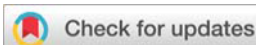


## COMMUNICATION



Cite this: *Photochem. Photobiol. Sci.*, 2018, **17**, 1018

Received 28th April 2018,

Accepted 2nd July 2018

DOI: 10.1039/c8pp00177d

rsc.li/pps

## Sustained production of H<sub>2</sub>O<sub>2</sub> in alkaline water solution using borate and phosphate-modified Au/TiO<sub>2</sub> photocatalysts†

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UV irradiation of Au/TiO<sub>2</sub> photocatalysts in the presence of borate and phosphate anions can produce H<sub>2</sub>O<sub>2</sub> at a millimolar level in alkaline water solution. The positive effect of the anions is ascribed to the anion-mediated hole transfer from Au/TiO<sub>2</sub> to an electron donor which thus accelerates the two-electron reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>.

Hydrogen peroxide has been widely utilized in the chemical industry and environmental remediation as a green oxidant, with only water and O<sub>2</sub> as the reaction byproducts.<sup>1</sup> At present, H<sub>2</sub>O<sub>2</sub> is mainly synthesized through anthraquinone oxidation.<sup>2</sup> This process requires significant organic solvents, hydrogen gas and energy input, and is not environmentally friendly. Another route is the direct synthesis of H<sub>2</sub>O<sub>2</sub> from O<sub>2</sub> and H<sub>2</sub> using metal-based catalysts (Pd or Pd/Au alloys).<sup>2–5</sup> However, this reaction suffers from the explosion risk, due to the mixture of H<sub>2</sub> and O<sub>2</sub>. As such, a novel and green method for the generation of H<sub>2</sub>O<sub>2</sub> is essentially needed.

Photocatalytic O<sub>2</sub> reduction offers a completely sustainable route to produce H<sub>2</sub>O<sub>2</sub> with only water, oxygen and solar energy as the input, which has attracted much attention in recent years.<sup>6–19</sup> For example, UV irradiation of a TiO<sub>2</sub> system in the presence of electron donors and O<sub>2</sub> can produce H<sub>2</sub>O<sub>2</sub>. However, the generated H<sub>2</sub>O<sub>2</sub> is limited to the micromolar level, which is ascribed to the slow oxygen reduction and fast H<sub>2</sub>O<sub>2</sub> decomposition *via* the surface Ti-OOH species with the excited electrons.<sup>7,8,20</sup> To improve the formation of H<sub>2</sub>O<sub>2</sub> in the TiO<sub>2</sub>-based photocatalytic system, numerous studies have been done, including the loading of noble metals (Au or Au/Ag alloys) on TiO<sub>2</sub>,<sup>6,7,10</sup> modification of TiO<sub>2</sub> with a reduced graphene oxide cocatalyst,<sup>8</sup> carbonate loading on Au/TiO<sub>2</sub>,<sup>9</sup> doping of TiO<sub>2</sub> with S or N,<sup>12</sup> the addition of Cu<sup>2+</sup> ions into a

TiO<sub>2</sub> suspension,<sup>13</sup> surface-fluorination of TiO<sub>2</sub>,<sup>14</sup> replacement of an aliphatic alcohol electron donor with benzylic alcohol<sup>15</sup> and designing of an SiO<sub>2</sub>-TiO<sub>2</sub>-Au core-shell structure.<sup>19</sup> Of particular note is the loading of Au nanoparticles on TiO<sub>2</sub>, which has been confirmed as one of the most effective methods to enhance the H<sub>2</sub>O<sub>2</sub> production at a millimolar level. The increased production of H<sub>2</sub>O<sub>2</sub> on Au/TiO<sub>2</sub> is due to the increase in the electron transfer from TiO<sub>2</sub> to Au through a Schottky junction, the increase in the two-electron reduction of O<sub>2</sub> on Au, and the decrease in the adsorption and decomposition of H<sub>2</sub>O<sub>2</sub> on Au as well.<sup>6,7,9–11</sup> However, to our knowledge, the solution used in most of these studies is acidic, probably due to the following two reasons. First, the rate of H<sub>2</sub>O<sub>2</sub> formation decreases with the increase of the solution pH, because H<sub>2</sub>O<sub>2</sub> is produced through the proton coupled electron transfer.<sup>10</sup> Second, the rate of H<sub>2</sub>O<sub>2</sub> decomposition increases with the solution pH.<sup>10</sup> Therefore, the production of H<sub>2</sub>O<sub>2</sub> with a larger steady-state concentration in a neutral or basic solution is a challenge.

