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# Enhanced visible light photocatalytic activity of Fe<sub>2</sub>O<sub>3</sub> modified TiO<sub>2</sub> prepared by atomic layer deposition

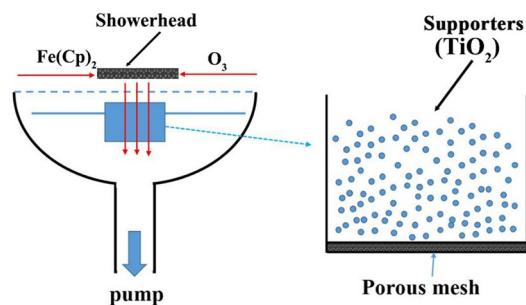
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In this work, commercial anatase TiO<sub>2</sub> powders were modified using ultrathin Fe<sub>2</sub>O<sub>3</sub> layer by atomic layer deposition (ALD). The ultrathin Fe<sub>2</sub>O<sub>3</sub> coating having small bandgap of 2.20 eV can increase the visible light absorption of TiO<sub>2</sub> supports, at the meantime, Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterojunction can effectively improve the lifetime of photogenerated electron–hole pairs. Results of ALD Fe<sub>2</sub>O<sub>3</sub> modified TiO<sub>2</sub> catalyst, therefore, showed great visible light driven catalytic degradation of methyl orange compared to pristine TiO<sub>2</sub>. A 400 cycles of ALD Fe<sub>2</sub>O<sub>3</sub> (~2.6 nm) coated TiO<sub>2</sub> powders exhibit the highest degradation efficiency of 97.4% in 90 min, much higher than pristine TiO<sub>2</sub> powders of only 12.5%. Moreover, an ultrathin ALD Al<sub>2</sub>O<sub>3</sub> (~2 nm) was able to improve the stability of Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalyst. These results demonstrate that ALD surface modification with ultrathin coating is an extremely powerful route for the applications in constructing efficient and stable photocatalysts.

A rapid industrial development driven by unsustainable technology advances can cause plenty of industrial sewage, spreading chemical hazards into water resources. As a result, water pollution has emerged as one of the most serious environmental issues worldwide<sup>1–4</sup>. Photocatalytic oxidation technology has shown great prospects in removing the toxic and harmful contaminants in aqueous environment<sup>5–7</sup>. Semiconductors (e.g. TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>) have been widely researched for organic pollutant degradation, however, the large band gap hinders their practical applications<sup>8–12</sup>. For example, TiO<sub>2</sub> with band gap of 3.2 eV can only absorb the ultra-violet light, accounting for only 4–5% of entire solar spectrum<sup>13</sup>. Therefore, various visible light sensitive photocatalysts has also been widely explored, such as g-C<sub>3</sub>N<sub>4</sub>, BiVO<sub>4</sub>, CdSe, Bi<sub>2</sub>WO<sub>6</sub><sup>14–19</sup>. On the other hand, TiO<sub>2</sub> is recognized as one of the excellent materials owing to its good inertness, eco-friendly, low cost, strong oxidizing power, and long-term stability against photo and chemical corrosion<sup>9,13,20–22</sup>. Thus, plenty of works have been made to extend the absorption spectrum of TiO<sub>2</sub> to visible light so to make a full use of solar spectrum. Several different approaches can be employed, including doping<sup>23–26</sup> and coupling with small band gap semiconductors or metals<sup>27–30</sup>.

Small band gap semiconductors not only increase the absorption of visible light but also inhibit photo-generated electrons–holes recombination when constructed as a semiconductor/semiconductor heterojunction structure, thus improving the photocatalytic performance dramatically<sup>31</sup>. Therefore, various TiO<sub>2</sub> based heterojunction photocatalysts have been proposed for visible light photocatalysis, including NiO/TiO<sub>2</sub><sup>32,33</sup>, Ag<sub>2</sub>O/TiO<sub>2</sub><sup>34</sup>, CdTe/TiO<sub>2</sub><sup>35</sup>, C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub><sup>36</sup>, Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub><sup>37</sup>, Cu<sub>2</sub>O/TiO<sub>2</sub><sup>38</sup>, Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub><sup>39</sup>, etc. For Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterojunction photocatalysts, a variety of composites have been investigated, such as Fe<sub>2</sub>O<sub>3</sub> nanoparticles on TiO<sub>2</sub> nanotube<sup>40</sup>, Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanoparticles<sup>41</sup>, TiO<sub>2</sub> coated cubic Fe<sub>2</sub>O<sub>3</sub><sup>42</sup>, Fe<sub>2</sub>O<sub>3</sub> nanosheet/TiO<sub>2</sub> hollow sphere<sup>39</sup>, and Fe<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub><sup>43</sup>. For instance, Lin et al. demonstrated that Fe<sub>2</sub>O<sub>3</sub> coating can effectively enhance the visible light photocatalytic

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**Figure 1.** The schematic diagram of coating  $\text{TiO}_2$  powders by ALD  $\text{Fe}_2\text{O}_3$ .

activity of  $\text{TiO}_2$ <sup>43</sup>. Various fabrication methods were applied, including hydrothermal or solvothermal process and sol-gel, to prepare the heterojunction photocatalysts<sup>44–46</sup>. Nevertheless, precise control of the interface between  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  at atomic level by conventional methods remain challenges.

