an opportunity to save energy during photocatalyst recovery for reuse via (low-pressure) microfiltration. The use of nanosheets as building blocks ensures a large specific surface area (even larger than Evonik P25). CD was anchored onto the surface of the spheres to provide hydrophobic sites to entrap and concentrate organic contaminants for more effective photocatalytic degradation. Various pollutants of dissimilar hydrophobicity (i.e., bisphenol A (BPA), bisphenol S (BPS), 2-naphthol, and 2,4-dichlorophenol (2,4-DCP)) were tested under different conditions to assess the applicability of CD-TiO<sub>2</sub>-HS. Recycling tests and surface chemistry (XPS) analyses were also conducted to assess photocatalyst stability. Photocatalytic performance and ease of separation for reuse were benchmarked against P25 to demonstrate the technical feasibility of this novel material for advanced water purification.

#### MATERIALS AND METHODS

**Chemicals.** Titanium isopropoxide  $[Ti(OCH(CH_3)_2)_4, TIP, \ge 97\%]$ , P25 ( $\ge 99.5\%$ ), triethanolamine ( $\ge 99\%$ ), diethanolamine ( $\ge 99\%$ ), oleylamine (70%), octylamine, hexamethylenetetramine ( $\ge 99\%$ ), *N*,*N*-dimethylformamide (DMF,  $\ge 99.8\%$ ), cyanamide ( $\ge 99\%$ ), bisphenol A (BPA,  $\ge 99\%$ ), bisphenol S (BPS,  $\ge 99\%$ ), 2-naphthol ( $\ge 99\%$ ), 2,4-dichlorophenol (2,4-DCP,  $\ge 99\%$ ),  $\beta$ -cyclodextrin ( $\ge 99\%$ ), monochloroacetic acid ( $\ge 99\%$ ), superoxide dismutase (SOD), and sodium hydroxide ( $\ge 99\%$ ) were purchased from Sigma-Aldrich and used as received. Hydrochloric acid (36.5%), sulfuric acid (98%), and absolute ethanol were purchased from Millipore-Sigma.

**Synthesis of Carboxymethyl-\beta-cyclodextrin (CD).** CD was prepared via a modified method reported by Chalasani.<sup>25</sup> Briefly, 6 g of  $\beta$ -cyclodextrin was dissolved in 10 mL of water and further mixed with 20 mL of NaOH solution (7 N). Monochloroacetic acid solution (16.3%) was then added into the above solution. This final mixture was then adjusted to pH = 4 with HCl, transferred to a flask, and water bathed at 60 °C

for 4 h. Methanol (50 mL) and acetone (100 mL) were added sequentially to precipitate CD out after the solution cooled to room temperature. The white CD was collected through centrifugation, washed with water thoroughly, and dried at 45  $^\circ$ C overnight.

Synthesis of TiO<sub>2</sub> Hierarchical Sphere (TiO<sub>2</sub>-HS) and CD-TiO<sub>2</sub>-HS. Triethanolamine (20 mL) was mixed with 10 mL of DMF under vigorous stirring for 30 min to obtain homogeneous solution. To this solution, 1.2 mL of TIP was added dropwise. This solution was stirred for another 30 min and then transferred to a 50 mL, Teflon-lined stainless-steel autoclave. The autoclave was then sealed and heated at 200 °C for 24 h. The white precipitate was harvested by centrifugation and washed thoroughly with ultrapure water and ethanol in sequence. TiO<sub>2</sub>-HS was then obtained through drying asobtained precipitate under 60 °C overnight. Samples were then calcinated in air at a ramp rate of 4 °C/min for 2 h and maintained at 500 °C for another 2 h in a tube furnace (STF 1200, Across International). Surface modification through CD anchoring was then used to treat as-prepared TiO<sub>2</sub>-HS. CD (100 mg) and TiO<sub>2</sub>-HS (200 mg) were dispersed in 25 mL of water that had been preadjusted to pH = 6 using phosphate buffer (0.1 M). To this dispersion, 200  $\mu$ L of cyanamide (50%) aqueous solution) was added. The reaction dispersion was then refluxed under 90 °C in oil bath for 6 h. The product was collected and washed with water thoroughly to remove possible free-standing CD molecules.

Characterization of CD-TiO<sub>2</sub>-HS. The morphology was observed with an environmental scanning electron microscope (ESEM, FEI Quanta 400F) with high voltage (20 kV) under high vacuum mode (chamber pressure  $1.45 \times 10^{-4}$  Pa). Transmission electron microscopy (TEM) images and highresolution TEM analyses were performed by using a JEOL-2010 TEM with an acceleration voltage of 200 kV. The composition and phase of CD-TiO2-HS were evaluated using powder X-ray diffraction (XRD, Rigaku DMAX) with Cu K $\alpha$ radiation ( $\lambda = 1.54178$  Å). The specific surface was measured using a Brunauer-Emmett-Teller (BET) surface analyzer (Autosorb-3B, Quantachrome Instruments). The characterization of surface-anchored CD was performed using a FTIR (Fourier transform infrared spectra) microscope (Nicolet iS50 FTIR, Thermo Scientific) scanning from 4000 to 400 cm<sup>-1</sup> in a KBr tablet. The CD-TiO<sub>2</sub>-HS particle size was determined by dynamic light scattering (DLS) using a FOQELS particle size analyzer (Brookhaven). Surface chemistry was analyzed by Xray photoelectron spectroscopy (XPS) using a PHI Quantera SXM scanning X-ray microprobe system using a 100  $\mu$ m X-ray beam of which the takeoff angle was 45°. The pass energy was 140 eV for the survey and 26 eV for the high-resolution elemental analysis. Thermogravimetric analysis (TGA) was performed on SDT Q600 (TA Instruments) at a heating rate of 10 °C/min from room temperature to 700 °C with a flowing air gas stream of 50 mL/min.

**Photocatalytic Treatment Tests.** Various contaminants with dissimilar hydrophobicity were selected to evaluate the photocatalytic performance of CD-TiO<sub>2</sub>-HS in aqueous systems. Tested contaminants included BPA, an endocrine disrupting chemical considered a contaminant of emerging concern;<sup>40,41</sup> BPS, a BPA substitute which has recently been reported to exhibit estrogenic effects;<sup>42</sup> 2-naphthol, a model compound for naphthol contaminants; and 2,4-DCP, a cytotoxic intermediate during preparation of herbicides.<sup>43</sup> A custom-designed photoreactor (Figure S1) was used for batch





Figure 1. Two-step synthesis of  $CD-TiO_2$ -HS. Fabrication of  $TiO_2$ -HS through one-pot hydrothermal reaction followed by surface anchoring of CD.



