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# Trace Amount CoFe<sub>2</sub>O<sub>4</sub> Anchored on a TiO<sub>2</sub> Photocatalyst Efficiently Catalyzing O<sub>2</sub> Reduction and Phenol Oxidation

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*Keywords:* Photocatalysis;  $O_2$  reduction; Organic oxidation; Ti $O_2$ ; CoFe<sub>2</sub> $O_4$ ; Semiconductor; Spinel.

**ABSTRACT:** Semiconducting TiO<sub>2</sub> is the most studied photocatalyst for organic oxidation by O<sub>2</sub>. To accelerate the reaction, a co-catalyst for O<sub>2</sub> reduction or for organic oxidation is often used, but the bifunctional one is rare. Herein we report a spinel CoFe<sub>2</sub>O<sub>4</sub> (CF) efficiently catalyzing O<sub>2</sub> reduction and phenol oxidation on TiO<sub>2</sub> in aqueous suspensions at pHs 3–11. The composite materials (CF/TiO<sub>2</sub>) were made by depositing o–5 wt% CF onto TiO<sub>2</sub> through a hydrothermal method. Solid characterization showed that CF nanoparticles (5 nm) homogenously distributed in CF/TiO<sub>2</sub>, whereas TiO<sub>2</sub> phase remained unchanged in crystal structure and crystallite size. For phenol oxidation under UV light, CF was nearly not active, but o.o1 wt % CF/TiO<sub>2</sub> was more active than TiO<sub>2</sub>, by approximately a factor of 3.6. Such trend in activity among the catalysts was also observed from the photocatalytic reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>, and from the electrochemical oxidation of phenol and H<sub>2</sub>O, respectively. An open circuit potential and photoluminescence measurement suggest that there is an interfacial electron transfer from TiO<sub>2</sub> to CF, followed by O<sub>2</sub> reduction. Accordingly, a possible mechanism is proposed, involving CF catalysis for O<sub>2</sub> reduction and phenol oxidation, respectively. Then the mutual promotion between electron and hole transfer results into great enhancement in the efficiency of charge separation, and hence in the rate of chemical reaction. Since spinel compounds have rich composition and unique structures, they are worthy of being further investigated as co-catalysts of a semiconductor photocatalysis.

#### **INTRODUCTION**

Titanium dioxide is the most studied photocatalyst for energy and environmental application, due to its low cost, good activity, and high stability.<sup>1,2</sup> The primary process occurring over the irradiated TiO<sub>2</sub> is generation of electrons  $(e_{cb})$  and holes  $(h_{vb})$  in the conduction and valence bands, respectively. Then these charge carriers recombine to heat, or migrate onto the surface to react with sorbents. For example,  $e_{cb}$  of anatase TiO<sub>2</sub> can reduce O<sub>2</sub> to O<sub>2</sub><sup>-•</sup>, whereas the counterpart  $h_{yb}^{+}$  can oxidize various organics to CO2 and other products. There are many factors influencing the efficiency of TiO<sub>2</sub> photocatalysis. Among them, the physical property of TiO<sub>2</sub> is the determining one.<sup>3,4</sup> In general, the apparent photocatalytic activity of TiO<sub>2</sub> greatly changes with its crystal structure, surface area, defect sites, and so on. But the intrinsic photocatalytic activity of TiO<sub>2</sub> exponentially increases with its synthesis temperature, regardless of the solid structures.<sup>5-9</sup> A high intrinsic photocatalytic activity means a large number of  $e_{cb}$  and  $h_{\rm vb}^{+}$ , which have migrated onto and reached the oxide surface. Due to fast charge recombination and slow surface reaction, however, the quantum efficiency of TiO<sub>2</sub> photocatalysis is still not high enough to enable practical application.<sup>10</sup> Therefore, how to speed up the interfacial charge transfer is the central issue in TiO<sub>2</sub> photocatalysis.

One of the strategies is modification of TiO<sub>2</sub> surface with a co-catalyst. For instance, a Fe<sub>2</sub>O<sub>3</sub> cluster deposited on TiO<sub>2</sub> can mediate the electron transfer to O<sub>2</sub> through a Fe<sup>III/II</sup> recycle, and hence accelerate phenol oxidation.<sup>11,12</sup> A cobalt phosphate (CoPi) deposited on TiO<sub>2</sub> can mediate the hole transfer to water,<sup>13</sup> and phenol,<sup>14</sup> through a Co<sup>IV/III</sup> recycle. But Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> is only 1.7 times more active than TiO<sub>2</sub>, whereas CoPi/TiO<sub>2</sub> is deactivated in absence of CoPi repairer and electron remover. Furthermore, previous catalysts rarely possess catalytic activity for both O<sub>2</sub> reduction and organic oxidation. Herein we report a bifunctional performance of CoFe<sub>2</sub>O<sub>4</sub> in TiO<sub>2</sub> photocatalysis for phenol oxidation in aqueous solutions at pHs 3–11.

