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## Selective dual-purpose photocatalysis for simultaneous H<sub>2</sub> evolution and mineralization of organic compounds enabled by a Cr<sub>2</sub>O<sub>3</sub> barrier layer coated on Rh/SrTiO<sub>3</sub>†

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**Dual-functional photocatalysis for H<sub>2</sub> evolution with the simultaneous mineralization of 4-chlorophenol was achieved under de-aerated conditions using a Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> photocatalyst which has Rh nanoparticles covered with a thin Cr<sub>2</sub>O<sub>3</sub> barrier layer to selectively control and maximize the dual-functional photocatalytic activity.**

Hydrogen is considered as an ideal energy storage medium and a promising energy carrier since it can be obtained from abundant natural resources such as water and biomass instead of fossil fuels.<sup>1–4</sup> In particular, photocatalytic water splitting is widely studied as a promising technology to produce hydrogen using solar light.<sup>5–7</sup> Another important application of photocatalysis is the degradation of organic compounds for the remediation of polluted water and air.<sup>8–12</sup> In photocatalytic H<sub>2</sub> production, organic electron donors are commonly used as sacrificial agents to scavenge photogenerated holes.<sup>13–17</sup> However, the intentional addition of organic electron donors (e.g., alcohols, organic acids, amines) for H<sub>2</sub> production is not practically acceptable since the electron donors themselves are another energy resource (often more expensive than H<sub>2</sub>). Therefore, a more desirable strategy is to use organic waste and pollutants in water as *in situ* electron donors. This is the concept of dual-functional photocatalysis which produces H<sub>2</sub> along with the simultaneous degradation of organic pollutants.<sup>18–20</sup> Recently, Kim *et al.* demonstrated that the simultaneous H<sub>2</sub> production with the anoxic photocatalytic degradation of organic compounds can be achieved by using TiO<sub>2</sub> modified by both surface fluorination and Pt deposition (F-TiO<sub>2</sub>/Pt).<sup>19,20</sup>

However, the total organic carbon (TOC) removal efficiency was negligible and TOC remained almost unchanged during the photocatalytic degradation of 4-chlorophenol (4-CP) on F-TiO<sub>2</sub>/Pt, because dioxygen was needed for mineralization. Meeting the optimal condition for dual-purpose photocatalysis is contradictory because the H<sub>2</sub> evolution requires anoxic conditions whereas the mineralization of organic compounds needs dioxygen.

In this study, a selective dual-purpose photocatalysis that achieves H<sub>2</sub> production and TOC removal simultaneously under anoxic conditions is reported. Instead of using the combination of TiO<sub>2</sub> (as a base photocatalyst) and Pt (as a cocatalyst for H<sub>2</sub> evolution), SrTiO<sub>3</sub> (base photocatalyst) and Rh@Cr<sub>2</sub>O<sub>3</sub> core-shell nanostructure (cocatalyst) were employed in this work. The photocatalytic activities of the composite materials of Cr<sub>2</sub>O<sub>3</sub>/Pt/SrTiO<sub>3</sub> and other Rh@Cr<sub>2</sub>O<sub>3</sub> (core-shell) loaded metal oxides have been previously demonstrated for the overall water splitting.<sup>21,22</sup> In this work, we demonstrate that Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> can be a promising dual-purpose photocatalyst that can produce H<sub>2</sub> along with TOC removal (mineralization) of aromatic pollutants in a de-aerated aqueous suspension which is considered an inappropriate condition to achieve the mineralization of organic pollutants.

Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> photocatalyst was prepared by step-wise photo-deposition of Rh nanoparticles on the SrTiO<sub>3</sub> surface as a core and then the Cr<sub>2</sub>O<sub>3</sub> nano-shell on the Rh core.<sup>22</sup> The loading amount of Rh and Cr<sub>2</sub>O<sub>3</sub> was 0.5 wt% and 0.75 wt%, respectively. Fig. S1 (ESI†) shows the HRTEM images of Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> and Rh/SrTiO<sub>3</sub> photocatalysts. Rh nanoparticles of 2–4 nm diameter were observed to be deposited on the surface of both photocatalysts and the Cr<sub>2</sub>O<sub>3</sub> shell was seen around the Rh core of the Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> catalyst. Rh/SrTiO<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> were compared for the photocatalytic degradation of 4-CP under de-aerated conditions as shown in Fig. 1. Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> exhibited a much higher activity than Rh/SrTiO<sub>3</sub> in both the removal of 4-CP and the concurrent production of chloride (Fig. 1a). The TOC removal was also highly enhanced with Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> (Fig. 1b). These results clearly indicate that the removal of 4-CP in the suspension of Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> proceeded along with the mineralization