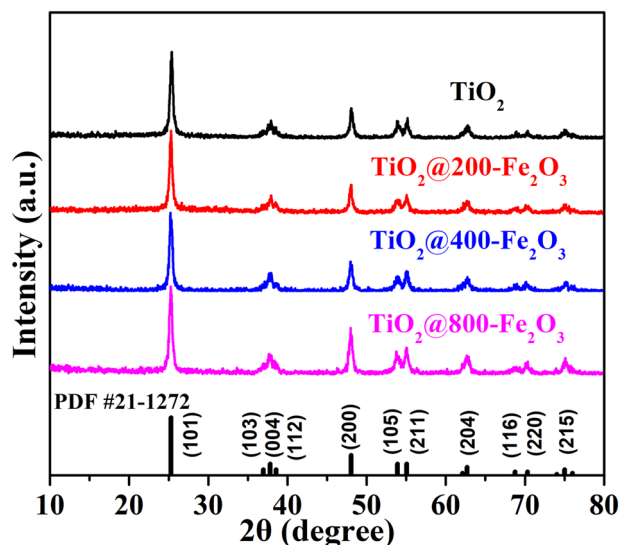
Atomic layer deposition (ALD) is a unique and promising thin film deposition technique based on self limited and saturated surface chemisorption reactions. It can deposit ultrathin, conformal, and uniform layers at sub-nanometer scale, which has attracted great attentions in surface engineering of nanostructures over the years<sup>47–49</sup>. In catalysts design, ALD enables a conformal layer with precise thickness control and tunable film composition onto another nanostructures with high aspect ratio<sup>50</sup>. The ALD coating can work as photo-active materials<sup>51,52</sup> or surface protection layer<sup>53,54</sup>. Herein, we modified the commercial anatase  $\text{TiO}_2$  powders with ultrathin  $\text{Fe}_2\text{O}_3$  surface coating by ALD. The photocatalytic performance was investigated by visible light degradation of methyl orange (MO). The ultrathin  $\text{Fe}_2\text{O}_3$  coating can enhance the absorption of  $\text{TiO}_2$  supports for visible light.  $\text{Fe}_2\text{O}_3$  modified  $\text{TiO}_2$  powders show much better visible light photocatalytic degradation of MO than pristine  $\text{TiO}_2$ . A possible mechanism for improved photocatalytic performance is proposed. In addition, an ultrathin ALD  $\text{Al}_2\text{O}_3$  ( $\sim 2$  nm) was used to promote the long-term durability of  $\text{TiO}_2@Fe_2O_3$  catalyst.

## Methods

**ALD deposition on  $\text{TiO}_2$  powders.** Commercial  $\text{TiO}_2$  powders with anatase phase (Nanjing Haitai nano materials Co.) were used as supports in this work. Ferrocene ( $\text{Fe}(\text{Cp})_2$ , Suzhou Fornano Corporation Ltd., 99.99%) and ozone were adopted as Fe and oxygen precursors for ALD  $\text{Fe}_2\text{O}_3$  deposition.  $\text{Fe}(\text{Cp})_2$  was vaporized at 85 °C. High purity nitrogen gas ( $\text{N}_2$ , 99.999%) was used as carrier gas at a total flow rate of 750 sccm and a pressure of 6 hPa in our ALD system (Picosun SUNALE™ R-150B). A particular container with porous mesh was used for ALD coating on powders, which has been reported elsewhere<sup>24,55</sup>, as shown in Fig. 1. Herein, precursors can flow through the  $\text{TiO}_2$  powders to achieve great conformality. X cycles of ALD  $\text{Fe}_2\text{O}_3$  ( $X = 200, 400, 600$ , and 800) were coated on  $\text{TiO}_2$  powder at 300 °C, the samples are marked as  $\text{TiO}_2@X\text{-Fe}_2\text{O}_3$ . One cycle of ALD  $\text{Fe}_2\text{O}_3$  contains the following four steps, 5 s  $\text{Fe}(\text{Cp})_2$  injection, 20 s  $\text{N}_2$  purge, 5 s  $\text{O}_3$  injection, and 20 s  $\text{N}_2$  purge. At the same system, 20 cycles of  $\text{Al}_2\text{O}_3$  were deposited on  $\text{TiO}_2@400\text{-Fe}_2\text{O}_3$  at 300 °C, where one ALD cycle of  $\text{Al}_2\text{O}_3$  is consisted of 5 s trimethylaluminum dose, 20 s  $\text{N}_2$  purging, 5 s  $\text{H}_2\text{O}$  dose, and 20 s  $\text{N}_2$  purging.

**Materials characterizations.** X-ray diffraction (XRD) using a Rigaku-D/MAX 2000 system was used for crystallinity and phase structure analysis. Scanning electron microscopy (SEM) images were taken using ZEISS Gemini SEM 500 instrument operated at 2 kV. The high-resolution transmission electron microscopy (HRTEM) was performed on a FEI Tecnai F20 S-Twin to observe the microstructures, where  $\text{TiO}_2$  powders were loaded on the ultra-thin carbon coated copper grids. The surface chemical features and valence band spectra were explored by X-ray photoelectron spectroscopy (XPS) using Thermo Fisher K-Alpha. The adventitious carbon signal ( $C 1s = 284.6$  eV) was adopted to calibrate the binding energies. UV-visible absorption spectra were conducted on a UV-vis-NIR spectrophotometer (UV-3600, Shimadzu, Japan). Photoluminescence (PL) spectra were collected on a Horiba Jobin Yvon HR800 spectrometer.

**Photocatalytic degradation.** The photocatalytic performance of  $\text{Fe}_2\text{O}_3$  coated  $\text{TiO}_2$  catalysts was investigated by visible light degradation of MO. 100 ml MO solution ( $4 \text{ mg L}^{-1}$ ) with 100 mg photocatalysts were loaded into a glass reactor, which was magnetically stirred at 500 rpm. In order to establish the adsorption/desorption equilibrium between MO and catalysts before irradiation, the MO solutions with catalysts were magnetically stirred for 30 min in darkness. Then, the suspension was irradiated under a 300 W Xe lamp (MircoSolar300, Perfect Light). A 420 nm filter was adopted to cut off UV light. The lamp was placed at 15 cm above the suspension, whose average visible light intensity is around  $80 \text{ mW cm}^{-2}$ . Water cooling was applied throughout the experiment to maintain the temperature at  $25 \pm 1$  °C. 3 mL solution was collected after each 15 min irradiation. The photocatalysts were removed by centrifugal separation. The residual MO concentration was determined using the absorption at 464 nm by UV-Vis-NIR spectrophotometer. The recycled usage experiment was performed for three times to explore the long-term stability of photocatalysts, e.g. after each photocatalytic experiment, the photocatalysts powders were gathered and rinsed by ethanol and water, then baked for 12 h at 100 °C. At last, a new MO solution was used to evaluate the photocatalytic activity of collected photocatalysts.