Recently, spinel compounds as catalysts for the reduction and evolution of  $O_2$  have received great attention.<sup>15</sup> For example,  $CoFe_2O_4$  (devoted as CF) has catalytic activity not only for a Ru(II) dye sensitized oxidation of  $H_2O$  to  $O_2$ , but also for the electrochemical reduction of  $O_2$  to  $H_2O_2$  or  $H_2O$ .<sup>16</sup> In structure, CF is a partially inverse spinel, where  $Co^{2+}$  and  $Fe^{3+}$  occupy both the tetrahedral (A) and octahedral (B) sites. Due to presence of an unpaired electron, CF also has ferrimagnetism. Therefore, CF has been widely used as a support of  $TiO_2$ .<sup>17-26</sup> The composite materials (devoted as CF/TiO<sub>2</sub>) was prepared by hydrolysis of a Ti(IV) precursor in the presence of CF,<sup>17,18,24-26</sup> or by formation of CF in the presence of  $TiO_2$ ,<sup>21-23</sup> and/or by co-

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formation of CF and TiO<sub>2</sub> from a mixed solution.<sup>19,20</sup> Since CF content was high (11-78 wt%),<sup>18,19</sup> these materials were magnetic, and separated easily from aqueous suspensions with an external magnet. Under UV and visible light, CF/TiO<sub>2</sub> is active for organic degradation, but a controversial result has been reported. On one hand, CF/TiO<sub>2</sub> was more active than TiO<sub>2</sub> for methyl blue and rhodamine B degradation.<sup>17,23,25,26</sup> On the other hand, CF/TiO<sub>2</sub> was less active than TiO<sub>2</sub> for methyl orange and rhodamine B degradation.<sup>18,19</sup> Such discrepancy is mostly due to the dye adsorption and sensitization that changes with the model dve and catalyst used. In aqueous solution, the adsorbed organic dyes on TiO<sub>2</sub> can degrade even under visible light, where dye is the light absorber, and  $TiO_2$  is a conducting mediator for O<sub>2</sub> reduction.<sup>21,27</sup> In other words, the role of CF in TiO<sub>2</sub> photocatalysis is yet to be explored.

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In this work, the effect of CF on the photocatalytic reactions of TiO<sub>2</sub> has been examined. To avoid the influence of organic photolysis and adsorption, phenol was selected as a model substrate. In aqueous solution, phenol photolysis and its dark adsorption on TiO<sub>2</sub> are both negligible. Then the observed difference between TiO<sub>2</sub> and CF/TiO<sub>2</sub> in the rate of phenol oxidation is surely due to CF effect on the photocatalytic reaction. Samples were prepared by depositing o-5 wt % CF onto a commercially available TiO<sub>2</sub>, via a hydrothermal method. Solid was characterized with several techniques. For phenol oxidation under UV light, CF was nearly not active, but the samples, containing 0.001-0.10 and 1-5 wt % CF, were more and less active than TiO<sub>2</sub>, respectively. To understand the role of CF, several experiments were carried out, including the catalyst stability test, the photocatalytic reduction of  $O_2$  to  $H_2O_2$ , the electrochemical reduction of O<sub>2</sub>, the photoelectrochemical oxidation of water and phenol, and the measurement of open circuit potential and photoluminescence. Furthermore, a possible mechanism responsible for the different effect of CF among samples is discussed.

#### RESULTS AND DISCUSSION

Solid structure was examined by X-ray diffraction (Figure 1A). The diffractions of  $TiO_2$  were strong, and matched those for anatase  $TiO_2$  (PDF#04-0477). The house-made CF showed a XRD pattern in good agreement with that for cubic  $CoFe_2O_4$  (PDF#02-1045). But the peak intensity of CF was much weaker than that of  $TiO_2$ . This is indicative of CF being poorly crystallized under the conditions used. The CF/TiO<sub>2</sub> samples were nearly the same as  $TiO_2$ , either in the diffraction position or peak width of anatase (Figure S1). As CF content was higher than 1 wt%, however, the diffractions due to CF became visible. These observations indicate that after CF loading,  $TiO_2$  phase remains intact in terms of the crystal structure and crystallite size, while CF in CF/TiO<sub>2</sub> is mostly in an amorphous form.



**Figure 1.** (A) XRD patterns of (a)  $TiO_2$ , (b) 5% CF/TiO<sub>2</sub>, and (c) CF. (B) Absorption spectra of CF and o-5% CF/TiO<sub>2</sub>.

Figure 1B shows the solid absorption spectra. In the spectrum of TiO<sub>2</sub>, there was an intensive absorption band at wavelengths shorter than 400 nm, due to the band-toband transition of TiO<sub>2</sub>. Through a Tauc plot, the band gap energy ( $E_g$ ) for TiO<sub>2</sub> was estimated to be 3.12 eV (Figure S2), well matching that for anatase TiO<sub>2</sub>.<sup>3</sup> In the spectrum of CF, there was a broad band from 200 nm to 800 nm. The estimated  $E_g$  for CF was 1.33 eV, similar to those reported.<sup>29-31</sup> In the spectrum of CF/TiO<sub>2</sub>, there was also a visible light absorption band, which increased with the increase of CF content. Meanwhile, the sample changed its color from white to yellow to brown (Figure S3).