Figure 2. SEM images of (a) CD-TiO<sub>2</sub>-HS single particle and (b) nanosheets building blocks show micrometer sized and hierarchical structure. HR-TEM images of (c) edge of CD-TiO<sub>2</sub>-HS and (d) magnification of selected spot illustrates the thinness (7.5-10 nm) of these nanosheets.

scale photocatalytic tests. Six UVA lamps (4 W, F4T5/BLB) were installed in the reactor; these provided a total light intensity of  $3.64 \times 10^{-6}$  einstein/L/s (their UVA spectrum is shown in Figure S2). The catalyst (10 mg) was dispersed in 40 mL of solution containing 20 ppm of contaminant at the beginning of photoreaction. Although such concentrations are relatively high compared to those encountered in national waters, they are within the range reported for industrial wastewater<sup>44</sup> and facilitate kinetic measurements. This suspension was stirred and equilibrated for 24 h, and the concentration of BPA was adjusted to 20 ppm before irradiation. Aliquots (1 mL) were taken after predetermined

intervals of irradiation time, and the catalysts were filtered out using a 0.22  $\mu$ m PTFE syringe filter. The contaminants in aliquots were measured using high-performance liquid chromatograph (HPLC, LC-20AT Shimadzu) equipped with a UV-vis detector (Table S1). To determine the adsorption isotherm, 0.25 mg/mL catalyst dispersion was prepared in which the BPA concentration was set to a range from 5 to 40 ppm. These dispersions were stirred vigorously for 24 h to reach adsorption equilibrium. BPA degradation tests were also conducted in the presence of various ROS (and h<sup>+</sup>) scavengers to determine the primary oxidant(s). The scavengers tested include 1 mM isopropanol (IPA) for  $\cdot$ OH, 50 kU/L superoxide



Figure 3. (a) XRD patterns of amorphous TiO<sub>2</sub>-HS, TiO<sub>2</sub>-HS, and CD-TiO<sub>2</sub>-HS with Cu K $\alpha$  radiation ( $\lambda$  = 1.54178 Å). A pure anatase phase was obtained after thermal treatment of amorphous TiO<sub>2</sub>-HS. (b) FTIR spectra of CD, CD-TiO<sub>2</sub>-HS, and CD-TiO<sub>2</sub>-HS exposed to UVA for 300 h indicates successful and stable surface anchoring of cyclodextrin. (c) Thermogravimetric analysis of CD-TiO<sub>2</sub>-HS before and after 300 h of UVA irradiation indicates no significant loss of CD after UV exposure.

dismutase (SOD) for  $\cdot O_2^-$ , and 1 mM sodium acetate (Acet) for electron holes (h<sup>+</sup>).

**Catalyst Recovery.** A separation test in batch scale was performed by filtering 200 mL of CD-TiO<sub>2</sub>-HS dispersion (0.25 mg/mL) through an Omnipore PTFE (polytetrafluoro-ethylene) membrane (JCWP04700, Millipore-Sigma) of different nominal pore sizes. The membrane was assembled into a Millipore Sigma Amicon filtration cell, and filtrate was collected for further TiO<sub>2</sub> quantification. To achieve over 99.5% recovery, a submicrometer (0.8  $\mu$ m) pore-size membrane was used for P25 separation, while an 11  $\mu$ m pore-size membrane is employed for CD-TiO<sub>2</sub>-HS. The differential pressure required for catalyst recovery was measured by a customized pressure vessel (Alloy Products Corp.).

Acid digestion of  $\text{TiO}_2$  was performed to turn potentially leached undissolved  $\text{TiO}_2$  into dissolved  $\text{Ti}^{4+}$ , in preparation for the inductively coupled plasma optical emission spectrometry (ICP-OES) measurement. Acid digestion followed the protocol described by Standard method 3030 G for water and wastewater analysis.<sup>45,46</sup> Ti<sup>4+</sup> concentration was evaluated by ICP 4300 with plasma flow of 15 mL/min and nebulizer flow of 0.7 mL/min.

**Catalyst Stability and Reuse Test.** The stability of CD-TiO<sub>2</sub>-HS photoactivity was tested through repeated usage for 10 cycles. At the beginning of each cycle, the BPA concentration in solution was 20 mg/L, and catalysts were collected and dried for next cycle after 2 h of UVA irradiation. The photoactivity of the catalyst was also evaluated after longterm use in water (100–500 h) to assess its stability. The catalyst after use was characterized with TGA, FTIR, and XPS to discern possible chemical changes of surface-anchored CD.

#### RESULTS AND DISCUSSION

Size Controlled Synthesis of Cyclodextrin-Anchored TiO<sub>2</sub> Hierarchical Sphere. A novel strategy to synthesize micrometer sized TiO<sub>2</sub>-HS was developed, and the photocatalyst was subsequently coated with CD (i.e., CD-TiO<sub>2</sub>-HS, Figure 1) to respectively address two common limitations of photocatalytic water treatment: (1) energy-intensive separation and recovery of the photocatalyst slurry and (2) inefficiency associated with scavenging of oxidation capacity by nontarget water constituents. First, TiO<sub>2</sub>-HS was fabricated through a simple one-pot hydrothermal method (Figure 1). Different synthesis conditions were used to better understand the

formation mechanism of this nanosheet assembled flowerlike sphere. It is postulated that nucleation sites were originally formed through Ostwald ripening.<sup>47</sup> Triethanolamine was used as structure-directing agent to induce randomly oriented anisotropic growth of TiO<sub>2</sub> nanosheets.<sup>48</sup> After extended hydrothermal reaction, these nanosheets readily self-organize and grow into hierarchical spheres with large diameters, since the nanosheets are fairly supple.<sup>49</sup> Further SEM analyses of samples collected at different intervals during hydrothermal reaction corroborated the postulated growth mechanism of TiO<sub>2</sub>-HS (Figure S3).