**Figure 2.** XRD patterns of pristine  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  coated  $\text{TiO}_2$ .

**Photoelectrochemical measurements.** Photoelectrochemical measurements were performed in a three-electrode electrochemical cell at room temperature using 1 M  $\text{Na}_2\text{SO}_4$  as the electrolyte. The  $\text{TiO}_2$  or  $\text{TiO}_2@400\text{-Fe}_2\text{O}_3$  on FTO were used as the working electrode. A Pt wire and  $\text{Ag}/\text{AgCl}$  were used as the counter electrode and the reference electrode, respectively. Photocurrent densities were collected by an electrochemistry workstation (CHI660E, Shanghai) using a potentiostatic method at 0.50 V. Light was chopped on and off cyclically. A solar simulator (300 W Xe lamp, MircoSolar300, Perfect Light) with a 420 nm cut-off filter provides the visible-light irradiation.

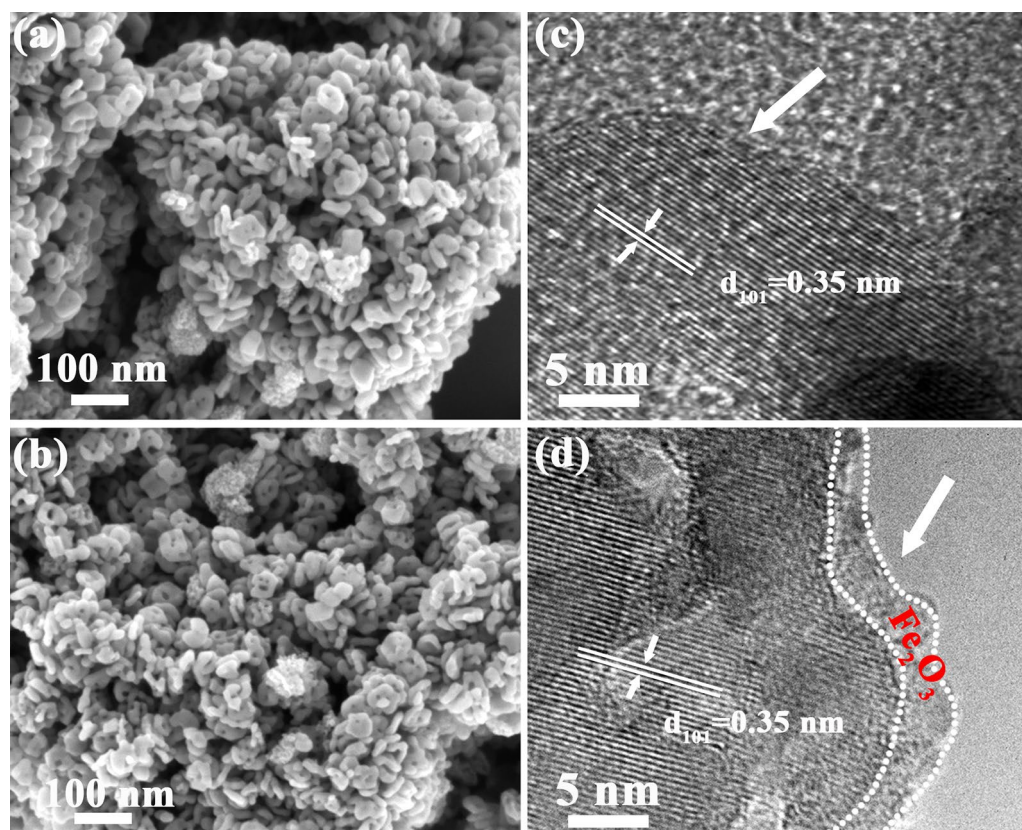
## Results

Figure 2 depicts the XRD patterns of pristine  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  coated  $\text{TiO}_2$  powders. All the samples show the similar characteristic diffraction peaks, in accord with anatase  $\text{TiO}_2$  (JCPDS No. 21-1,272). This result indicates that ultrathin ALD  $\text{Fe}_2\text{O}_3$  would not affect the crystal structure of  $\text{TiO}_2$ , consistent with our previous finding<sup>24,55</sup>. In addition, signals related to  $\text{Fe}_2\text{O}_3$  were absent.

SEM images of  $\text{TiO}_2$  powders without and with 400 cycles ALD  $\text{Fe}_2\text{O}_3$  deposition are shown in Fig. 3a,b. It can be seen that the pristine  $\text{TiO}_2$  powder exhibits a disk-like morphology with a diameter of approximately 40 nm and a thickness of approximately 10 nm, with severe aggregation. After ALD  $\text{Fe}_2\text{O}_3$  deposition, it was observed that  $\text{Fe}_2\text{O}_3$  coated  $\text{TiO}_2$  exhibited almost identical morphology, indicating that ultra-thin  $\text{Fe}_2\text{O}_3$  coating did not have significant influence on particle size and morphology of  $\text{TiO}_2$ . HRTEM was further conducted to observe the microstructure of  $\text{TiO}_2@400\text{-Fe}_2\text{O}_3$  and pristine  $\text{TiO}_2$  powders as shown in Fig. 3c,d. While pristine  $\text{TiO}_2$  shows a sharp well-ordered surface with good crystallinity (Fig. 3c), an amorphous layer of  $\sim 2.6$  nm formed on the  $\text{TiO}_2$  surface was observed which was contributed to ultra-thin  $\text{Fe}_2\text{O}_3$  layer (400 cycles) formed by ALD deposition. Moreover, both samples exhibit the lattice spacing of 0.35 nm, corresponding to (101) planes of anatase  $\text{TiO}_2$ . Based on above XRD and TEM data, it was speculated that an ultra-thin amorphous  $\text{Fe}_2\text{O}_3$  is coated on  $\text{TiO}_2$  nanoparticles surface without significantly modifying the morphology of the catalyst supports.