Figure 2 shows the solid images of transmission electron microscopy (TEM). TiO<sub>2</sub> particles were flake-shaped, with a length of ca. 30-40 nm. CF particles were sphere-like, with a diameter of ca. 5 nm. But most of CF particles seriously agglomerated, due to magnetism and small size. In 5% CF/TiO<sub>2</sub>, there were small particles (CF) present on large particles (TiO<sub>2</sub>). In the high resolution TEM image, there were two interlayer distances at 0.35 and 0.21 nm, corresponding to the (1 o 1) facet of anatase TiO<sub>2</sub> (PDF#04-0477), and the (4 o 0) facet of CoFe<sub>2</sub>O<sub>4</sub> (PDF#02-1045), respectively. An element mapping with 5% CF/TiO<sub>2</sub> showed that Fe and Co species homogenously distributed in the sample (Figure S4). These observations indicate that CoFe<sub>2</sub>O<sub>4</sub> has been successfully deposited onto TiO<sub>2</sub> via a simple hydrothermal method.



**Figure 2**. TEM images of (A)  $TiO_2$ , (B) CF, and (C) 5% CF/TiO<sub>2</sub>, and (D) HRTEM image of 5% CF/TiO<sub>2</sub>.

The chemical state of CF was examined by X-ray photoelectron spectroscopy (XPS), and the results are shown in Figure S5. In the spectrum of Co 2p, the peak at 780.20 eV (a satellite at 786.30 eV) is assigned to Co  $2p_{3/2}$ , while the peak at 796.20 eV (a satellite at 804.00 eV) is assigned to Co  $2p_{1/2}$ . These peaks correspond to  $Co^{2+}$  in  $CoFe_2O_4$ .<sup>32,33</sup> Moreover, a small peak at 782.90 eV corresponds to Co<sup>3+</sup>. In the spectrum of Fe 2p, there were five peaks, characteristics of Fe<sup>3+</sup>. The peaks at 710.30 eV and 713.00 eV (a satellite at 718.50 eV), and 723.50 eV (a satellite at 726.22 eV) are assigned to Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$ , respectively.<sup>34</sup> The measured valences of Co and Fe elements in CF are in agreement with the formula of CoFe<sub>2</sub>O<sub>4</sub>. Moreover, the cation distribution of CF was examined by Mössbauer spectroscopy at room temperature,<sup>35-37</sup> and the results are shown in Figure S6 and Table S1. There were 25.44 and 74.56% of Fe ions occupying the tetrahedral (tet) and octahedral (oct) sites of CF, respectively. By using a literature model,<sup>38</sup> Co ions in A and B sites were calculated to be 16.85 and 83.15%, respectively. Then CF is assigned as  $(Co_{0.17}Fe_{0.51})_{tet}[Co_{0.83}Fe_{1.49}]_{oct}O_4$ . Note that after CF was calcined at 500 °C, its cation distribution changed to be  $(Co_{0.26}Fe_{0.75})_{tet}[Co_{0.70}Fe_{1.25}]_{oct}O_4$ . That is, the CoFe2O4 sample obtained in this work is partially inverse spinel.

The porosity and surface area of solid was measured by  $N_2$  adsorption, and the results are shown in Figure S7 and Table S2. All samples showed a hypothesis loop in the isotherms of  $N_2$  adsorption–desorption. This is indicative of mesopores present in those samples. In a comparison with pure CF, pure TiO<sub>2</sub> had a smaller surface area, but a larger pore volume and average pore size. As CF content in CF/TiO<sub>2</sub> increased, the surface area and pore volume decreased initially, and then increased. However, the average pore size regularly decreased with the increase of CF

content. With each sample, moreover, the measured surface area was always lower than the sum of the surface area calculated from individual CF and  $TiO_2$ , respectively. These observations indicate that the micro- and mesopores of  $TiO_2$  are occupied or blocked by CF nanoparticles, together with construction of a large porous network.



**Figure 3.** (A) Photocatalytic degradation of phenol, (B) the formation of hydroquinone, and (C) the production of  $H_2O_2$ , measured in aqueous phase of (a) TiO<sub>2</sub>, (b) 0.01% CF/TiO<sub>2</sub>, (c) CF, (d) CoO/TiO<sub>2</sub>, and (e) Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>.

Figure 3A shows the results of phenol degradation on different catalysts in aqueous solution. At first glance, phenol degradation on CF was very slow. Notably the reaction on 0.01% CF/TiO<sub>2</sub> was much faster than that on TiO<sub>2</sub>. To verify the effect of CF, control experiments were performed. In the dark, phenol adsorption on solid was a

little (around 2%). Under UV light without catalyst, the change of phenol concentration with time was negligible. Then the observed change of phenol concentration with time is surely due to a reaction initiated by photocatalysis. Moreover, CoO/TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> were only a little more active than TiO<sub>2</sub>. These observations indicate that the activity of CF/TiO<sub>2</sub> much higher than that of TiO<sub>2</sub> mostly originates from CF, rather than CoO and Fe<sub>2</sub>O<sub>3</sub>.

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To quantitatively describe the CF effect, the time profile of phenol degradation fit the pseudo first-order rate equation. The resulting rate constants ( $k_{obs}$ ) from CF, TiO<sub>2</sub>, and CF/TiO<sub>2</sub> were 0.19, 2.24, and 8.10, respectively, in a unit of 10<sup>-3</sup> min<sup>-1</sup>. Accordingly, CF is 11.8 times less active than TiO<sub>2</sub>, whereas CF/TiO<sub>2</sub> is 3.6 times more active than TiO<sub>2</sub>. These observations indicate that trace CF (0.01 wt.%) can greatly improve the photocatalytic activity of TiO<sub>2</sub>.