Figure 2 shows the SEM images of CD-TiO<sub>2</sub>-HS, in which the constituent nanosheets and mesoporous structure are clearly visible. The diameter of TiO2-HS particles was in the range  $3-5 \ \mu m$  (Figure 2a,b), which was corroborated by dynamic light scattering (DLS) (i.e., the average hydrodynamic diameter of 3.75  $\mu$ m, Table S2). These particles are much larger than previously reported TiO<sub>2</sub> spheres with hierarchical structures (10 nm to submicrometer sizes).<sup>36,38,50</sup> This relatively large size was achieved without sacrificing large surface area due to the nanosheet-based hierarchical structure. Specifically, CD-TiO<sub>2</sub>-HS had a BET surface area of 145.2  $m^2/$ g compared to 50.8 m<sup>2</sup>/g for P25 TiO<sub>2</sub> (Table S3) and 49.6-170  $\text{m}^2/\text{g}$  for previously reported TiO<sub>2</sub> spheres with hierarchical structures.<sup>36,37,50</sup> The benefits of the larger particle size related to more facile photocatalyst recovery with lower energy consumption are discussed later. Figure 2c shows highresolution transmission electron microscopy (HR-TEM) image of CD-TiO<sub>2</sub>-HS surface with irregularly oriented nanosheets. This corroborates that CD-TiO2-HS had a hierarchical structure assembled from nanosheets. The typical thickness of nanosheets was 7.5-10 nm based on the TEM image (Figure 2d). Similar nanosheet thicknesses have been reported for submicrometer sized TiO<sub>2</sub> photocatalyst with hierarchical structures (7-20 nm).<sup>36-38</sup>

The hydrothermal reaction product was amorphous, based on its XRD pattern (Figure 3a). TiO<sub>2</sub>-HS after calcination is composed of pure anatase crystallites (JCPDS 21-1272) and shows a typical major peak at  $2\theta = 25^{\circ}$  (101), along with five minor peaks at  $2\theta = 37.87^{\circ}$  (004),  $48.24^{\circ}$  (200),  $54.86^{\circ}$  (211),  $63.01^{\circ}$  (204), and  $69.10^{\circ}$  (220)<sup>51</sup> in the XRD pattern. Surface capping with CD did not affect the crystallites, as indicated by the virtually identical XRD patterns for both TiO<sub>2</sub>-HS and CD-TiO<sub>2</sub>-HS (Figure 3a). Successful anchoring of CD was confirmed through peak identification from the FTIR spectrum

(Figure 3b). Three bands at 2929, 1157, and 1029 cm<sup>-1</sup> were identified from the spectra of CD-TiO<sub>2</sub>-HS which represent C-H stretch, C-O stretch of cyclodextrin, and the O-C-O antisymmetric glycosidic vibrational modes, respectively.<sup>25</sup> CD was anchored onto TiO<sub>2</sub>-HS through covalent Ti-O-C bonds.<sup>52</sup> TGA analysis shows that 20% (w/w) of CD-TiO<sub>2</sub>-HS was composed of CD molecules (Figure 3c).

Improved Photocatalytic Treatment by  $TiO_2$ -HS through CD Anchoring. CD anchoring significantly enhanced the photoactivity of  $TiO_2$ -HS (Figure 4a). Using



**Figure 4.** Photocatalytic degradation of bisphenol A enhanced by cyclodextrin coating. (a) CD-TiO<sub>2</sub>-HS degraded BPA (20 ppm) faster than TiO<sub>2</sub>-HS. All tests were conducted with 0.25 mg/mL TiO<sub>2</sub>-HS and CD-TiO<sub>2</sub>-HS under UVA irradiation (365 nm, 0.675 mW/cm<sup>2</sup>) at pH = 6.86. (b) TOC (initial concentration of 16 ppm) removal within 3 h without catalyst and in the presence of TiO<sub>2</sub>-HS and CD-TiO<sub>2</sub>-HS.

an identical amount (0.25 mg/mL) of catalysts, 90% removal of BPA was achieved within 1 h with CD-TiO<sub>2</sub>-HS versus 2.5 h with TiO<sub>2</sub>-HS. BPA degradation followed first-order kinetics with a rate constant (k) of 0.049  $\pm$  0.006 min<sup>-1</sup> for CD-TiO<sub>2</sub>-HS, which is 2.6-fold higher than that for TiO<sub>2</sub>-HS (0.019  $\pm$  0.002 min<sup>-1</sup>) (Table S4). About 85.1% of BPA was mineralized within 3 h in the presence of CD-TiO<sub>2</sub>-HS (versus 65.6% for CD-TiO<sub>2</sub>) as indicated by the removal of total organic carbon (TOC) (Figure 4b). BPA degradation tests were also conducted in the presence of various ROS (and h<sup>+</sup>) scavengers to determine the primary oxidant(s). Results indicate that hydroxyl radicals were the dominant oxidant responsible for photocatalytic degradation of BPA (Figure S4).

The improved photoactivity of CD-TiO<sub>2</sub>-HS was likely due to BPA sorption by CD near photocatalytic sites.<sup>23,53</sup> The central cavity of CD is composed of glucose monomers linked with skeletal carbon and ethereal oxygen.<sup>54</sup> Therefore, the anchored CD molecules create hydrophobic cavities that can sorb BPA<sup>29</sup> and concentrate it on the particle surface where heterogeneous photocatalysis takes place. The photogenerated ROS (with typical lifetimes of only a few microseconds)<sup>55–57</sup> would, therefore, have a higher likelihood of oxidizing BPA (or other adsorbed priority pollutants) rather than being scavenged by other constituents in the bulk solution. Enhanced BPA sorption capacity as a result of CD surface capping was confirmed through adsorption kinetics and isotherm analyses (Figure 5). BPA adsorption followed pseudo-second-order



**Figure 5.** Cyclodextrin coating enhanced BPA sorption by  $TiO_2$ -HS. (a) Equilibrium is reached in about 24 h for both systems and (b) anchoring CD onto  $TiO_2$ -HS (i.e., CD- $TiO_2$ -HS) significantly increases the sorption capacity.

kinetics (Figure S5), and equilibrium was reached at about 20 h. Equilibrium adsorption was adequately described by the Langmuir isotherm, and the maximum adsorption capacity was 2.5-fold higher for CD-TiO<sub>2</sub>-HS than pristine  $TiO_2$ -HS.

Photocatalytic degradation tests were also conducted with BPS, 2-naphthol, and 2,4-DCP to evaluate removal of contaminants with different hydrophobicity (Figure S6 and Table S5). First-order rate constants for degradation of BPS, 2-naphthol, and 2,4-DCP by CD-TiO<sub>2</sub>-HS were 0.034  $\pm$  0.004, 0.033  $\pm$  0.002, and 0.060  $\pm$  0.010 min<sup>-1</sup>, respectively. Compared with TiO<sub>2</sub>-HS, CD anchoring increased the removal rate of BPS, 2-naphthol, and 2,4-DCP by 2.6-, 1.5-, and 6-fold, respectively. This is consistent with our hypothesis that enhanced contaminant entrapment by CD close to photocatalytic sites enhances treatment and supports our

"bait—hook—destroy" strategy to enhance photocatalytic water treatment.  $^{58}$ 

Tests were also conducted with a mixture of the aforementioned contaminants to gain further insight into the removal process when several competing species are present (Figure S7). The photodegradation of each contaminant was inhibited in the presence of other compounds competing for ROS, though CD anchoring (and associated entrapment) again enhanced degradation kinetics relative to uncoated TiO<sub>2</sub>-HS (Table S5). This enhancement was not correlated to the hydrophobicity of the contaminants (indicated by log  $K_{ow}$ ) (Figure S8), which is consistent with a previous report that CD can entrap a wide range of pollutants with different hydrophobicity.<sup>29</sup>