To further determine the successful deposition of ALD  $\text{Fe}_2\text{O}_3$ , XPS was performed to characterize the surface chemical features of ALD  $\text{Fe}_2\text{O}_3$  coated  $\text{TiO}_2$  powders. Figure 4a shows the Ti 2p spectra of  $\text{TiO}_2@400\text{-Fe}_2\text{O}_3$  and pristine  $\text{TiO}_2$  powders. The spectra can be fitted into two peaks at 464.3 eV and 458.5 eV, which can be assigned to  $\text{Ti } 2p_{1/2}$  and  $\text{Ti } 2p_{3/2}$  peaks<sup>28</sup>. In O 1s spectra (Fig. 4b), both samples present the main peak at 529.9 eV related to Ti–O bonding from  $\text{TiO}_2$ . In addition, there is a peak at 531.7 eV can be ascribed to the surface –OH<sup>56</sup>. Figure 4c exhibits the Fe 2p spectrum of  $\text{TiO}_2@400\text{-Fe}_2\text{O}_3$ , Fe  $2p_{1/2}$  and Fe  $2p_{3/2}$  peaks locate at 723.8 eV and 710.5 eV, in accord with Fe–O bonding value in  $\text{Fe}_2\text{O}_3$ <sup>57</sup>. Based on XPS data, the Fe atom ratio (Fe/Fe + Ti) is determined to be 1.1% in  $\text{TiO}_2@400\text{-Fe}_2\text{O}_3$ . It is anticipated that an ultra-thin amorphous  $\text{Fe}_2\text{O}_3$  is coated on  $\text{TiO}_2$  nanoparticles surface successfully. Due to the low content of  $\text{Fe}_2\text{O}_3$ , Fe 2p spectrum shows a bad signal to noise ratio. Therefore, the Fe 2p spectrum of ALD  $\text{Fe}_2\text{O}_3$  film is also presented for reference, as shown in Fig. 4d which can exhibit much better signal to noise ratio.

The influence of ultra-thin  $\text{Fe}_2\text{O}_3$  coating on absorption of  $\text{TiO}_2$  powders in visible light was explored using UV–Vis diffuse reflectance spectra, as illustrated in Fig. 5a. The spectrum of pristine  $\text{TiO}_2$  powders is also plotted for comparison. Pristine  $\text{TiO}_2$  powders exhibit the absorption edge of around 371 nm without noticeable visible light absorption. However, noticeable absorption in the visible light region from 390 to 750 nm can be observed after ultra-thin  $\text{Fe}_2\text{O}_3$  surface modification. The relationship of the absorption edge with the photon energy ( $h\nu$ ) for the indirect bandgap semiconductor is shown in the following formula:  $(\alpha h\nu)^{1/2} = A(h\nu - E_g)$ , where  $\alpha$  and A are the absorption coefficient and absorption constant, respectively. Since the absorption coefficient  $\alpha$  is determined by the scattering and reflectance spectra based on Kubelka–Munk theory, therefore, the bandgap values

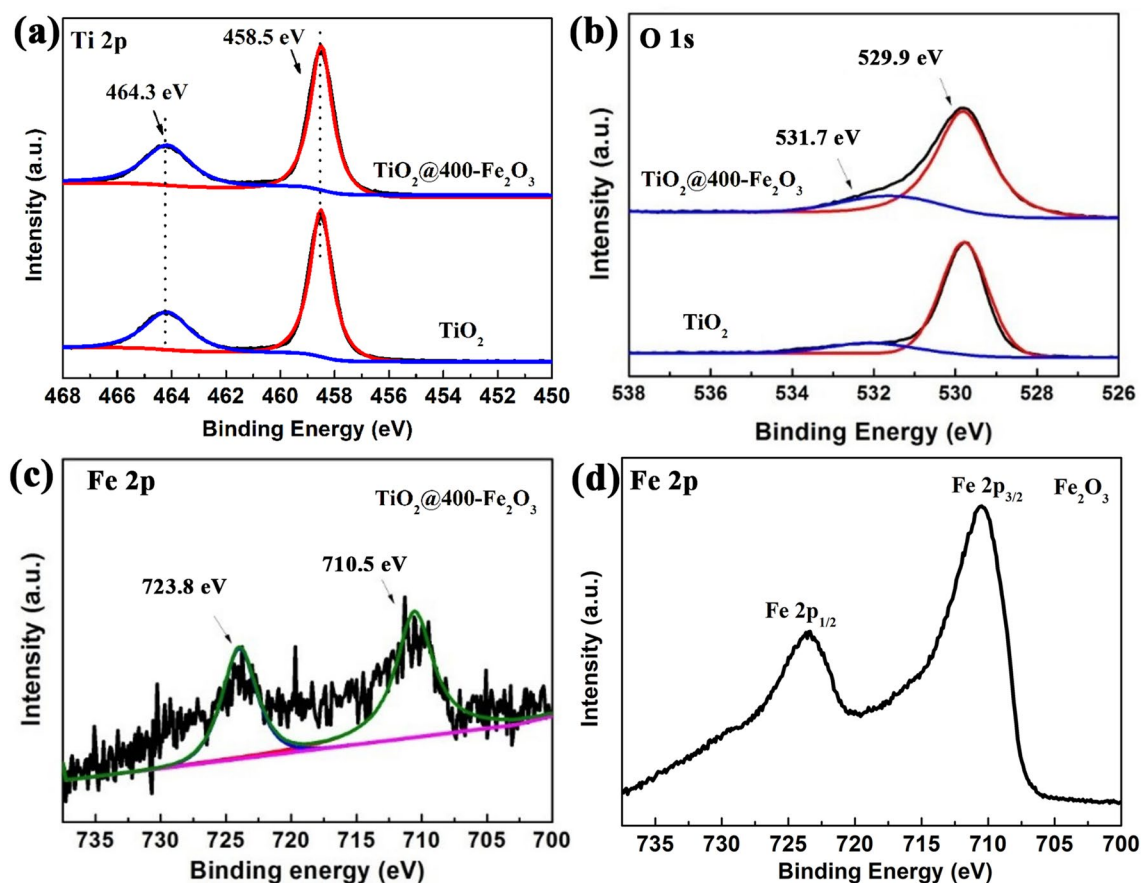


**Figure 3.** SEM images of (a) pristine TiO<sub>2</sub> and (b) TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub>. TEM images of (c) pristine TiO<sub>2</sub> and (d) TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub>.