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† Electronic supplementary information (ESI) available: Experimental details of the synthesis of Rh/SrTiO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> and F-TiO<sub>2</sub>/Pt, experimental details of photocatalytic reaction and photoelectrochemical tests, and Fig. S1–S7. See DOI: 10.1039/c6cc04260k



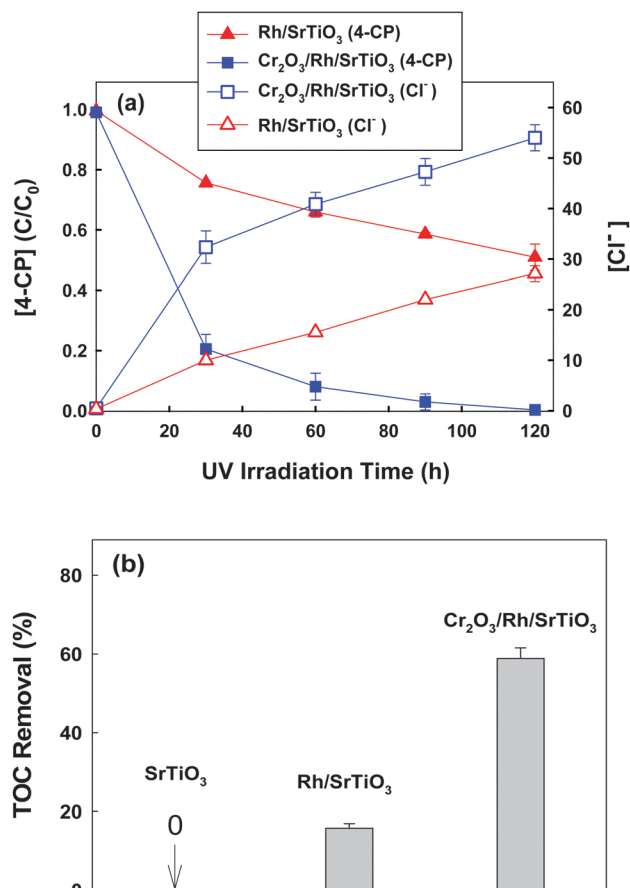


Fig. 1 (a) Photocatalytic degradation of 4-CP and the concurrent production of chloride in a de-aerated catalyst suspension. (b) Comparison of TOC removal efficiencies after 2 h photocatalytic reaction. Experimental conditions: [catalyst] = 0.5 g L<sup>-1</sup>, [4-CP]<sub>0</sub> = 100 μM, pH<sub>0</sub> = 7, λ > 320 nm, air-tight, and initially Ar-purged for 1 h before UV irradiation.

(i.e., TOC removal) even under the de-aerated conditions, where the initial dissolved O<sub>2</sub> was measured to be less than 0.1 ppm using a dissolved O<sub>2</sub> meter. In the absence of O<sub>2</sub> that serves as a main electron scavenger, the photocatalytic oxidation and mineralization should be inhibited on a bare semiconductor but the loading of Rh and Cr<sub>2</sub>O<sub>3</sub> changes the photocatalytic reaction mechanism.