Photocatalytic degradation tests with BPA were also conducted in the context of secondary effluent polishing. The secondary effluent (TOC = 17 mg/L) was collected from an activated sludge treatment plant (West University Place, Houston, TX) (Table S6). A decrease in degradation efficiency was observed for BPA spiked into the effluent compared to DI water, possibly due to the presence of background ROS scavengers.<sup>59,60</sup> In DI water, 99.7% of BPA was removed within 2 h, while only 79.6% of BPA was degraded after 3 h treatment in secondary effluent. BPA degradation by CD-TiO<sub>2</sub>-HS in secondary effluent was monitored over four cycles (Figure S9). Progressive loss of photoactivity was observed in these tests, with BPA removal decreasing to 29.8% by the fourth cycle. This loss of photocatalytic activity can be partly attributed to organic matter present in the secondary effluent (EfOM), which not only scavenges photogenerated ROS but also competes with BPA for CD sorption sites. These data corroborate that photocatalytic water treatment efficiency generally decreases from ideal systems (e.g., DI water) to more realistic scenarios in the presence of inhibitory com-pounds.<sup>20,61</sup> Nevertheless, whereas secondary effluent polishing with CD-TiO<sub>2</sub>-HS experienced a significant decrease in efficiency, this decrease was not as dramatic as that observed with P25 slurry, which exhibited only 10.6% BPA removal after the first cycle (Figure S9). Apparently, photocatalytic treatment with P25 is more susceptible to inhibition by EfOM because (unlike CD-TiO2-HS) it does not concentrate BPA near photocatalytic sites to minimize ROS scavenging.

Photoactive stability of P25 in a secondary effluent was also evaluated through similar cycling tests. P25 lost its photoactivity faster than CD-TiO<sub>2</sub>-HS (e.g., only 10.5% of BPA was removed by P25 on the second cycle (Figure S9)). Significant aggregation of P25 (Table S2), possibly exacerbated by multivalent ions such as  $Ca^{2+}$ ,  $6^{62}$  is conducive to decreased surface area and photoactivity. 62,63 Aggregation of CD-TiO<sub>2</sub>-HS was less favorable due to its micrometer-sized primary particle structure, 64 which is an important advantage.

Low-Energy Photocatalyst Recovery via Microfiltration. The application of commercial TiO<sub>2</sub> nanoparticles (such as P25 and P90) as photocatalytic slurries requires separation (often via ultrafiltration or nanofiltration) to prevent release into treated water and recover for reuse. This consumes significant amounts of energy which, in some cases, can even exceed the energy consumption of the UV lamps needed to induce photocatalytic degradation.<sup>17</sup> The relatively large size of CD-TiO<sub>2</sub>-HS without sacrificing surface area relative to nanosized particles would therefore be critical to lower the energy requirements for photocatalyst recovery (Table S3). Using an 11  $\mu$ m pore membrane, CD-TiO<sub>2</sub>-HS was much easier to recover than P25, with over 99.5% retained compared to 75% for P25 (88% P25 retention with 6  $\mu$ m membrane) (Figure 6a). Although the primary particle size of P25 is 21 nm, its agglomerated average hydrodynamic diameter over 300 nm (Table S2), which facilitated its retention by micro-filtration.



**Figure 6.** CD-TiO<sub>2</sub>-HS is much easier to recover than suspended P25 powder using filter paper with various pore sizes, ranging from 6 to 25  $\mu$ m. (a) 100% leaching means no TiO<sub>2</sub> nanoparticle was retained by filtration. (b) Pressure needed for particle separation by filtration and resulting permeate flux. To achieve over 99.5% recovery of the photocatalyst, 0.8  $\mu$ m pore-size PTFE membrane was used for P25 and 11  $\mu$ m pore-size membrane for CD-TiO<sub>2</sub>-HS.

Transmembrane pressure measurements show that a 6-fold higher pressure was required for P25 recovery (15.6 psi) compared to CD-TiO<sub>2</sub>-HS (2.56 psi) using microfiltration with the 11  $\mu$ m pore filters. The permeate flux for CD-TiO<sub>2</sub>-HS (5.56 mL/s) was 50 times higher than that for P25 (0.12 mL/ s) (Figure 6b), which was corroborated by the combined pore blockage-cake filtration model<sup>65</sup> (Figure S10). Furthermore, note that ultrafiltration is needed to retain TiO<sub>2</sub> nanoparticles that do not agglomerate, including those stabilized to maintain high surface area and photoactivity.<sup>66,67</sup> The transmembrane pressure needed to separate 30 nm TiO<sub>2</sub> nanoparticles using cross-flow ultrafiltration has been previously evaluated,<sup>67</sup> and a permeate flux of  $6.8 \times 10^{-3}$  mL/s was measured under a transmembrane pressure of 14.5 psi. This permeate flux is 3 orders of magnitude lower than that for CD-TiO<sub>2</sub>-HS (5.56 mL/s). Moreover, CD-TiO<sub>2</sub>-HS is more amenable to separation by settling than P25 (Figure S11). These findings reinforce that the relatively large primary particle size of CD-TiO<sub>2</sub>-HS represents a significant advantage related to faster separation with much lower pressure (and thus less energy) requirements.

To assess the stability and durability of CD-TiO<sub>2</sub>-HS, particles were dispersed in a modular continuous flow reactor (Figure S1c,d), and the outflow was filtered through an inline filter. A microfiltration membrane with 11  $\mu$ m pore size was similarly selected for CD-TiO<sub>2</sub>-HS separation. The TiO<sub>2</sub> concentration in leachate was monitored after the 1st, 2nd, 5th, and 10th backwash cycles (Figure S12). Less than 1.6% of the photocatalyst was lost after 10 cycles. The average equivalent Ti concentration in effluent was about 0.06 mg/L (Table S8 and eq S2), which is lower than recommended Ti concentration in drinking water (0.1 mg/L).<sup>68</sup> The contribution to TOC from potential disintegration of CD was also estimated to be negligible (Table S8).