During phenol degradation, hydroquinone (HQ) was formed as the major intermediate, and the result is shown in Figure 3B. As the irradiation time increased, HQ concentration in aqueous phase increased toward a limit. Among samples, the rate of HQ formation became larger in the order of 0.01% CF/TiO<sub>2</sub> > TiO<sub>2</sub> > CF. This trend in the rate of intermediate production is in agreement with that in the rate of phenol degradation. In all cases, however, the amount of HQ formed was much lower than that of phenol consumed. For example, at 120 min, the mole ratio of HQ produced to phenol disappeared was 24, 17, and 6% for CF/TiO<sub>2</sub>, TiO<sub>2</sub>, and CF, respectively. These observations indicate that HQ also degrades *in situ*.

During phenol degradation,  $H_2O_2$  was also detectable, and the results are shown in Figure 3C. As the irradiation time increased,  $H_2O_2$  concentration in aqueous phase increased. This is because the electron reduction of  $O_2$  and the hole of phenol oxidation over TiO<sub>2</sub> occur at the same time.<sup>39,40</sup> At given time, interestingly,  $H_2O_2$  concentration formed from 0.01% CF/TiO<sub>2</sub> was approximately 3 times more than that produced from TiO<sub>2</sub>. However,  $H_2O_2$  in aqueous solution can adsorb and decompose on TiO<sub>2</sub>.<sup>41,42</sup> Then the real amount of  $H_2O_2$  produced from catalyst should be larger than that measured in aqueous phase.

To assess the fate of  $H_2O_2$ , separate experiment with 10 mM  $H_2O_2$  was performed, and the result is shown in Figure S8. In the dark, there was approximately 5% of  $H_2O_2$  adsorbed on TiO<sub>2</sub> or 0.01% CF/TiO<sub>2</sub>. This is due to formation of a peroxide complex on the surface Ti(VI) sites.<sup>37</sup> Under UV light,  $H_2O_2$  concentration in aqueous phase decreased with time. This is because  $H_2O_2$  decomposes over the irradiated TiO<sub>2</sub>, through a reductive and oxidative pathway.<sup>39-42</sup> However, the photocatalytic decomposition of  $H_2O_2$  on 0.01% CF/TiO<sub>2</sub> was approximately 1.23 times faster than that on TiO<sub>2</sub>. In combination with the result of  $H_2O_2$  formation, it follows that CF/TiO<sub>2</sub> is surely more active than TiO<sub>2</sub> for the photocatalytic reduction of  $O_2$ . This trend in activity between two catalysts, obtained





**Figure 4**. Apparent rate constants of phenol degradation, (A) over o-5% CF/TiO<sub>2</sub>, measured at initial pH7.0, and (B) over TiO<sub>2</sub> and o.01% CF/TiO<sub>2</sub>, obtained at different initial pHs.

Since 0.01% CF/TiO<sub>2</sub> is more active than TiO<sub>2</sub>, it is necessary to examine the effect of CF content. To do this, the samples containing o-5 % CoFe<sub>2</sub>O<sub>4</sub> were prepared under similar conditions. Figure 4A shows the results of phenol degradation over those samples in aqueous suspensions. As CF content in CF/TiO<sub>2</sub> increased, the rate of phenol degradation increased initially, and then decreased. A maximum reaction rate was observed from 0.01% CF/TiO<sub>2</sub>. Since the catalysts in aqueous suspensions may have different surface area, the rate constant of phenol degradation  $(k_{obs})$  was normalized tentatively with the solid surface area  $(A_{sp})$ , measured by N<sub>2</sub> gas (Table S<sub>2</sub>). However, the change of  $k_{\rm obs}/A_{\rm sp}$  with CF content well resembles that of  $k_{obs}$  (Figure 4A). Then the observed difference in activity among the samples due to the different surface area is less likely. Since CF strongly absorbs UV light (Figure 1B), the decreased rate of phenol degradation at high CF loading is ascribed to excess CF, that reduces the number of photons reaching TiO<sub>2</sub>, and hence slows down the TiO<sub>2</sub>photocatalyzed reaction. These observations indicate that only trace amount CF is beneficial to TiO<sub>2</sub> photocatalysis. This result is quite different from those reported in the literature.<sup>17-26</sup> Previous samples containing 11-78 % CF

The higher activity of 0.01% CF/TiO<sub>2</sub> than that of TiO<sub>2</sub> was observed in the wide range of initial pH from 3 to 11, which is shown in Figure 4B. As the initial pH increased, the rate constant of phenol degradation increased initially, and then decreased. A maximum rate was observed at approximately pH 7.0 from 0.01% CF/TiO<sub>2</sub> and at pH 9.0 from TiO<sub>2</sub>. These observations imply that CF/TiO<sub>2</sub> is stable in a weakly acidic and basic aqueous solution. This is important to water treatment by TiO<sub>2</sub> photocatalysis.



**Figure 5.** (A) Stability test of 0.01% CF/TiO2 for phenol degradation. (B) The corresponding formation of hydroquinone.