Inorganic anions have been widely used as a hole transfer cocatalyst for the TiO<sub>2</sub>-photocatalyzed degradation of organic pollutants in aqueous solution.<sup>21,22</sup> For example, we have recently reported that borate anions have a positive effect on the photocatalytic degradation of phenol over TiO<sub>2</sub> (brookite or anatase)<sup>23,24</sup> and Pt/TiO<sub>2</sub> (anatase)<sup>25</sup> in aqueous suspensions from pH 5 to 9. We have also reported that the addition of phosphate anions into the suspension of brookite TiO<sub>2</sub><sup>23</sup> and Pt/Bi<sub>2</sub>WO<sub>6</sub><sup>26</sup> can enhance the photocatalytic degradation of phenol in the initial pH range of 3–9. The anion-induced rate enhancement of phenol degradation is ascribed to the hole oxidation of anions to produce the anion radicals, followed by phenol oxidation to regenerate the anions.<sup>24–26</sup> Based on the results reviewed above, we guess that the anion-mediated hole transfer may cooperate with the Au-mediated electron transfer from TiO<sub>2</sub> to Au. This would accelerate the two-electron reduction of O<sub>2</sub> on Au particles and consequently enhance the photocatalytic formation of H<sub>2</sub>O<sub>2</sub>.

In this study, we report a significant enhancement of H<sub>2</sub>O<sub>2</sub> production at the millimolar level upon the addition of 2 mM

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† Electronic supplementary information (ESI) available: Experimental details, XRD patterns, N<sub>2</sub> adsorption-desorption isotherms, diffuse reflectance spectra, physical parameters of the catalysts, SEM images, EDS spectra, high-resolution TEM, and the XPS spectrum. See DOI: 10.1039/c8pp00177d

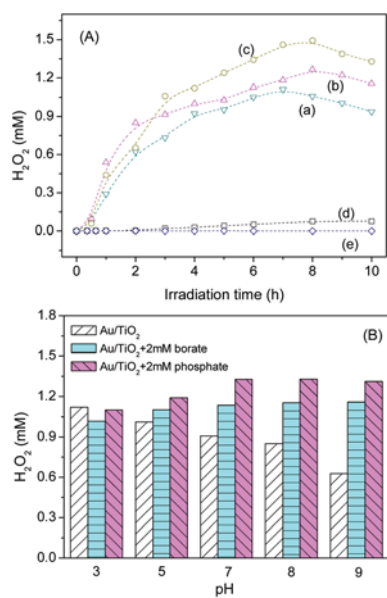
borate or phosphate anions into an air-saturated methanol water solution of Au/TiO<sub>2</sub> in a wide range of pH from 5 to 9. Au particles were deposited on commercial anatase TiO<sub>2</sub> (Sigma-Aldrich) by the deposition-precipitation method described in the literature.<sup>7,10</sup> The synthetic procedures and sample characterization are shown in the ESI.† In brief, the loading amount of Au in Au/TiO<sub>2</sub> was 0.61 wt%, measured by inductively coupled plasma mass spectroscopy. The X-ray diffraction patterns of TiO<sub>2</sub> and Au/TiO<sub>2</sub> (Fig. S1A†) well matched those of standard anatase TiO<sub>2</sub> (PDF #65-5714). The specific surface areas of TiO<sub>2</sub> and Au/TiO<sub>2</sub> were calculated to be 49.5 and 42.7 m<sup>2</sup> g<sup>-1</sup> (Table S1†), respectively. Additionally, scanning electron microscopy images showed that the particles greatly aggregated together, with an average particle size of 40 nm (Fig. S2†). Elemental analysis showed that Au particles were uniformly distributed on the surface of TiO<sub>2</sub> (Fig. S3†). Using high-resolution transmission electron microscopy, the Au particles were found to be spherical with an average diameter of 13 nm. The lattice distances were 0.35 nm for the anatase TiO<sub>2</sub> (101) and 0.24 nm for the Au (111) facet (Fig. S4†). In the X-ray photoelectron spectroscopy of Au/TiO<sub>2</sub> (Fig. S5†), there appeared the binding energies of Au 4f<sub>7/2</sub> at 83.79 eV and Au 4f<sub>5/2</sub> at 87.37 eV, in accordance with those of metallic Au.<sup>6</sup>