Stability Considerations. Ensuring stable photoactivity under UV irradiation is critical to practical water treatment applications, especially for surface-modified nanoparticles that could lose their coating. CD has been reported to degrade in aqueous solutions linearly with time under harsher UVC irradiation conditions ( $\lambda = 254$  nm and  $1.41 \times 10^{-5}$  einstein/ L/s,<sup>69</sup> with complete mineralization of 1 g/L within 250–300 h. Because CD degradation hinders the ability of CD-TiO<sub>2</sub>-HS to adsorb BPA close to ROS generation sites for enhanced photocatalytic efficiency, we examined the potential loss of photocatalytic activity over 10 consecutive cycles under milder UVA irradiation ( $\lambda$  = 365 nm and 3.6 × 10<sup>-6</sup> einstein/L/s). In these tests, no loss of photocatalytic BPA degradation activity by UVA-irradiated CD-TiO<sub>2</sub>-HS was observed (>99% removal over 2 h) (Figure 7a). To better assess the stability of CD-TiO<sub>2</sub>-HS after extended usage, photoactivity of CD-TiO<sub>2</sub>-HS after prolonged exposure was also tested. BPA removal efficiency was stable for the first 300 h of UVA exposure, decreasing only slightly from 99.7% to ca. 97.4% after CD-TiO<sub>2</sub>-HS was pre-exposed to UVA for 300 h (Figure 7b). However, a significant loss of photoactivity was observed after 400 h. BPA removal within 2 h was 83.6%, which is similar to the removal efficiency with uncoated TiO<sub>2</sub>-HS.

Further analyses were conducted to discern chemical changes on the CD-TiO<sub>2</sub>-HS structure after use. CD-TiO<sub>2</sub>-HS were collected after exposure to UVA irradiation and analyzed with XPS (Figure 8). A new peak at 288.9 eV was observed after UVA irradiation, corresponding to O=C-OH bonds likely produced from oxidation of C-OH groups (Table 1). During the first 300 h, a minor decrease in percentage of carbon atoms indicates insignificant loss of CD coating. This is consistent with FTIR spectra (where no significant change in the relative abundance of surface functional groups was observed) and TGA analysis (where only a small (2.5%) weight loss of anchored CD occurred after 300 h UVA exposure (Figure 3c)). XPS data indicate that the relative abundance of ether (C-O-C) groups (286.35 eV), which are mainly present in glucopyranose units in the central cavity of CD,<sup>52</sup> increased after exposure to UVA for 300 h from 19.0 to 24.7% (Table 1). This increase was mainly due to carbon losses during CD degradation, such as carboxylic groups that are prone to be released as  $\rm CO_2^{.69}$  As a result of CD degradation, the carbon content (i.e., elemental composition (%), C 1s) present in the photocatalyst decreased from 15.8% to 13.6% (Table 1). However, the total abundance of C-O-Cgroups in the photocatalyst (calculated as its relative abundance in CD times carbon content in the photocatalyst<sup>70</sup>) remained constant at about 3% (Table 1). Thus, glucopyranose units were retained in the central cavity of CD, which is



**Figure 7.** Reusability and stable activity of CD-TiO<sub>2</sub>-HS after repeated photocatalytic degradation of BPA in DI water using (a) CD-TiO<sub>2</sub>-HS recaptured for 10 cycles and (b) CD-TiO<sub>2</sub>-HS preexposed to continuous UVA irradiation for various durations (20, 45, 100, 145, and 300 h).

consistent with the observed BPA sorption and enhanced photocatalytic activity within the first 300 h (Figure 7).

Carbon loss became significant (70%) after 500 h of UVA irradiation (Table 1 and Figure S14). This is likely due to the cleavage of glucopyranose units. The central cavity would have been deconstructed generating smaller organic molecules (e.g., formic acid and acetic acid).<sup>69</sup> Destruction of the central cavity results in significant loss of sorption capacity. This corresponds well with the loss of removal efficiency with CD-TiO<sub>2</sub>-HS observed after 400 h, which approached that of uncoated TiO<sub>2</sub>-HS.

Although CD degradation is likely to begin at the onset of UV irradiation, the rate, extent, and significance of these transformations on CD-TiO<sub>2</sub>-HS performance depend on the irradiation wavelength and intensity. Because CD-TiO<sub>2</sub>-HS retains its relatively high activity for up to 400 h of UVA irradiation, it is a promising candidate for repeated use. The eventual deterioration of CD-TiO<sub>2</sub>-HS would require its replacement—or reanchoring of CD to the spent catalyst, which would be a relatively simple "rejuvenation" process. Around 70% of CD was degraded and detached from CD-TiO<sub>2</sub>-HS after 500 h according to XPS analysis (Table 1 and Figure S14). Moreover, the residual coating is mainly composed of short chain carboxylic acids originating from CD cleavage.<sup>69</sup> Therefore, a relatively accessible surface would be left after long-term usage, and multilayer coating by CD



Figure 8. XPS spectra of C 1s region for CD-TiO2-HS after exposure to UVA for (a) 0, (b) 100, (c) 300, and (d) 500 h.

Table 1. Elemen	ntal and Chemica	l Bonds Composition	of CD-TiO <sub>2</sub> -HS afte	r Different Exposure Times
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	elemental composition of photocatalyst (%)			chemical bond composition (relative abundance, %)		omposition ance, %)		
UVA irradiation time (h)	Ti 2p	O 1s	C 1s	C-C	С-О-С	О=С-ОН	C–O–C abundance in photocatalyst <sup><math>a</math></sup> (%)	
0	$24.0 \pm 1.07$	$60.2 \pm 1.43$	$15.8 \pm 0.21$	69.2	19.0	NA	3.0	
100	$25.1 \pm 0.89$	$61.7 \pm 1.50$	$13.2 \pm 0.16$	67.2	22.4	10.4	3.0	
300	$24.3 \pm 1.02$	$62.1 \pm 1.27$	$13.6 \pm 0.11$	65.4	24.7	9.9	3.3	
500	$27.1 \pm 1.11$	$68.0 \pm 1.76$	$4.9 \pm 0.04$	63.3	23.1	13.6	1.1	
${}^{a}$ [C-O-C abundance in photocatalyst] = [carbon content (% C 1s) in photocatalyst] × [relative abundance of C-O-C]. <sup>70</sup>								

(which would reduce the contact between adsorbed contaminants and  $TiO_2$ -HS) is unlikely to occur through reanchoring. Here, CD reanchoring, which is a relatively simple process, fully replenished enhanced photocatalytic degradation by CD-TiO<sub>2</sub>-HS, with 90.4% (w/w) of the catalyst regenerated (Figure S15 and Table S9).

In photocatalytic water treatment, materials costs tend to be small compared to energy costs, and separation and recovery of a TiO<sub>2</sub> slurry generally requires more energy than the UV lamps used for photoexcitation.<sup>17</sup> Thus, periodic replacement or replenishment of CD-TiO<sub>2</sub>-HS would be offset by significant savings in photocatalyst separation. Further research could improve our approach to enhance TiO<sub>2</sub> affinity for nonpolar pollutants (and bring them closer to reactive sites) through coatings that are more resistant to radical attack (e.g., porous fluorinated polymers) that increase the sorption capacity and photocatalytic stability of easily separable TiO<sub>2</sub>-HS.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b04301.