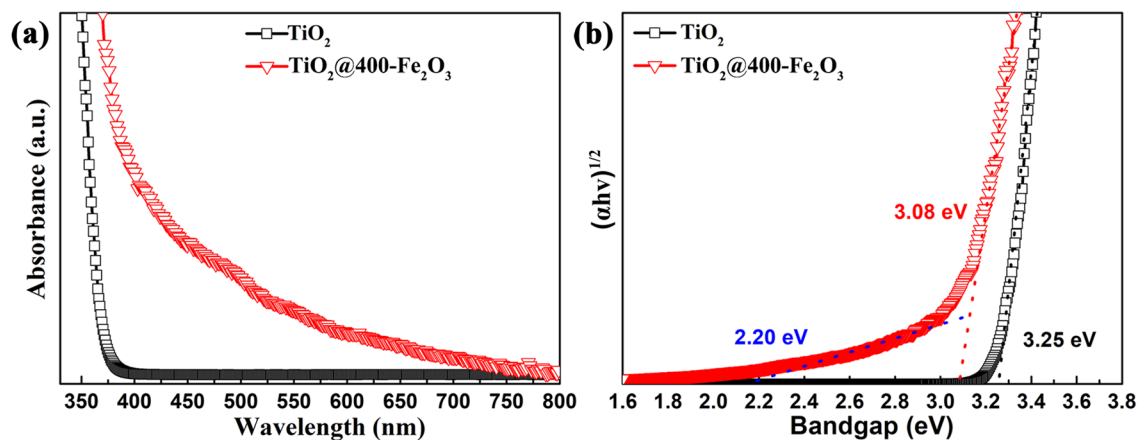
can be determined by the intercept of the tangent lines. As depicted from Fig. 5b, only one tangent line can be extrapolated for pristine TiO<sub>2</sub> powders showing a bandgap of 3.25 eV, while two bandgap values can be obtained from the plots for TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub> powders, attributing to Fe<sub>2</sub>O<sub>3</sub> coating with a bandgap value of ~2.20 eV and TiO<sub>2</sub> supports with a bandgap value of ~3.08 eV. It can be concluded that ultra-thin Fe<sub>2</sub>O<sub>3</sub> coating results in a smaller bandgap which can increase the absorption of TiO<sub>2</sub> powder support in visible light.

The visible light photocatalytic activity of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub> catalysts was compared by degrading MO. All samples exhibit low adsorption capacity of MO molecules. As reported in our previous work, MO is selected here for its stability under visible light irradiation in the absence of catalysts<sup>24</sup>. Figure 6a shows the evolution of UV-vis absorption spectra of MO solution in the presence of pristine TiO<sub>2</sub> under visible light irradiation. It can be seen that the absorption peaks at 464 nm decreases slightly after 90 min, exhibiting very poor photocatalytic activity due to its large bandgap. In contrast, the peak intensity at 464 nm fades rapidly for TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub> with the irradiation time extending, as shown in Fig. 6b. In addition, the orange MO solution turns into colorless after 90 min, as presented in the insert of Fig. 6b, indicating the degradation of MO. Figure 6c compares visible light photocatalytic activity of Fe<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub> catalysts. It can be found that a much-improved photocatalytic degradation efficiency of ~86.2% can be achieved with only 200 cycles of ALD Fe<sub>2</sub>O<sub>3</sub> modification. And the TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub> photocatalysts display the highest photocatalytic degradation efficiency of 97.4%. In comparison with reported Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterojunction catalysts for photodegradation of organic pollutants and antibiotics, ALD Fe<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub> (TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub>) in this work exhibit excellent removal efficiency for MO degradation, as summarized in Table 1. The photocatalytic degradation efficiency decreases to 95.8% and 90.4% for TiO<sub>2</sub>@600-Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>@800-Fe<sub>2</sub>O<sub>3</sub> samples, respectively, along with further increasing the thickness of ALD Fe<sub>2</sub>O<sub>3</sub> coating. The reduced efficiency can be ascribed to the fact that more Fe<sub>2</sub>O<sub>3</sub> coating would introduce more recombination sites for photoinduced electron-hole pairs<sup>42</sup>, diminishing the photocatalytic efficiency.

The degradation data were also fitted by the pseudo-first-order kinetics. The rate constant  $k$  can be determined by  $\ln(C_t/C_0) = -kt$  at low initial pollutant concentration. Herein,  $C_0$  is the initial MO concentration, while the  $C_t$  is the MO concentration after irradiation time of  $t$ .  $k$  is the first-order rate constant ( $\text{min}^{-1}$ ). The  $-\ln(C_t/C_0)$  vs.  $t$  curves are plotted in Fig. 6d. It can be seen that  $-\ln(C_t/C_0)$  has a linear relationship with  $t$ , indicating the photocatalytic degradation of MO by Fe<sub>2</sub>O<sub>3</sub> modified TiO<sub>2</sub> catalysts obeys the first-order kinetics. The first-order rate constant ( $k$ ) is determined to be  $3.8 \times 10^{-2} \text{ min}^{-1}$  for TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub>, which is much larger than pristine TiO<sub>2</sub> of  $1.3 \times 10^{-3} \text{ min}^{-1}$ . The result indicates that ALD Fe<sub>2</sub>O<sub>3</sub> modification can effectively enhance the visible light photocatalytic performance of TiO<sub>2</sub> supports.