The photocatalytic reaction was carried out in a Pyrex glass reactor, irradiated externally with a 300 W high-pressure mercury lamp at  $\lambda > 320$  nm. Fig. 1A shows the time profiles of H<sub>2</sub>O<sub>2</sub> formation over different catalysts in a 4 vol% CH<sub>3</sub>OH

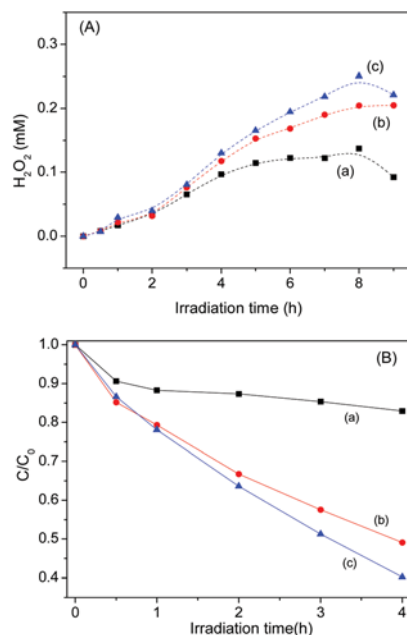
aqueous suspension, performed at 20 °C and an initial pH of 8. The H<sub>2</sub>O<sub>2</sub> concentration was measured through the horse-radish peroxide-catalyzed oxidation of *N,N*-diethyl-*p*-phenylenediamine.<sup>27</sup> With bare TiO<sub>2</sub>, the H<sub>2</sub>O<sub>2</sub> production was rather low, with only 77.8  $\mu$ M after the suspension was irradiated for 10 h. With Au/TiO<sub>2</sub>, the H<sub>2</sub>O<sub>2</sub> production was increased by an order of magnitude. However, with Pt/TiO<sub>2</sub>, the H<sub>2</sub>O<sub>2</sub> production was even lower than that measured from TiO<sub>2</sub>, which is probably ascribed to the Pt-catalyzed decomposition of H<sub>2</sub>O<sub>2</sub>.<sup>28</sup> These observations indicate that Au is a better cocatalyst for the production of H<sub>2</sub>O<sub>2</sub> over TiO<sub>2</sub>, which is in good agreement with the literature results.<sup>6,7,9,10</sup> Upon the addition of 2 mM borate or phosphate anions, interestingly, the formation of H<sub>2</sub>O<sub>2</sub> over Au/TiO<sub>2</sub> was greatly increased. For example, after photoirradiation for 3 hours, the amount of H<sub>2</sub>O<sub>2</sub> followed the order of Au/TiO<sub>2</sub>/phosphate (1.06 mM) > Au/TiO<sub>2</sub>/borate (0.91 mM) > Au/TiO<sub>2</sub> (0.73 mM). In other words, the H<sub>2</sub>O<sub>2</sub> production at the millimolar level over Au/TiO<sub>2</sub> can be achieved in alkaline water solution with the assistance of inorganic anions. In all cases, moreover, the H<sub>2</sub>O<sub>2</sub> concentration increased with the irradiation time, and then decreased after reaching a maximum. This is indicative of a competition between the formation and the decomposition of H<sub>2</sub>O<sub>2</sub>.

Fig. 1B shows the results of H<sub>2</sub>O<sub>2</sub> production under UV illumination for 10 h in aqueous solution as a function of initial pH. As the initial pH of the suspension was increased, the production of H<sub>2</sub>O<sub>2</sub> over Au/TiO<sub>2</sub> rapidly declined. The H<sub>2</sub>O<sub>2</sub> concentration at pH 3 was 1.13 mM, but it decreased to 0.63 mM at pH 9. This trend is in good agreement with the results reported by Tada and coworkers.<sup>10</sup> In contrast, the production of H<sub>2</sub>O<sub>2</sub> over Au/TiO<sub>2</sub> in the presence of 2 mM borate and phosphate anions gradually increased with the increase of the suspension pH. Strikingly, at pH 9, the H<sub>2</sub>O<sub>2</sub> concentration in the presence of borate and phosphate anions can still reach 1.16 and 1.31 mM, respectively. These observations indicate that these anions have a positive effect on the H<sub>2</sub>O<sub>2</sub> production in a methanolic aqueous solution from an initial pH of 5 to an initial pH of 9.