Schematic diagram of photoreactor, dynamic light scattering (DLS), pseudo-second-order modeling of BPA adsorption, pore blockage and cake filtration modeling, and catalyst recovery through cycling test (PDF)

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The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This research is supported by the NSF ERC on Nanotechnology-Enabled Water Treatment (EEC-1449500).

#### REFERENCES

(1) Zhang, H.; Lv, X.; Li, Y.; Wang, Y.; Li, J. P25-graphene composite as a high performance photocatalyst. *ACS Nano* **2010**, *4* (1), 380–386.

(2) Lee, J.; Mackeyev, Y.; Cho, M.; Wilson, L. J.; Kim, J.-H.; Alvarez, P. J.  $C_{60}$  aminofullerene immobilized on silica as a visible-light-activated photocatalyst. *Environ. Sci. Technol.* **2010**, 44 (24), 9488–9495.

(3) Ling, L.; Tugaoen, H.; Brame, J.; Sinha, S.; Li, C.; Schoepf, J. J.; Hristovski, K.; Kim, J.-H.; Shang, C.; Westerhoff, P. Coupling light emitting diodes with photocatalyst-coated optical fibers improves quantum yield of pollutant oxidation. *Environ. Sci. Technol.* **2017**, *51* (22), 13319–13326.

(4) Pelaez, M.; Nolan, N. T.; Pillai, S. C.; Seery, M. K.; Falaras, P.; Kontos, A. G.; Dunlop, P. S.; Hamilton, J. W.; Byrne, J. A.; O'shea, K.; Entezari, M. H.; Dionysiou, D. D. A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl. Catal., B* **2012**, *125*, 331–349.

(5) Iliev, V.; Tomova, D.; Rakovsky, S.; Eliyas, A.; Puma, G. L. Enhancement of photocatalytic oxidation of oxalic acid by gold modified  $WO_3/TiO_2$  photocatalysts under UV and visible light irradiation. *J. Mol. Catal. A: Chem.* **2010**, 327 (1–2), 51–57.

(6) Chen, H.; Chen, S.; Quan, X.; Zhang, Y. Structuring a  $TiO_2$ based photonic crystal photocatalyst with Schottky junction for efficient photocatalysis. *Environ. Sci. Technol.* **2010**, 44 (1), 451–455.

(7) Choi, H.; Sofranko, A. C.; Dionysiou, D. D. Nanocrystalline  $TiO_2$  photocatalytic membranes with a hierarchical mesoporous multilayer structure: synthesis, characterization, and multifunction. *Adv. Funct. Mater.* **2006**, *16* (8), 1067–1074.

(8) Rincón, A.; Pulgarin, C. Photocatalytical inactivation of E. coli: effect of (continuous-intermittent) light intensity and of (suspended-fixed)  $TiO_2$  concentration. *Appl. Catal., B* **2003**, *44* (3), 263–284.

(9) Marks, R.; Yang, T.; Westerhoff, P.; Doudrick, K. Comparative analysis of the photocatalytic reduction of drinking water oxoanions using titanium dioxide. *Water Res.* **2016**, *104*, 11–19.

(10) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric field effect in atomically thin carbon films. *Science* **2004**, *306* (5696), 666– 669.

(11) Wang, W.-S.; Wang, D.-H.; Qu, W.-G.; Lu, L.-Q.; Xu, A.-W. Large ultrathin anatase  $TiO_2$  nanosheets with exposed {001} facets on graphene for enhanced visible light photocatalytic activity. *J. Phys. Chem. C* **2012**, *116* (37), 19893–19901.

(12) Zhang, H. Ultrathin two-dimensional nanomaterials. *ACS Nano* **2015**, *9* (10), 9451–9469.

(13) Sun, Z.; Liao, T.; Dou, Y.; Hwang, S. M.; Park, M.-S.; Jiang, L.; Kim, J. H.; Dou, S. X. Generalized self-assembly of scalable twodimensional transition metal oxide nanosheets. *Nat. Commun.* **2014**, *5*, 3813.

(14) Yamamoto, T.; Saso, N.; Umemura, Y.; Einaga, Y. Photoreduction of prussian blue intercalated into titania nanosheet ultrathin films. J. Am. Chem. Soc. **2009**, *131* (37), 13196–13197.

(15) Chen, Z.; Xu, Y.-J. Ultrathin  $TiO_2$  layer coated-CdS spheres core-shell nanocomposite with enhanced visible-light photoactivity. ACS Appl. Mater. Interfaces **2013**, 5 (24), 13353–13363.

(16) Li, C.; Koenigsmann, C.; Ding, W.; Rudshteyn, B.; Yang, K. R.; Regan, K. P.; Konezny, S. J.; Batista, V. S.; Brudvig, G. W.; Schmuttenmaer, C. A.; Kim, J.-H. Facet-dependent photoelectrochemical performance of TiO<sub>2</sub> nanostructures: an experimental and computational study. *J. Am. Chem. Soc.* **2015**, *137* (4), 1520–1529. (17) Cates, E. L. Photocatalytic water treatment: so where are we going with this? *Environ. Sci. Technol.* **2017**, *51*, 757–758.

(18) Chong, M. N.; Jin, B.; Chow, C. W.; Saint, C. Recent developments in photocatalytic water treatment technology: a review. *Water Res.* **2010**, *44* (10), 2997–3027.

(19) Nalbandian, M. J.; Greenstein, K. E.; Shuai, D.; Zhang, M.; Choa, Y.-H.; Parkin, G. F.; Myung, N. V.; Cwiertny, D. M. Tailored synthesis of photoactive  $TiO_2$  nanofibers and Au/TiO<sub>2</sub> nanofiber composites: structure and reactivity optimization for water treatment applications. *Environ. Sci. Technol.* **2015**, 49 (3), 1654–1663.

(20) Carbonaro, S.; Sugihara, M. N.; Strathmann, T. J. Continuous-flow photocatalytic treatment of pharmaceutical micropollutants: activity, inhibition, and deactivation of  $TiO_2$  photocatalysts in wastewater effluent. *Appl. Catal., B* **2013**, *129*, 1–12.

(21) Bolis, V.; Busco, C.; Ciarletta, M.; Distasi, C.; Erriquez, J.; Fenoglio, I.; Livraghi, S.; Morel, S. Hydrophilic/hydrophobic features of TiO<sub>2</sub> nanoparticles as a function of crystal phase, surface area and coating, in relation to their potential toxicity in peripheral nervous system. *J. Colloid Interface Sci.* **2012**, *369* (1), 28–39.

(22) Kamegawa, T.; Shimizu, Y.; Yamashita, H. Superhydrophobic surfaces with photocatalytic self-cleaning properties by nanocomposite coating of TiO<sub>2</sub> and polytetrafluoroethylene. *Adv. Mater.* **2012**, *24* (27), 3697–3700.