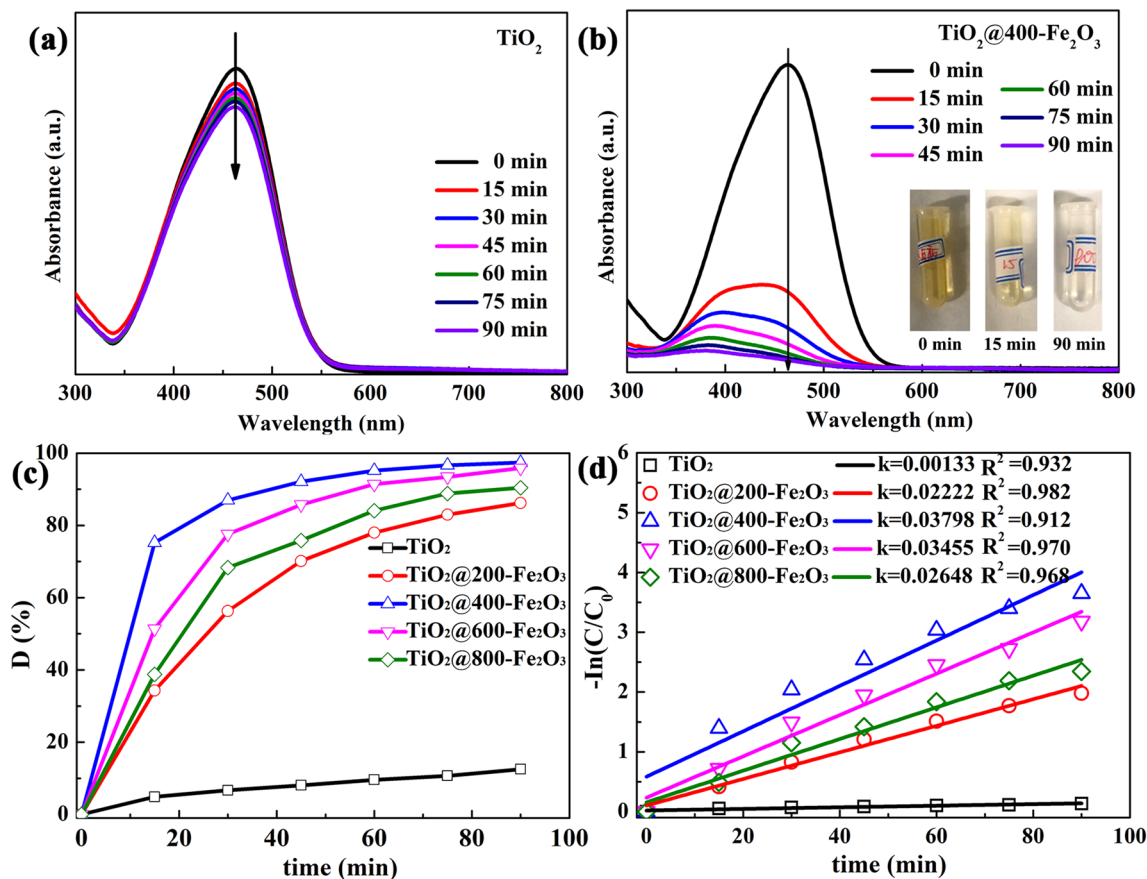


**Figure 4.** XPS spectra of (a) Ti 2p and (b) O 1s for  $\text{TiO}_2$  and  $\text{TiO}_2@400\text{-Fe}_2\text{O}_3$ , Fe 2p XPS spectra for (c)  $\text{TiO}_2@400\text{-Fe}_2\text{O}_3$  and (d)  $\text{Fe}_2\text{O}_3$  film.



**Figure 5.** (a) UV-Vis diffuse reflectance spectra and (b) Tauc plot of  $\text{TiO}_2$  with and without 400 cycles  $\text{Fe}_2\text{O}_3$  coating.

PL and photocurrent response measurements were conducted to explore the recombination rate of photo-generated electron-hole pairs. The lower the PL intensity, the higher separation efficiency of electron-hole pairs in the catalysts. Figure 7a shows the PL spectra of pristine  $\text{TiO}_2$  and various cycles of ALD  $\text{Fe}_2\text{O}_3$  coated  $\text{TiO}_2$ . It can be seen that all the  $\text{Fe}_2\text{O}_3$  coated  $\text{TiO}_2$  exhibit lower intensity than pristine  $\text{TiO}_2$ , indicating that the coupling of  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  can effectively inhibit the recombination of the photo-generated electron-hole pairs. Moreover, it can be seen that the 400 cycles  $\text{Fe}_2\text{O}_3$  coating results in the lowest intensity, thicker  $\text{Fe}_2\text{O}_3$  coating would increase the recombination of the photo-generated electron-hole pairs. The PL data are consistent well with the results of photocatalytic degradation of MO. Figure 7b presents the photocurrent response curves of  $\text{TiO}_2$  and

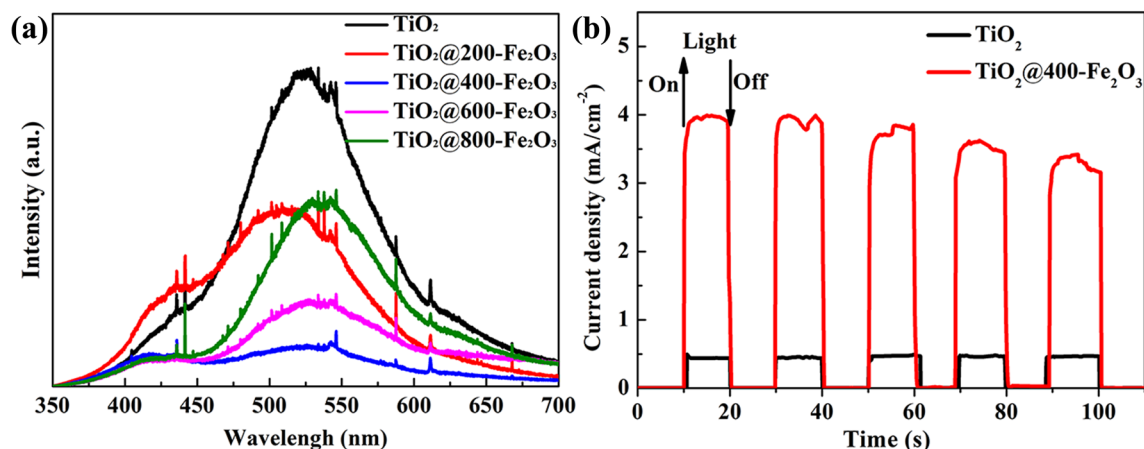


**Figure 6.** UV-vis absorption spectra of MO exposed to different irradiation time in the presence of (a) pristine  $\text{TiO}_2$  and (b)  $\text{TiO}_2@400\text{-Fe}_2\text{O}_3$  catalysts under visible light irradiation. The inserts are the photos of MO solution before and after irradiation. (c) Visible light photocatalytic degradation curves of MO and (d)  $-\ln(C/C_0)$  vs. time curves by using  $\text{TiO}_2$  with and without  $\text{Fe}_2\text{O}_3$  coating as catalysts.