To produce H<sub>2</sub>O<sub>2</sub> through a more sustainable route, it is better to replace the alcoholic electron donor with environmental pollutants. Phenol is a representative environmental pollutant due to the robust nature of its aromatic structure. Fig. 2 shows the result of H<sub>2</sub>O<sub>2</sub> production over Au/TiO<sub>2</sub> using phenol as the electron donor. As the irradiation time increased, the H<sub>2</sub>O<sub>2</sub> concentration in the aqueous phase increased, and then decreased. At 8 h, the H<sub>2</sub>O<sub>2</sub> concentration was 137  $\mu$ M, which was much higher than that (10  $\mu$ M) previously obtained from anatase TiO<sub>2</sub> in the presence of phenol.<sup>29</sup> This observation indicates that Au is indeed an effective cocatalyst for the TiO<sub>2</sub>-photocatalyzed production of H<sub>2</sub>O<sub>2</sub>. Upon the addition of 2 mM borate and phosphate anions into Au/TiO<sub>2</sub>, the H<sub>2</sub>O<sub>2</sub> production at 9 h was increased by 1.21 and 1.39 fold (Fig. 2), respectively. These observations further confirm that the borate and phosphate anions do have a positive effect on the production of H<sub>2</sub>O<sub>2</sub> over Au/TiO<sub>2</sub>.



**Fig. 1** (A) Time profile of the photocatalytic formation of H<sub>2</sub>O<sub>2</sub> under UV irradiation in air-saturated water solution at initial pH 8.0. The catalysts are (a) Au/TiO<sub>2</sub>, (b) Au/TiO<sub>2</sub> + 2 mM borate, (c) Au/TiO<sub>2</sub> + 2 mM phosphate, (d) TiO<sub>2</sub> and (e) Pt/TiO<sub>2</sub>. (B) Effect of solution pH on the photocatalytic formation of H<sub>2</sub>O<sub>2</sub> under photoirradiation for 10 h over Au/TiO<sub>2</sub> in the presence or the absence of 2 mM borate or phosphate anions. Note: H<sub>2</sub>O<sub>2</sub> production was measured in the presence of 4 vol% CH<sub>3</sub>OH as the electron donor at 20 °C.



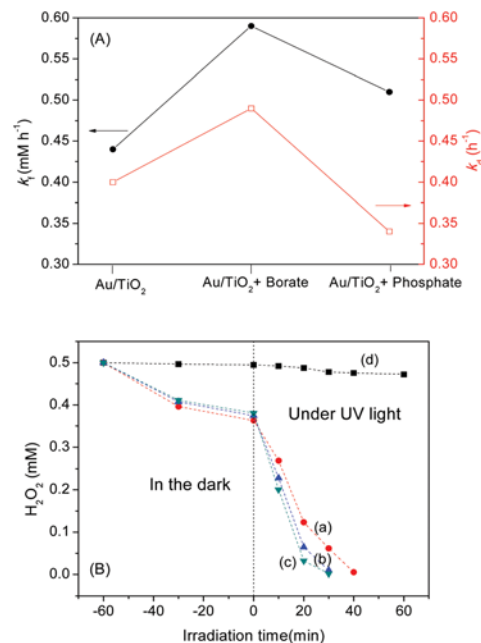
**Fig. 2** Time profile of  $\text{H}_2\text{O}_2$  production (A) and phenol degradation (B) under UV irradiation in air-saturated water solution at initial pH 8.0, measured with phenol (0.86 mM) as the electron donor over different catalysts: (a)  $\text{Au}/\text{TiO}_2$ , (b)  $\text{Au}/\text{TiO}_2 + 2 \text{ mM borate}$  and (c)  $\text{Au}/\text{TiO}_2 + 2 \text{ mM phosphate}$ .