To illustrate the catalyst stability, a repeated experiment was performed, and the results are shown in Figure 5A. During five cycles, the photocatalytic performance of 0.01 %CF/TiO<sub>2</sub> was excellent. From the first run to the fifth, the rate constant of phenol degradation decreased only by a factor of 1.33. The decreased reaction rate is mostly due to the accumulated intermediates in suspensions, competing with phenol for reactive species. In fact, HQ concentration in aqueous phase increased with time, and then decreased after reaching a maximum (Figure 5B). After the last run, total HQ accumulated (48  $\mu$ M) was

only 2.5% of total phenol degraded (1.91 mM). Moreover, the possible change in chemical state was examined with 5% CF/TiO<sub>2</sub>. After illumination with UV light for 6 h, the sample showed negligible change in the XPS spectra of Co 2p and Fe 2p, respectively (Figure S5). These observations indicate that CF is not only stable, but also helps degradation of both phenol and HQ over the irradiated TiO<sub>2</sub>.



**Figure 6.** LSV curves of the film electrodes of (a)  $TiO_2$ , (b) 0.01% CF/TiO<sub>2</sub>, and (c) CF, measured in 0.5 M NaClO<sub>4</sub>. (A) Under O<sub>2</sub> (solid lines) or N<sub>2</sub> (dotted lines) in the dark. (B) Under N<sub>2</sub> and UV light in presence of 0.43 mM phenol. (C) The corresponding current recorded at 0.90 V vs. NHE.

To understand the role of CF in  $\text{TiO}_2$  photocatalysis, the reduction and oxidation reactions were examined, independently, by a linear sweep voltammetry (LSV). Figure 6A shows the result of O<sub>2</sub> reduction over  $\text{TiO}_2$ , CF, and 0.01% CF/TiO<sub>2</sub> film electrodes. As the bias swept negatively, the dark current of each electrode increased. But the

electrode current obtained under air was much larger than that measured under N<sub>2</sub>. This is indicative of O<sub>2</sub> reduction being the dominant process under air.

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Among the electrodes, however, the onset potential  $(E_{on})$ , and dark current of O<sub>2</sub> reduction were different. The  $E_{\rm on}$  value became more positive in the order of CF >  $CF/TiO_2 > TiO_2$ , whereas the electrode current also became larger in the order of  $CF > CF/TiO_2 > TiO_2$ . As CF content in CF/TiO<sub>2</sub> increased, the dark current of CF/TiO<sub>2</sub> increased, together with a positive shift in  $E_{on}$  (Figure S10). By using a literature method,<sup>43</sup>  $E_{on}$  was estimated, which was -0.023, 0.011, 0.037, 0.047, and 0.249 V vs. NHE, respectively, for the samples containing o, o.oo1, o.o1, o.1, and 100% CF. A more positive  $E_{on}$  and a larger current correspond to an easier of reduction of O<sub>2</sub>. These observations indicate that trace CF (0.01%) is also capable of efficiently catalyzing the electrochemical reduction of O<sub>2</sub> on a TiO<sub>2</sub> electrode, as does CF on a FTO or glassy carbon electrode.<sup>16</sup> Note that when a graphite rod was used as counter electrode (Figure S11), and/or infrared compensation was considered (Figure S12, no significant change was observed in LSV or  $E_{on}$  trend among samples (Table S<sub>3</sub>).

Figure 6B shows the results of phenol oxidation in 0.5 M NaClO<sub>4</sub>, measured under N<sub>2</sub> and UV light. As the bias swept positively, the electrode current increase initially, and then increased toward a limit. Interestingly, the onset potential and limit photocurrent of phenol oxidation became more negative and larger, respectively, in the order of  $CF/TiO_2 > TiO_2 > CF$ . Similar observations were also obtained from water oxidation (Figure S13). But the onset potential of water oxidation was slightly more positive than that of phenol oxidation. That is, under the present conditions, phenol oxidation is easier than water oxidation. Moreover, at a fixed potential, the electrode photocurrent remained stable during four light-on and light-off cycles (Figure 6C). Note that the photocurrent for each catalyst was the average from four parallel electrodes (Figure S14), and therefore the present result is reliable. These observations indicate that trace CF (0.01%) is also capable of efficiently catalyzing the hole oxidation of phenol, as observed from a dye sensitized water oxidation.<sup>10</sup>

The fate of the photogenerated electrons was also examined with an open circuit potential (OCP) method. Figure 7A shows the time profiles of OCP for TiO<sub>2</sub>, and o.o1% CF/TiO<sub>2</sub> film electrodes, measured in o.5 M NaClO<sub>4</sub> under N<sub>2</sub>. Once the electrode was illuminated, the electrode potential dropped, due to formation of the photoelectrons. When the potential was stable, the light was blocked off. Immediately, the electrode potentials quickly raised, due to fast recombination of electrons and holes in ns–µs domain.<sup>44</sup> Then OCP decayed slowly with time, due to the electron scavenging by an acceptor present in electrolyte solution. However, CF/TiO<sub>2</sub> showed a decay of OCP faster than that of TiO<sub>2</sub>. By using a literature equation,<sup>45</sup> the constant of OCP decay with time was estimated, which was 0.0061, and 0.011 s<sup>-1</sup> for TiO<sub>2</sub> and CF/TiO<sub>2</sub>, respectively (Figure S15). That is, the electron transfer from TiO<sub>2</sub> to an acceptor is increased by a factor of 1.8, on the deposition of 0.01% CF. Since proton reduction was negligible (Figure 6A), it is possible that the "photogenerated" electrons of TiO<sub>2</sub> are transferred into CF (Figure 2D).