H<sub>2</sub> evolution was also monitored during the anoxic degradation of 4-CP. As seen in Fig. 2a, markedly increased H<sub>2</sub> production was observed with the Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> photocatalyst compared with Rh/SrTiO<sub>3</sub>. The initial rate of H<sub>2</sub> production on Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> was around 12 μmol h<sup>-1</sup>. The apparent photonic efficiency of H<sub>2</sub> evolution (with 300 μM 4-CP) was separately measured under the irradiation centered around λ = 330 ± 10 nm and determined to be 0.7%. Concurrent O<sub>2</sub> evolution was also observed in the case of Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub>, whereas no O<sub>2</sub> production was observed with Rh/SrTiO<sub>3</sub>. Such a difference can be ascribed to the fact that the Cr<sub>2</sub>O<sub>3</sub> layer over Rh can suppress the back reaction of H<sub>2</sub> with O<sub>2</sub> to produce H<sub>2</sub>O.<sup>23</sup> The fact that O<sub>2</sub> was evolved along with the degradation of 4-CP on Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> indicates that holes react with both 4-CP and water molecules. The *in situ* generated O<sub>2</sub> should be subsequently consumed during the



Fig. 2 (a) Time-profiled production of H<sub>2</sub> and O<sub>2</sub> in the suspension of Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> and Rh/SrTiO<sub>3</sub> with 4-CP (300 μM) in the initially de-aerated suspension. (b) Comparison of photocatalytic O<sub>2</sub> evolution in the suspension of Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> (after 3 h reaction) in the presence and absence of 4-CP.

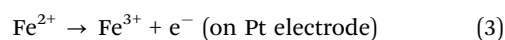
mineralization of 4-CP,<sup>19,24,25</sup> which explains why the degradation of 4-CP was possible under de-aerated conditions. As a result, the *in situ* O<sub>2</sub> evolution was significantly enhanced in the absence of 4-CP (Fig. 2b). The mineralization of 4-CP can be expressed by eqn (1).



During the initial stage (for 1 h) of photo-irradiation, the rates of H<sub>2</sub> and O<sub>2</sub> evolution were determined to be around 12 μmol h<sup>-1</sup> and 1.2 μmol h<sup>-1</sup>, respectively. The O<sub>2</sub> evolution rate is much lower than the expected stoichiometric rate (6 μmol h<sup>-1</sup>) in the dual-purpose photocatalysis, which should be ascribed to the *in situ* consumption of O<sub>2</sub> in the mineralization (as mentioned above). In this case, the average TOC removal rate was 5.0 μmol h<sup>-1</sup>, which corresponds to 5.4 μmol h<sup>-1</sup> of the O<sub>2</sub> consumption rate (according to eqn (1)). Therefore, the sum of the apparent O<sub>2</sub> evolution (1.2 μmol h<sup>-1</sup>) and the *in situ* consumption of O<sub>2</sub> (5.4 μmol h<sup>-1</sup>) is 6.6 μmol h<sup>-1</sup>, which is close to the stoichiometric O<sub>2</sub> evolution rate of 6.0 μmol h<sup>-1</sup>. Incidentally, from a practical point of view, dual-functional photocatalysts working under air-saturated conditions would be desirable. Therefore, H<sub>2</sub> evolution in an aerated suspension of Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> was



To investigate the role of the Cr<sub>2</sub>O<sub>3</sub> shell on the Rh core and its effects on the interfacial electron transfer on Cr<sub>2</sub>O<sub>3</sub>/Rh/SrTiO<sub>3</sub> and Rh/SrTiO<sub>3</sub>, the Fe<sup>3+/2+</sup> redox couple-mediated photocurrent was collected (*via* reactions (2) and (3)) in the UV-irradiated suspension of each catalyst.<sup>27</sup>



Catalyst Samples	H <sub>2</sub> evolution rate (μmol/h)
Cr <sub>2</sub> O <sub>3</sub> /Rh/SrTiO <sub>3</sub> (pH 7)	~11.8
Cr <sub>2</sub> O <sub>3</sub> /Rh/SrTiO <sub>3</sub> (pH 3)	~10.8
F-TiO <sub>2</sub> /Pt (pH 7)	~1.8
F-TiO <sub>2</sub> /Pt (pH 3)	~4.8