Meanwhile, the phenol concentration also gradually decreased with the increase of irradiation time (Fig. 2B). The rates of phenol degradation obtained from different catalysts followed the order of  $\text{Au}/\text{TiO}_2/\text{phosphate} > \text{Au}/\text{TiO}_2/\text{borate} > \text{Au}/\text{TiO}_2$ , the trend of which is in good agreement with that observed from  $\text{H}_2\text{O}_2$  production in Fig. 2A. These observations clearly indicate that photocatalysis can provide a good solution for the simultaneous production of  $\text{H}_2\text{O}_2$  and the elimination of hazardous environmental pollutants.

To understand the positive effect of borate and phosphate anions on  $\text{H}_2\text{O}_2$  generation over  $\text{Au}/\text{TiO}_2$ , a kinetics analysis was carried out by assuming that the formation and decomposition rates of  $\text{H}_2\text{O}_2$  follow the zero-order and the first-order kinetics, respectively. Then the following equation for the time-dependent concentration of  $\text{H}_2\text{O}_2$  is obtained (ESI†),<sup>7,9,10</sup> where  $k_f$  and  $k_d$  are the formation rate constant and the decomposition rate constant, respectively.

$$[\text{H}_2\text{O}_2] = \frac{k_f}{k_d} [1 - \exp(-k_d t)]$$

By using this equation, the data at the first 7 hours as shown in Fig. 1A were well fitted, and the results are shown in Fig. 3A. It is clear that the  $k_f$  value is increased upon the addition of either borate or phosphate anions. This provides direct evidence for the positive effect of the anions on the  $\text{Au}/\text{TiO}_2$ -photocatalyzed formation of  $\text{H}_2\text{O}_2$ . However, upon the addition of borate and phosphate anions, the  $k_d$  value is increased and decreased, respectively. This might be due to the rate of  $\text{H}_2\text{O}_2$  decomposition that changes with the  $\text{H}_2\text{O}_2$



**Fig. 3** (A) Formation rate constant ( $k_f$ , solid symbol) and the decomposition rate constant ( $k_d$ , open symbol) for  $\text{H}_2\text{O}_2$  production. (B) Dark adsorption and photocatalytic decomposition of 0.50 mM  $\text{H}_2\text{O}_2$ . All experiments were carried out in an aerated aqueous suspension at initial pH 8.0, under the conditions of (a)  $\text{Au}/\text{TiO}_2$ , (b)  $\text{Au}/\text{TiO}_2 + 2 \text{ mM borate}$ , (c)  $\text{Au}/\text{TiO}_2 + 2 \text{ mM phosphate}$  and (d)  $\text{H}_2\text{O}_2$ .

concentration. Since the total concentration of  $\text{H}_2\text{O}_2$  in the aqueous phase and on the catalyst surface is unknown, it's difficult to distinguish the decomposition rate of  $\text{H}_2\text{O}_2$  by using  $k_d$ . Then, we conducted a  $\text{H}_2\text{O}_2$  decomposition experiment by using  $\text{H}_2\text{O}_2$  as the reacting substrate, and the result is shown in Fig. 3B. In the dark,  $\text{H}_2\text{O}_2$  in the aqueous solution greatly adsorbed onto  $\text{Au}/\text{TiO}_2$ , due to the formation of a surface  $\text{Ti}(\text{IV})$  complex. Upon the addition of borate or phosphate anions, the amount of  $\text{H}_2\text{O}_2$  adsorption on  $\text{Au}/\text{TiO}_2$  was slightly decreased, indicative of the anion species occupying the oxide surface. Under UV illumination, the concentration of  $\text{H}_2\text{O}_2$  decreased with time. Surprisingly, the rate of  $\text{H}_2\text{O}_2$  decomposition in the presence of the anions was higher than that in the absence of the anions. In previous studies, Maurino *et al.* found that the surface fluorination of  $\text{TiO}_2$  led to a significant increase of  $\text{H}_2\text{O}_2$  production, which is ascribed to the decrease of  $\text{H}_2\text{O}_2$  adsorption and decomposition.<sup>14</sup> Tada *et al.* found that the carbonate-modified  $\text{Au}/\text{TiO}_2$  has a high visible-light activity for  $\text{H}_2\text{O}_2$  production, and they also ascribed it to the decrease of  $\text{H}_2\text{O}_2$  adsorption and decomposition.<sup>9</sup> In the present study, however, an opposite effect of the anions was observed from the  $\text{H}_2\text{O}_2$  decomposition on  $\text{Au}/\text{TiO}_2$ . In the alkaline solution, the surface of  $\text{Au}/\text{TiO}_2$  would be negatively charged. This would disfavor the adsorption of the negatively charged borate and phosphate anions onto  $\text{Au}/\text{TiO}_2$ , due to the electrostatic repulsion. In fact, the dark adsorption of  $\text{H}_2\text{O}_2$  on  $\text{Au}/\text{TiO}_2$  changed a little upon the addition of borate and phosphate anions (Fig. 3B). Then, the observed

increase of  $\text{H}_2\text{O}_2$  production upon the addition of borate and phosphate anions (Fig. 1A and 2A) must be attributed to other factors, as will be discussed below.