**Figure 7**. (A) OCP curves measured in 0.5 M NaClO<sub>4</sub> under N<sub>2</sub>. (B) Photoluminesce spectra of powders under air. (C) M–S plots measured at 1 kHz in a 0.5 M NaClO<sub>4</sub> solution at pH 5. Samples were (a) TiO<sub>2</sub>, (b) 0.01% CF/TiO<sub>2</sub>, and (c) CF.

To further examine the CF effect, the solid photoluminescence (PL) spectrum was recorded, and the results are shown in Figure 7B. After  $\text{TiO}_2$  was excited with 325 nm light, there were several emission peaks, centered at 393, 449, 467, 480, and 492 nm, respectively. The peak at 393 nm (3.16 eV) well matches the band gap of anatase  $\text{TiO}_2$ (Figure 1B), while other peaks at 449–492 nm (2.52–2.76

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eV) are assigned to  $e_{cb}^{-}$  recombination with the trapped  $h_{VB}^{+}$  within band gap, and/or to  $e_{cb}^{-}$  reaction with the adsorbed  $O_2$  on the oxide surface.<sup>46</sup> Comparatively, the emissions of CF were rather weak, while the PL spectrum of 0.01% CF/TiO<sub>2</sub> was similar to that of TiO<sub>2</sub>. But at given wavelength, the peak intensity of CF/TiO<sub>2</sub> was lower than that of TiO<sub>2</sub>. In combination with OCP, it follows that the photogenerated electrons of TiO<sub>2</sub> are transferred into CF, followed by O<sub>2</sub> reduction. As a result, the emissions are reduced, either at 393 nm, or at 449–492 nm. On the other hand, it is also possible that the trapped  $h_{VB}^{++}$  of TiO<sub>2</sub> transfers into CF, suppressing its recombination with  $e_{cb}^{--}$ .

To understand the photocatalytic mechanism of a semiconductor (SC), one needs to know the conduction band edge potential ( $E_{CB}$ ), and the valence band edge potential ( $E_{VB}$ ). But such data for CoFe<sub>2</sub>O<sub>4</sub> are not found in the literature. Figure 7C shows the Mott–Schottky (M–S) plots of three film electrodes in 0.5 M NaClO<sub>4</sub> at pH 5.0. First, the plot slope was positive for TiO<sub>2</sub>, but negative for CF. It means that TiO<sub>2</sub> and CF are n-type and p-type SC, respectively.<sup>45</sup> Second, the plot intercept with the potential axis corresponds to the flat potential ( $E_{fb}$ ). In general,  $E_{fb}$  is close to  $E_{CB}$  for n-type SC, and to  $E_{VB}$  for p-type SC. From  $E_g = E_{VB} - E_{CB}$ ,  $E_{CB}$  of CF was calculated to be 0.46 V, more positive than that of TiO<sub>2</sub>. The M–S plot of 0.01% CF/TiO<sub>2</sub> was similar to that of TiO<sub>2</sub>. But  $E_f$  of 0.01% CF/TiO<sub>2</sub> was approximately 50 mV more negative than that of TiO<sub>2</sub>.

In aqueous solution at pH o, the literature values of  $E_{CB}$ and  $E_{VB}$  for anatase TiO<sub>2</sub> are –0.12 and 3.08 V vs. normal hydrogen electrode (NHE), respectively.<sup>47,48</sup> Then  $E_{CB}$  and  $E_{VB}$  of CF are estimated to be 0.34 and 1.67 V vs. NHE, respectively. In thermodynamics, the holes of both TiO<sub>2</sub> and CF are capable of oxidizing phenol (1.44 V vs. NHE) or H<sub>2</sub>O (1.23 V vs. NHE).<sup>49,50</sup> But the electron reduction of O<sub>2</sub> to HO<sub>2</sub> (-0.05 V vs. NHE) is allowed on TiO<sub>2</sub>,<sup>46</sup> but not on CF. This is one of the reasons why CF is much less active than TiO<sub>2</sub> for the photocatalytic degradation of phenol in aqueous suspensions (Figure 3A). Recall that CF and CF/TiO<sub>2</sub> used in photocatalysis were prepared at 160 °C, whereas TiO<sub>2</sub> is industrially made at a temperature lower than 450 °C.<sup>7</sup> Then the low activity of CF is also due to its poor crystallinity, as compared with TiO<sub>2</sub> (Figure 1A).

To verify the crystallinty effect, the solid was further calcined at 500 °C for 2 h. After that, all solids had an enhanced XRD diffraction (Figure Si6). Meanwhile, the rates of phenol degradation on  $TiO_2$  and CF were increased by factors of 1.3 and 1.6, respectively (Figure Si7). These observations confirm that the reaction rate does increase with the crystallinity of SC ( $TiO_2$  or CF).<sup>5-9</sup> After thermal treatment, however, the rate of phenol degradation on 0.01% CF/TiO<sub>2</sub> decreased by a factor of 1.6. The changes in the reaction rate on the thermal treatment are not due to changes in the solid surface area (Table S4 and Figure Si7).