(23) Xing, M.; Qi, D.; Zhang, J.; Chen, F.; Tian, B.; Bagwas, S.; Anpo, M. Super-hydrophobic fluorination mesoporous  $MCF/TiO_2$  composite as a high-performance photocatalyst. *J. Catal.* **2012**, 294, 37–46.

(24) Makarova, O. V.; Rajh, T.; Thurnauer, M. C.; Martin, A.; Kemme, P. A.; Cropek, D. Surface modification of  $TiO_2$  nanoparticles for photochemical reduction of nitrobenzene. *Environ. Sci. Technol.* **2000**, 34 (22), 4797–4803.

(25) Chalasani, R.; Vasudevan, S. Cyclodextrin-functionalized  $Fe_3O_4$ @ TiO<sub>2</sub>: reusable, magnetic nanoparticles for photocatalytic degradation of endocrine-disrupting chemicals in water supplies. *ACS Nano* **2013**, 7 (5), 4093–4104.

(26) Crini, G.; Morcellet, M. Synthesis and applications of adsorbents containing cyclodextrins. *J. Sep. Sci.* **2002**, 25 (13), 789–813.

(27) Alsbaiee, A.; Smith, B. J.; Xiao, L.; Ling, Y.; Helbling, D. E.; Dichtel, W. R. Rapid removal of organic micropollutants from water by a porous  $\beta$ -cyclodextrin polymer. *Nature* **2016**, *529* (7585), 190.

(28) Crini, G.; Morcellet, M. Synthesis and applications of adsorbents containing cyclodextrins. *J. Sep. Sci.* **2002**, *25* (13), 789–813.

(29) Alsbaiee, A.; Smith, B. J.; Xiao, L.; Ling, Y.; Helbling, D. E.; Dichtel, W. R. Rapid removal of organic micropollutants from water by a porous  $\beta$ -cyclodextrin polymer. *Nature* **2016**, *529* (7585), 190–194.

(30) Lindsey, M. E.; Xu, G.; Lu, J.; Tarr, M. A. Enhanced Fenton degradation of hydrophobic organics by simultaneous iron and pollutant complexation with cyclodextrins. *Sci. Total Environ.* **2003**, 307 (1–3), 215–229.

(31) Zhu, Y.; Yue, M.; Natarajan, V.; Kong, L.; Ma, L.; Zhang, Y.; Zhao, Q.; Zhan, J. Efficient activation of persulfate by Fe 3 O 4@  $\beta$ -cyclodextrin nanocomposite for removal of bisphenol A. *RSC Adv.* **2018**, 8 (27), 14879–14887.

(32) Chen, W.; Zou, C.; Liu, Y.; Li, X. The experimental investigation of bisphenol A degradation by Fenton process with different types of cyclodextrins. *J. Ind. Eng. Chem.* **2017**, *56*, 428–434. (33) Challa, R.; Ahuja, A.; Ali, J.; Khar, R. Cyclodextrins in drug

delivery: an updated review. *AAPS PharmSciTech* **2005**, *6* (2), E329–E357.

(34) Administration, U. S. F. D., GRAS Notice 000074: Betacyclodextrin, 2016.

(35) Administration, U. S. F. D., GRAS Notice 687, Alphacyclodextrin, 2016.

(36) Tao, Y.-g.; Xu, Y.-q.; Pan, J.; Gu, H.; Qin, C.-y.; Zhou, P. Glycine assisted synthesis of flower-like TiO<sub>2</sub> hierarchical spheres and

its application in photocatalysis. *Mater. Sci. Eng., B* 2012, 177 (18), 1664–1671.

(37) Zhu, T.; Li, J.; Wu, Q. Construction of  $TiO_2$  hierarchical nanostructures from nanocrystals and their photocatalytic properties. *ACS Appl. Mater. Interfaces* **2011**, *3* (9), 3448–3453.

(38) Li, H.; Li, T.; Liu, H.; Huang, B.; Zhang, Q. Hierarchical flower-like nanostructures of anatase  $TiO_2$  nanosheets dominated by {001} facets. J. Alloys Compd. **2016**, 657, 1–7.

(39) Luo, X.; Deng, F.; Min, L.; Luo, S.; Guo, B.; Zeng, G.; Au, C. Facile one-step synthesis of inorganic-framework molecularly imprinted  $TiO_2/WO_3$  nanocomposite and its molecular recognitive photocatalytic degradation of target contaminant. *Environ. Sci. Technol.* **2013**, 47 (13), 7404–7412.

(40) Rosenfeldt, E. J.; Linden, K. G. Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes. *Environ. Sci. Technol.* **2004**, 38 (20), 5476–5483.

(41) Snyder, S. A.; Westerhoff, P.; Yoon, Y.; Sedlak, D. L. Pharmaceuticals, personal care products, and endocrine disruptors in water: implications for the water industry. *Environ. Eng. Sci.* **2003**, 20 (5), 449–469.

(42) Grignard, E.; Lapenna, S.; Bremer, S. Weak estrogenic transcriptional activities of Bisphenol A and Bisphenol S. *Toxicol. In Vitro* **2012**, *26* (5), 727–731.

(43) Chiron, S.; Minero, C.; Vione, D. Occurrence of 2, 4dichlorophenol and of 2, 4-dichloro-6-nitrophenol in the Rhône river delta (Southern France). *Environ. Sci. Technol.* **2007**, *41* (9), 3127– 3133.

(44) Dsikowitzky, L.; Schwarzbauer, J. Organic Contaminants from Industrial wastewaters: identification, toxicity and fate in the environment. In *Pollutant Diseases, Remediation and Recycling*; Springer: 2013; pp 45–101.

(45) Federation, W. E.; Association, A. P. H. Standard Methods for the Examination of Water and Wastewater; American Public Health Association (APHA): Washington, DC, 2005.

(46) Kiser, M.; Westerhoff, P.; Benn, T.; Wang, Y.; Perez-Rivera, J.; Hristovski, K. Titanium nanomaterial removal and release from wastewater treatment plants. *Environ. Sci. Technol.* **2009**, *43* (17), 6757–6763.

(47) Xie, J.; Zhang, X.; Zhang, H.; Zhang, J.; Li, S.; Wang, R.; Pan, B.; Xie, Y. Intralayered ostwald ripening to ultrathin nanomesh catalyst with robust oxygen-evolving performance. *Adv. Mater.* **2017**, 29 (10), 1604765.

(48) Peng, L.; Xiong, P.; Ma, L.; Yuan, Y.; Zhu, Y.; Chen, D.; Luo, X.; Lu, J.; Amine, K.; Yu, G. Holey two-dimensional transition metal oxide nanosheets for efficient energy storage. *Nat. Commun.* **2017**, *8*, 15139.