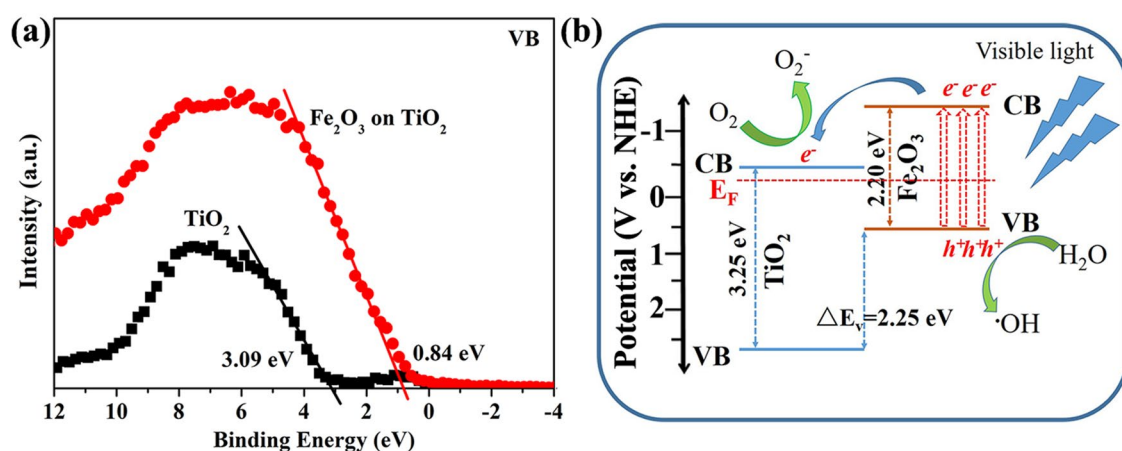
| Catalysts   | Method                        | Power of Xe lamp (W) | Organic pollutants |                         | Time (min) | D (%) | Ref       |
|---|-------------------------------|----------------------|--------------------|-------------------------|------------|-------|-----------|
|   |                               |                      | type               | C (mg L <sup>-1</sup> ) |            |       |           |
| $\text{Fe}_2\text{O}_3$ decorated $\text{TiO}_2$    | calcination                   | 350                  | MB <sup>a</sup>    | 3.2                     | 80         | 64.5  | 58        |
| $\text{Fe}_2\text{O}_3$ -Doped $\text{TiO}_2$       | Sol-gel                       | 500                  | MB                 | 10                      | 120        | 100   | 44        |
| $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanofibers     | Electrospinning + calcination | 800                  | RhB <sup>b</sup>   | 5                       | 180        | 53.6  | 59        |
| $\text{Fe}_2\text{O}_3$ decorated $\text{TiO}_2$    | hydrothermal                  | 500                  | RhB                | 4.8                     | 270        | 77.8  | 45        |
| $\text{Fe}_2\text{O}_3@/\text{SiO}_2@/\text{TiO}_2$ | vapor-thermal                 | 300                  | RhB                | 4.8                     | 60         | 100   | 46        |
| $\text{Fe}_2\text{O}_3$ coated $\text{TiO}_2$       | solvothermal                  | 300                  | TC <sup>c</sup>    | 50                      | 90         | 100   | 39        |
| Core-shell $\text{Fe}_2\text{O}_3@/\text{TiO}_2$    | Precipitation                 | 350                  | RhB                | 10                      | 360        | 71.0  | 60        |
| Core-shell $\text{TiO}_2@/\text{Fe}_2\text{O}_3$    | hydrothermal                  | 300                  | MO                 | 10                      | 16         | 96.6  | 43        |
| Core-shell C@ $\text{TiO}_2@/\text{Fe}_2\text{O}_3$ | Impregnation                  | 500                  | MB                 | 20                      | 240        | 80.8  | 61        |
| $\text{Fe}_2\text{O}_3/\text{TiO}_2$ composites     | Impregnation                  | 500                  | Orange II          | 20                      | 240        | 53.4  | 62        |
| $\text{Fe}_2\text{O}_3$ coated $\text{TiO}_2$       | ALD                           | 300                  | MO                 | 4                       | 90         | 97.4  | This work |

**Table 1.** Comparison of photocatalytic activity for degradation of organic pollutants using  $\text{TiO}_2\text{-Fe}_2\text{O}_3$  based catalysts. <sup>a</sup> MB is Methylene Blue, <sup>b</sup> RhB is Rhodamine B, <sup>c</sup> TC is Tetracycline.

$\text{TiO}_2@400\text{-Fe}_2\text{O}_3$ , it can be seen that  $\text{TiO}_2@400\text{-Fe}_2\text{O}_3$  exhibits a much higher photocurrent density than pristine  $\text{TiO}_2$ , indicating a more efficient separation of the photoexcited electron-hole pairs.



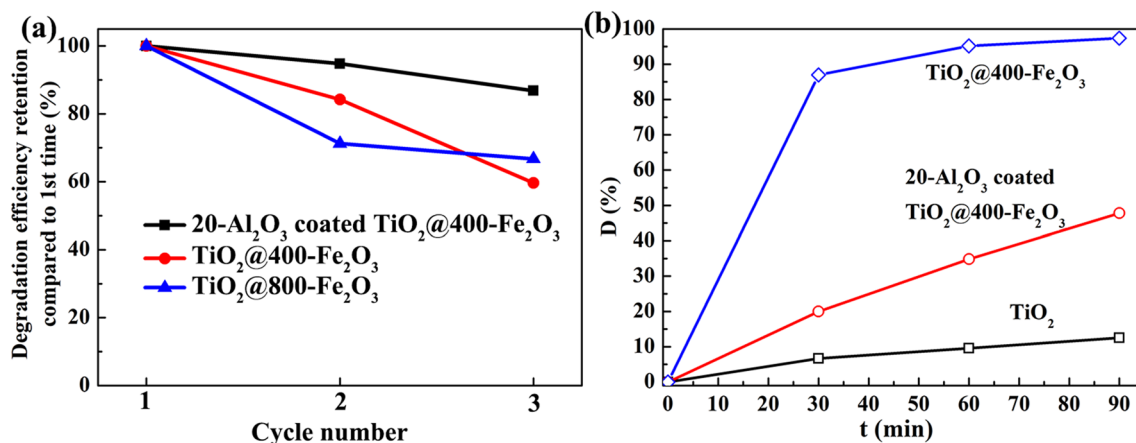
**Figure 7.** (a) PL spectra and (b) photocurrent response curves of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub>.



**Figure 8.** (a) Valence band spectra of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>. (b) Schematic illustration of energy band structure of Fe<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub> and proposed charge transfer mechanism during visible light irradiation.