These observations imply that in CF/TiO<sub>2</sub>, the amorphous CF is more efficient than the crystallized CF, in participation of the  $TiO_2$ -photocatalyzed reaction. In other words, CF acts as a molecular cocatalyst of  $TiO_2$  photocatalysis, instead of a semiconductor coupling with  $TiO_2$ .



**Scheme 1.** Possible mechanism for the enhanced photocatalytic activity of CF/TiO<sub>2</sub>, where small balls represent CF.

Accordingly, a possible role of CF in TiO<sub>2</sub> photocatalysis is proposed in Scheme 1. First, the photogenerated electrons and holes of TiO<sub>2</sub> are captured by the Fe<sup>3+</sup> and Co<sup>2+</sup> species of CF, respectively. Then, the reduced CF (Fe<sup>2+</sup> species) is oxidized by  $O_2$ , and the oxidized CF ( $Co^{3+}$  species) is reduced by phenol. As a result, CF is regenerated. These processes resemble those of Fe<sub>2</sub>O<sub>3</sub> and CoPi deposited on TiO<sub>2</sub>, respectively.<sup>11-14</sup> However, the photocatalytic reactions are different from the (photo)electrochemical reactions. The former occurs on the same particles in an air-exposed aqueous suspension, whereas the latter occurs on different electrodes in a N<sub>2</sub>-purged electrolyte under an external potential. Then one may worry about the fast recombination of  $e_{cb}^{-}$  (Fe<sup>2+</sup>) and  $h_{vb}^{+}$  (Co<sup>3+</sup>) on TiO<sub>2</sub>, making CF in null cycle. This possibly is argued as follows. First, the electron reduction of O<sub>2</sub> and the hole oxidation of phenol on the irradiated TiO<sub>2</sub> can occur simultaneously. Second, the rate of phenol degradation is proportional to the crystallite size of TiO<sub>2</sub>.<sup>7</sup> Third, CoFe<sub>2</sub>O<sub>4</sub> has a unique structure, where both Fe and Co ions occupy the tetraand octahedral sites (Figure S6). Forth, a XPS study shows that in CoFe<sub>2</sub>O<sub>4</sub>, there are also Fe<sup>2+</sup> and Co<sup>3+</sup> species, peacefully coexisting together without redox reaction.<sup>16,33</sup> Then the reduction and oxidation of CF can occur on the different particles of TiO<sub>2</sub>, and/or at different sites of CF. Therefore, the proposed role of CF as a bifunctional cocatalyst in TiO<sub>2</sub> photocatalysis is highly plausible.

In the suspensions, both  $TiO_2$  and CF are the light absorbing species. But the observed reaction on CF/TiO<sub>2</sub> is predominantly initiated by  $TiO_2$ . This is inferred from the fact that CF is nearly not active and that 0.01% CF/TiO<sub>2</sub> is more active than  $TiO_2$ . Furthermore, in  $TiO_2$  photocatalysis, the electrons and holes are photogenerated and consumed in pairs. Any action that accelerates the electron

transfer would promote the hole transfer, and vice visa. In the present case, CF acts as a co-catalyst for both electron and hole transfer. As a result, the efficiency of charge separation is greatly improved, and CF/TiO<sub>2</sub> is much more active TiO<sub>2</sub> for the photocatalytic degradation of phenol.

#### CONCLUSIONS

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In this work, a novel photocatalyst of TiO2 has been successfully deposited with trace CF (0.01 %) through a simple hydrothermal method. This material is much more active than parent TiO, for the photocatalytic oxidation of phenol in an air-saturated aqueous suspension. Impressively, the composite photocatalyst is not only stable, but also operative in both a weakly acidic and alkaline aqueous solution. An independent study of electrochemistry clearly indicates that trace CF can efficiently catalyze O<sub>2</sub> reduction and phenol oxidation, respectively. With the aid of an OCP and PL, it is proposed that CF acts as a bifunctional co-catalyst for both O<sub>2</sub> reduction and organic oxidation in TiO<sub>2</sub> photocatalysis. There are many spinel compounds with different compositions and unique properties.15 The present work of CoFe<sub>2</sub>O<sub>4</sub> effect would help further study of spinel compounds as co-catalysts of a semiconductor photocatalysis for water splitting, organic oxidation, and environmental remediation.

#### EXPERIMENTAL SECTION

**Material.** Anatase TiO<sub>2</sub>, peroxidase, and *N*,*N*-diethyl-1,4-phenylenediamine (DPD) were purchased from Sigma-Aldrich. FeCl<sub>3</sub>· $6H_2O$ , Co(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$ , and others in analytic grade were purchased from Shanghai Chemicals. A Milli-Q ultrapure water was used, and solution pH was adjusted with a dilution solution of NaOH or HClO<sub>4</sub>.

**Synthesis.** Pure CF was synthesized using a literature method.<sup>16</sup> Briefly, KOH solution (2.24 g, 50 mL) was slowly added into a mixed solution of iron salt (1.53 g, 15 mL), and cobalt salt (0.62 g, 15 mL). Then the suspension was transferred into a Teflon-lined autoclave, and heated at 160 °C for 6 h. After the autoclave cooled down, the solid was collected, and washed several times with water and ethanol, and dried at 50 °C overnight.