Our recent studies demonstrated that the  $\text{TiO}_2$  modified with both Pt and fluoride ( $\text{F-TiO}_2/\text{Pt}$ ) exhibited a dual-functional photocatalytic activity for the simultaneous production of  $\text{H}_2$  and degradation of 4-CP.<sup>19,20</sup> In Fig. 3, the  $\text{H}_2$  production on  $\text{Cr}_2\text{O}_3/\text{Rh}/\text{SrTiO}_3$  was compared with  $\text{F-TiO}_2/\text{Pt}$  under neutral and acidic pH conditions. The photocatalytic activity of  $\text{Cr}_2\text{O}_3/\text{Rh}/\text{SrTiO}_3$  is higher than that of  $\text{F-TiO}_2/\text{Pt}$  and less affected by the pH change. It should be noted that the activity of  $\text{F-TiO}_2/\text{Pt}$  is markedly reduced at neutral pH whereas that of  $\text{Cr}_2\text{O}_3/\text{Rh}/\text{SrTiO}_3$  was little influenced by pH. As a result,  $\text{Cr}_2\text{O}_3/\text{Rh}/\text{SrTiO}_3$  is a better dual-functional photocatalyst from a practical point of view. In terms of the charge transfer characteristics, the following two major features make  $\text{Cr}_2\text{O}_3/\text{Rh}/\text{SrTiO}_3$  a practical dual-functional photocatalyst. For the electron transfer part, CB electrons are selectively consumed by protons only and their transfer to  $\text{O}_2$  and other electron acceptors (EA) is hindered because the  $\text{Cr}_2\text{O}_3$  barrier layer is selectively permeable only to protons. On the other hand, VB holes are utilized to oxidize both  $\text{H}_2\text{O}$  (to  $\text{O}_2$ ) and 4-CP (organic pollutants) simultaneously and the *in situ* generated  $\text{O}_2$  is immediately consumed for the mineralization of the organic pollutants.<sup>19,24,28</sup> The reaction mechanisms described above are schematically illustrated in Scheme 1. In the absence of the  $\text{Cr}_2\text{O}_3$  layer, the CB electrons can be consumed by not only protons but also *in situ* generated  $\text{O}_2$  and other reaction intermediates, which would reduce the overall dual-photocatalysis activity.

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**Scheme 1** Schematic illustrations of photocatalytic reaction mechanisms occurring on the surface of  $\text{Cr}_2\text{O}_3/\text{Rh}/\text{SrTiO}_3$ .

the accumulation of organic degradation intermediates on the catalyst surface.<sup>29,30</sup> To further investigate the effect of organic compounds in this dual functional photocatalysis, the evolution of  $\text{H}_2$  and  $\text{O}_2$  was simultaneously measured with repeated photocatalysis cycles. In this case, 100  $\mu\text{M}$  4-CP was initially added but not replenished in the subsequent cycles. Fig. S7 (ESI<sup>†</sup>) shows that  $\text{H}_2$  production was higher in the first cycle than in the subsequent cycles: the difference in  $\text{H}_2$  production should be ascribed to the organic electron donor (*i.e.*, 4-CP) effect. The extra holes scavenged by 4-CP make an equal number of electrons to be used for  $\text{H}_2$  production. At the same time,  $\text{O}_2$  evolved in the first cycle is immediately consumed for the mineralization of 4-CP. As a result, the ratio of  $\text{H}_2$  to  $\text{O}_2$  in the first cycle was significantly higher ( $\text{H}_2/\text{O}_2(r) = 6.9$ ) than the stoichiometric water splitting ratio ( $r = 2.0$ ). The ratio progressively approached the stoichiometric ratio as the cycle was repeated ( $r: 6.9 \rightarrow 2.7 \rightarrow 2.5 \rightarrow 2.2$ ).

In conclusion, this study demonstrated that the mineralization of organic pollutants can be achieved under the de-aerated conditions with the simultaneous  $\text{H}_2$  production over a  $\text{Cr}_2\text{O}_3/\text{Rh}/\text{SrTiO}_3$  photocatalyst. The present study showed the highest  $\text{H}_2$  evolution efficiency in dual-purpose photocatalysis to our knowledge. It is proposed that the  $\text{Cr}_2\text{O}_3$  shell on the Rh nanoparticle core markedly enhances the  $\text{H}_2$  production and TOC removal of aromatic pollutants, which makes  $\text{Cr}_2\text{O}_3/\text{Rh}/\text{SrTiO}_3$  an active dual-functional photocatalyst.

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