(49) Chen, J. S.; Tan, Y. L.; Li, C. M.; Cheah, Y. L.; Luan, D.; Madhavi, S.; Boey, F. Y. C.; Archer, L. A.; Lou, X. W. Constructing hierarchical spheres from large ultrathin anatase  $TiO_2$  nanosheets with nearly 100% exposed {001} facets for fast reversible lithium storage. *J. Am. Chem. Soc.* **2010**, 132 (17), 6124–6130.

(50) Tian, G.; Chen, Y.; Zhou, W.; Pan, K.; Tian, C.; Huang, X.-r.; Fu, H. 3D hierarchical flower-like  $TiO_2$  nanostructure: morphology control and its photocatalytic property. *CrystEngComm* **2011**, *13* (8), 2994–3000.

(51) Guo, N.; Liang, Y.; Lan, S.; Liu, L.; Ji, G.; Gan, S.; Zou, H.; Xu, X. Uniform  $TiO_2$ -SiO<sub>2</sub> hollow nanospheres: synthesis, characterization and enhanced adsorption-photodegradation of azo dyes and phenol. *Appl. Surf. Sci.* **2014**, *305*, 562–574.

(52) Shown, I.; Ujihara, M.; Imae, T. Synthesis of Cyclodextrin-Modified Water Dispersible Ag-TiO<sub>2</sub> Core–Shell Nanoparticles and Their Photocatalytic Activity. *J. Nanosci. Nanotechnol.* **2011**, *11* (4), 3284–3290.

(53) Yu, H.; Xiao, P.; Tian, J.; Wang, F.; Yu, J. Phenylaminefunctionalized  $rGO/TiO_2$  photocatalysts: spatially separated adsorption sites and tunable photocatalytic selectivity. *ACS Appl. Mater. Interfaces* **2016**, 8 (43), 29470–29477. (54) Morin-Crini, N.; Crini, G. Environmental applications of waterinsoluble  $\beta$ -cyclodextrin–epichlorohydrin polymers. *Prog. Polym. Sci.* **2013**, 38 (2), 344–368.

(55) Young, R. H.; Brewer, D.; Keller, R. A. Determination of rate constants of reaction and lifetimes of singlet oxygen in solution by a flash photolysis technique. *J. Am. Chem. Soc.* **1973**, *95* (2), 375–379. (56) Arakaki, T.; Faust, B. C. Sources, sinks, and mechanisms of hydroxyl radical ( $\bullet$  OH) photoproduction and consumption in authentic acidic continental cloud waters from Whiteface Mountain, New York: The role of the Fe(r)(r = II, III) photochemical cycle. *J. Geophys. Res-Atmos.* **1998**, *103* (D3), 3487–3504.

(57) Burns, J. M.; Cooper, W. J.; Ferry, J. L.; King, D. W.; DiMento, B. P.; McNeill, K.; Miller, C. J.; Miller, W. L.; Peake, B. M.; Rusak, S. A.; Rose, A. L.; Waite, T. D. Methods for reactive oxygen species (ROS) detection in aqueous environments. *Aquat. Sci.* **2012**, *74* (4), 683–734.

(58) Lee, C.-G.; Javed, H.; Zhang, D.; Kim, J.-H.; Westerhoff, P.; Li, Q.; Alvarez, P. J. Porous electrospun fibers embedding  $TiO_2$  for adsorption and photocatalytic degradation of water pollutants. *Environ. Sci. Technol.* **2018**, *52* (7), 4285–4293.

(59) Dong, M. M.; Mezyk, S. P.; Rosario-Ortiz, F. L. Reactivity of effluent organic matter (EfOM) with hydroxyl radical as a function of molecular weight. *Environ. Sci. Technol.* **2010**, *44* (15), 5714–5720.

(60) Zhang, D.; Yan, S.; Song, W. Photochemically induced formation of reactive oxygen species (ROS) from effluent organic matter. *Environ. Sci. Technol.* **2014**, *48* (21), 12645–12653.

(61) Lee, C.-G.; Javed, H.; Zhang, D.; Kim, J.-H.; Westerhoff, P.; Li, Q.; Alvarez, P. J. Porous electrospun fibers embedding  $TiO_2$  for adsorption and photocatalytic degradation of water pollutants. *Environ. Sci. Technol.* **2018**, *52* (7), 4285–4293.

(62) Katz, A.; McDonagh, A.; Tijing, L.; Shon, H. K. Fouling and inactivation of titanium dioxide-based photocatalytic systems. *Crit. Rev. Environ. Sci. Technol.* **2015**, 45 (17), 1880–1915.

(63) Zhang, Y.; Chen, Y.; Westerhoff, P.; Crittenden, J. Impact of natural organic matter and divalent cations on the stability of aqueous nanoparticles. *Water Res.* **2009**, *43* (17), 4249–4257.

(64) Sharma, V. K. Aggregation and toxicity of titanium dioxide nanoparticles in aquatic environment—a review. J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 2009, 44 (14), 1485–1495.

(65) Lee, S.-J.; Dilaver, M.; Park, P.-K.; Kim, J.-H. Comparative analysis of fouling characteristics of ceramic and polymeric micro-filtration membranes using filtration models. *J. Membr. Sci.* **2013**, *432*, 97–105.

(66) Lee, S.-A.; Choo, K.-H.; Lee, C.-H.; Lee, H.-I.; Hyeon, T.; Choi, W.; Kwon, H.-H. Use of ultrafiltration membranes for the separation of  $TiO_2$  photocatalysts in drinking water treatment. *Ind. Eng. Chem. Res.* **2001**, *40* (7), 1712–1719.

(67) Xue, X.-d.; Fu, J.-f.; Zhu, W.-f.; Guo, X.-c. Separation of ultrafine  $TiO_2$  from aqueous suspension and its reuse using cross-flow ultrafiltration (CFU). *Desalination* **2008**, 225 (1–3), 29–40.

(68) Dong, S.; Chen, C.; Li, D.; Sun, Y. A study of hygienic standard for titanium in the source of drinking water. *Chin. J. Prev. Med.* **1993**, 27 (1), 26–28.

(69) Lannoy, A.; Kania, N.; Bleta, R.; Fourmentin, S.; Machut-Binkowski, C.; Monflier, E.; Ponchel, A. Photocatalysis of Volatile Organic Compounds in water: Towards a deeper understanding of the role of cyclodextrins in the photodegradation of toluene over titanium dioxide. *J. Colloid Interface Sci.* **2016**, *461*, 317–325.

(70) Kim, K.; Zhu, P.; Li, N.; Ma, X.; Chen, Y. Characterization of oxygen containing functional groups on carbon materials with oxygen K-edge X-ray absorption near edge structure spectroscopy. *Carbon* **2011**, *49* (5), 1745–1751.