The above method was used to prepare o-5% CF/TiO<sub>2</sub>. Typically, 0.5 g of TiO<sub>2</sub> was suspended in KOH solution KOH (2.24 g, 60 mL). Then 58 µL of Fe<sup>3+</sup> solution (2 g/L), 31 µL of Co<sup>2+</sup> solution(2 g/L), and 20 mL H<sub>2</sub>O were mixed, and slowly added into the TiO<sub>2</sub> suspension. After that, the suspension was treated as described above. In this sample, the content of CF was calculated to be 0.01% in weight. Moreover, by mimicking 0.01% CF/TiO<sub>2</sub>, two reference samples of CoO/TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> were also prepared, without the addition of Fe<sup>3+</sup> and Co<sup>2+</sup>, respectively.

**Characterizations.** Powder X-ray diffraction (XRD) pattern was recorded on an Ultima IV X-ray diffractometer (Rigaku, Japan). Diffuse reflectance spectra were rec-

orded on a Shimadzu UV-2600 with BaSO<sub>4</sub> as a reference. Reflectance (R) was transferred into Kubelka–Munk absorbance,  $F_R = (1-R)^2/(2R)$ . X-ray photoelectron spectroscopy (XPS) was made on an ESCA Lab 220i-XL. The spectrum was calibrated with C 1s at 284.6 eV. Adsorption isotherms of N<sub>2</sub> on solid were measured at 77 K on a Micromeritics ASAP2020. The solid surface area was calculated using Brunauer-Emmett-Teller (BET) equation. Photoluminescence (PL) spectrum was recorded in air at room temperature, on a Shimadzu F-2500 spectrophotometer. Scanning electron microscope (SEM) measurement was performed on a Hitachi SU-8010. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on a JEM-2100F field-emission instrument. 57Fe Mössbauer spectroscopy was recorded on a spectrometer operating in constant acceleration mode at 300K. The source used was a <sup>57</sup>Co (Rh), and the isomer shift was referred to  $\alpha$ -Fe.

Photocatalysis. Reactions were carried out on a XPA-7 photochemical reactions instrument (Xujiang Nanjing). Reactor was a quartz glass tube (50 mL), thermostated at 25 °C. Light source was a high pressure mercury lamp (300W), attached with a 365 nm cut-off filter, whose intensity reaching the reactor surface was 4.5 mW/cm<sup>2</sup>. Unless stated otherwise, experiments were performed under fixed conditions (1.00g/L catalyst, 0.43mM phenol, and pH 7). A suspension containing necessary components was stirred in the dark for 1 h, and then irradiated with UV light. At given intervals, 2 mL of sample was withdrawn, and filtered through a 0.22 µm membrane. The filtrate was analyzed by HPLC (high-performance liquid chromatography) on a Dionex P68o (Apollo C18 reverse column, and 50% CH<sub>3</sub>OH as an eluent). H<sub>2</sub>O<sub>2</sub> was analyzed using the literature method.<sup>28</sup> Briefly, 2.7 mL of the filtrate was mixed with 0.3 mL buffer solution (0.5 M  $NaH_2PO_4/Na_2HPO_4$ ), 25 µL DPD, and 25 µL peroxidase in order. The solution absorbance at 553 nm was recorded on an Agilent 8453 UV-visible spectrophotometer.

**Stability Test.** In the first run, a suspension containing 2.00 g/L 0.01% CF/TiO<sub>2</sub> and 0.22 mM phenol at pH 7.0 was stirred in the dark for 1 h, and then irradiated for 90 min. Sample was analyzed as the above. In the second run, a certain amount of the non-irradiated catalyst suspension (2 g/L) and phenol stock solution (10.75 mM) was injected into the above irradiated suspension, as so to restore previous conditions. After stirring in the dark for 30 min, new suspension was irradiated with light for 90 min. The above procedure was repeated five times.

(Photo)electrochemical Measurement. A working electrode was fabricated by doctor blade method. First, a fluorinated tin oxide (FTO) substrate ( $12-14 \Omega/sq$ , and 2.2 mm thick), purchased from Pilkington Glass, was cleaned with ethanol and water, and dried in N<sub>2</sub>. Second, the FTO substrate was coated with a gel containing 0.5 wt % cata-

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lysts and 3.9 wt % PVA, and then sintered at 500 °C for 2 h. Third, the film glass was cut into several parts. Each part had an exposed area of  $1 \times 1$  cm<sup>2</sup>. Measurements were performed in 0.5M NaClO<sub>4</sub> (pH 7) at 10 mV/s, using a platinum gauze as counter electrode, and an Ag/AgCl electrode as reference electrode. Instrument was a CHI660E Electrochemical Station (Chenghua, Shanghai), attached with a 500 W Xenon lamp and a 320 nm cut-off filter.

# ASSOCIATED CONTENT

**Supporting Information**. Tables of solid parameters in Mössbauer, N<sub>2</sub> adsorption, O<sub>2</sub> reduction onset potentials, XRD patterns, integrated data, Tauc plots, SEM images, photographs, Mössbauer plots, XPS spectra, N<sub>2</sub> adsorption isotherm, H<sub>2</sub>O<sub>2</sub> decomposition, magnetization curves, dark LSV curves for IR compensation and carbon rod counter electrode, LSV curves for water oxidation, four parallel LSV curves for phenol oxidation, OCP data fitting, XRD patterns and phenol degradation on calcined samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors.

## Notes

The authors declare no competing financial interest.

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