The band alignment for Fe<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub> was determined by measuring the valence band offset  $\Delta E_v$  (VBO) using XPS. Figure 8a shows VB spectra of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> determined by linear extrapolation method, respectively. The VB of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> are found to be 3.09 eV and 0.84 eV, respectively. The VB of Fe<sub>2</sub>O<sub>3</sub> is higher than that of TiO<sub>2</sub>, and  $\Delta E_v$  at the interface of Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> is estimated to be 2.25 eV. The optical bandgaps of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> have been determined to be 3.25 and 2.20 eV, respectively, in Fig. 5. Therefore, the conduction band offset  $\Delta E_c$  (CBO) at the interface of Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> is estimated to be 1.20 eV. Considering the band structure of TiO<sub>2</sub> vs. standard hydrogen electrode (NHE)<sup>62–64</sup>, the energy band structure of Fe<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub> can be depicted in Fig. 8b. Under visible light, TiO<sub>2</sub> shows no photo-electronic response due to its large band gap. Only Fe<sub>2</sub>O<sub>3</sub> can be excited, yielding photo-generated electron from its VB to CB. Due to the aligned equilibrium of Fermi level at the interface of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>, as shown in Fig. 8b, the photogenerated electrons can transfer from CB of Fe<sub>2</sub>O<sub>3</sub> to that of TiO<sub>2</sub> driven by the built-in electric field and the concentration gradient of electrons, while remaining the holes in VB of Fe<sub>2</sub>O<sub>3</sub><sup>60,62–64</sup>. Therefore, the separation efficiency of photoinduced electron-hole pairs can be improved, which has been demonstrated by PL and photocurrent response results in Fig. 7. There are a large number of literatures focusing on the photocatalytic activity of Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> composites catalyst<sup>60,62–64</sup>. It is widely accepted that OH<sup>•</sup> radicals can be formed via the reaction of water and photogenerated holes in VB of Fe<sub>2</sub>O<sub>3</sub>. And electrons in CB of TiO<sub>2</sub> can react with oxygen to form O<sub>2</sub><sup>•-</sup>. These radicals with high activities can degrade organic molecules into harmless substances.

The stability of photocatalysts is one of the significant factors for practical applications, therefore, TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>@800-Fe<sub>2</sub>O<sub>3</sub> catalysts were tested in recycling experiments of MO photodegradation. As shown in Fig. 9a, compared to the first usage, both TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>@800-Fe<sub>2</sub>O<sub>3</sub> catalysts exhibit a declining degradation efficiency. The degradation efficiency retention compared to the first usage is only 59.6% and 66.7% for TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>@800-Fe<sub>2</sub>O<sub>3</sub>, respectively. It may be ascribed to the fact that stability of Fe<sub>2</sub>O<sub>3</sub> during photocatalytic reactions is reduced due to photo-corrosion<sup>42,65</sup>. ALD coatings have been widely used as surface protection layer to protect active materials from photo-corrosion<sup>53,54</sup>. Therefore, an ultrathin Al<sub>2</sub>O<sub>3</sub> (~2 nm) protective layer was deposited on catalysts surface by ALD in the same system to



**Figure 9.** (a) Three cycles of MO degradation for TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>@800-Fe<sub>2</sub>O<sub>3</sub> and 20 cycles Al<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub> in 90 min. (b) Comparison of MO degradation curves for pristine TiO<sub>2</sub>, TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub>, and 20 cycles Al<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub>.

improve the stability of Fe<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub> catalysts. Figure 9b shows the photocatalytic degradation of MO using both TiO<sub>2</sub>@400-Fe<sub>2</sub>O<sub>3</sub> with Al<sub>2</sub>O<sub>3</sub> passivation. The photocatalytic degradation efficiency decreases to 47.8% in 90 min, which is ascribed to the fact that Al<sub>2</sub>O<sub>3</sub> coating with large band gap would also hinder the photogenerated carriers from migrating to the surface of electrode<sup>62,66</sup>. But it is still much better than that of pristine TiO<sub>2</sub>. More importantly, the stability of catalysts is persistent, as there is limited decline of degradation efficiency after three usage as shown in Fig. 8a, retaining 86.8% compared to the first usage. The results indicate that thin Al<sub>2</sub>O<sub>3</sub> can act as a physical shell to protect Fe<sub>2</sub>O<sub>3</sub> from photo-corrosion. This can be ascribed to that Al<sub>2</sub>O<sub>3</sub> can prevent the direct contact between solution and Fe<sub>2</sub>O<sub>3</sub>.

**Conclusions.** In summary, commercial anatase TiO<sub>2</sub> powders were modified using ultrathin ALD Fe<sub>2</sub>O<sub>3</sub> surface coating. The ultrathin Fe<sub>2</sub>O<sub>3</sub> layer with small bandgap of ~2.20 V can increase the absorption of TiO<sub>2</sub> supports in visible light. In addition, Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterojunction can suppress the photoinduced electron-hole pairs recombination. The above results indicate excellent visible light photocatalytic activity for the Fe<sub>2</sub>O<sub>3</sub> modified TiO<sub>2</sub> powders. 400 cycles Fe<sub>2</sub>O<sub>3</sub> (~2.6 nm) coated TiO<sub>2</sub> photocatalysts show excellent degradation efficiency of 97.4% in 90 min, far above the performance of pristine TiO<sub>2</sub> powders with only 12.5%. Moreover, an ultrathin Al<sub>2</sub>O<sub>3</sub> (~2 nm) can improve the recycling usage performance of Fe<sub>2</sub>O<sub>3</sub> coated TiO<sub>2</sub> catalyst effectively. As conclusions, ALD surface modification with ultrathin film is a promising route for improving the visible light activity and long-term stability of photocatalysts.

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## Author contributions

\*Y.Q.C. and T.Q.Z. contributed equally in this work. X.R.Z., T.Q.Z. and Y.Q.C. prepared samples and tested the photocatalytic performance. C.L. conducted the SEM test. C.L. and Q.R. performed XPS characterization. J.B.F. performed TEM test. Y.Q.C. drafted the manuscript. A.D.L. supervised the whole work. W.M.L. and A.D.L. revised the manuscript. All authors critically read and commented on the manuscript. All authors read and approved the final manuscript.

## Competing interests

The authors declare no competing interests.

## Additional information

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