To further understand the anion effect, a photoelectrochemical measurement with an Au/TiO<sub>2</sub> film electrode was carried out. Fig. 4 shows the linear sweep voltammetry of Au/TiO<sub>2</sub> in the absence and the presence of 2 mM borate or phosphate anions. The experiment was carried out in a three-electrode configuration using 0.43 mM phenol as the hole scavenger. In the dark, the electrode currents were very weak, either in the absence or the presence of the anions. Under UV light, the Au/TiO<sub>2</sub> electrode exhibited an anodic photocurrent, which started at approximately  $-0.25$  V (vs. Ag/AgCl) and then increased as the bias anodically shifted. This is indicative of phenol oxidation by the photogenerated holes of Au/TiO<sub>2</sub>. Upon the addition of borate and phosphate anions, interestingly, the onset potentials for phenol oxidation were negatively shifted by 60 and 40 mV, respectively. Meanwhile, the photocurrents were also significantly increased. These observations suggest that the borate and phosphate anions are capable of mediating the hole transfer from irradiated Au/TiO<sub>2</sub> to phenol, and thus increase the photocurrent of phenol oxidation. The same mechanism would hold for the photocatalytic system, in which both  $\text{H}_2\text{O}_2$  production (Fig. 2A) and phenol degradation (Fig. 2B) are notably accelerated upon the anion addition. Such anion-mediated hole transfer would improve the charge separation of Au/TiO<sub>2</sub>, and consequently increase the electron accumulation on the Au particles. As a result, the  $\text{H}_2\text{O}_2$  formation is enhanced, because the two-electron reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$  preferentially occurs on the Au sites of Au/TiO<sub>2</sub>.<sup>11,30</sup>

In conclusion, we have presented a simple method of anion addition for the sustained production of  $\text{H}_2\text{O}_2$  at the millimolar level in a methanol aqueous suspension of Au/TiO<sub>2</sub> in the initial pH range of 5–9. It is proposed that the borate and phosphate anions can mediate the hole transfer, and hence accelerate the electron transfer from TiO<sub>2</sub> to Au for the  $\text{O}_2$  reduction to  $\text{H}_2\text{O}_2$ . This addresses the dilemma how to produce a large amount of  $\text{H}_2\text{O}_2$  in an alkaline aqueous solu-

tion. Moreover, we have also shown that  $\text{H}_2\text{O}_2$  production and phenol degradation on Au/TiO<sub>2</sub> can be simultaneously enhanced upon the anion addition. This provides a sustainable route for pollution treatment and  $\text{H}_2\text{O}_2$  production.

## Conflicts of interest

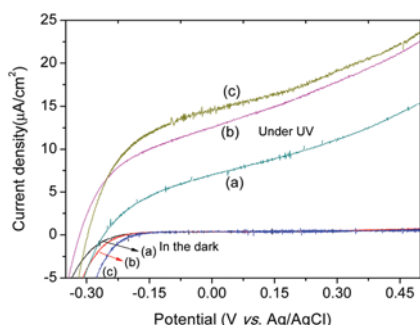
There are no conflicts to declare.

## Acknowledgements

This work was supported by the Creative Research Group of the National Natural Science Foundation of China (No. 21621005).

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**Fig. 4** Linear sweep voltammetry of the Au/TiO<sub>2</sub> film electrode in the presence of 0.43 mM phenol, recorded in the dark (black, red and blue lines), and under UV light (upper lines), at a scan rate of 20 mV s<sup>-1</sup>. The experiments were carried out in 0.5 M NaClO<sub>4</sub> at pH 8, in the absence (a), and the presence of 2.0 mM borate (b) or 2.0 mM phosphate (c).

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