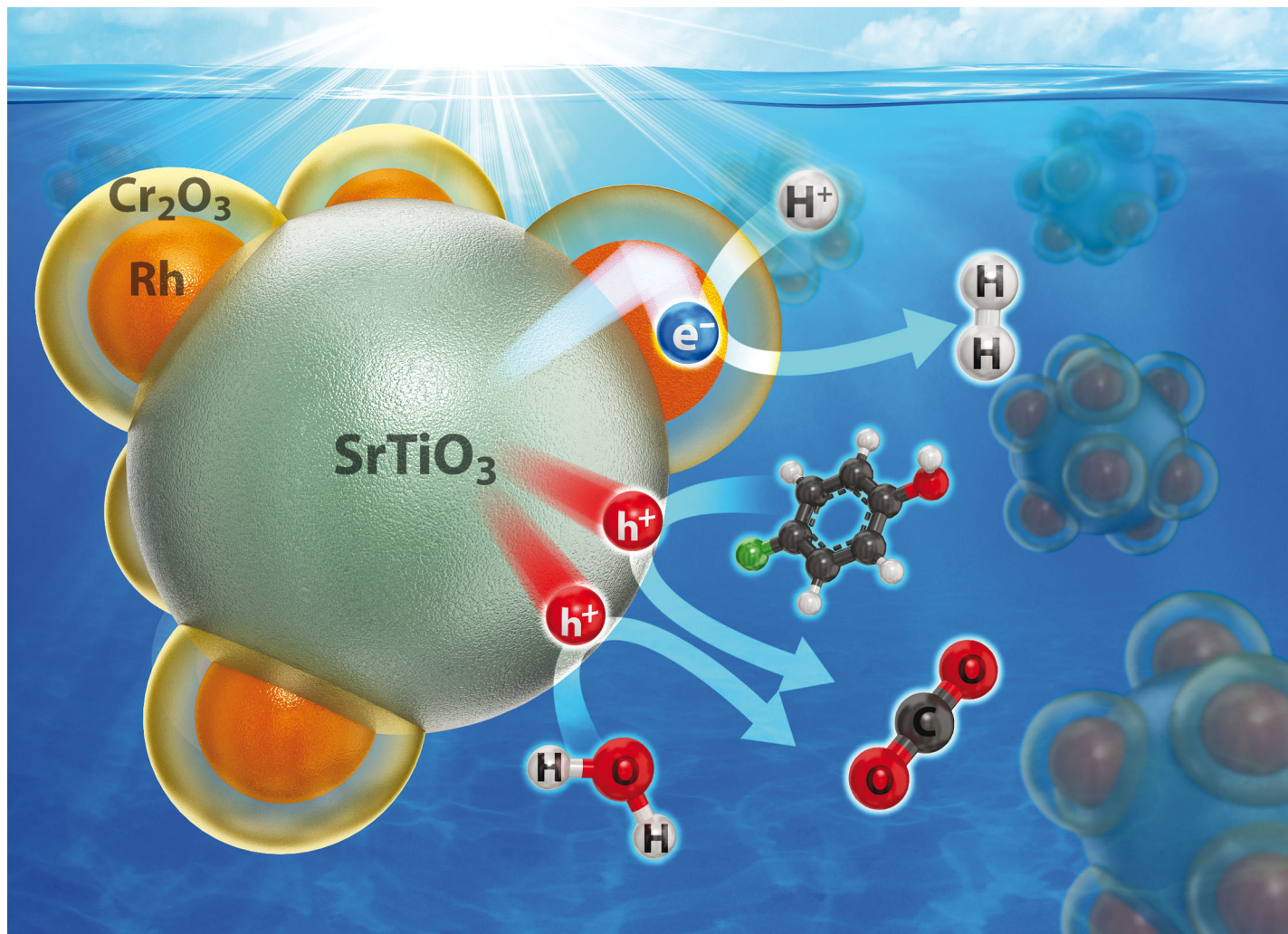




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Selective dual-purpose photocatalysis for simultaneous H_2 evolution and mineralization of organic compounds enabled by a Cr_2O_3 barrier layer coated on Rh/SrTiO_3

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Selective dual-purpose photocatalysis for simultaneous H₂ evolution and mineralization of organic compounds enabled by a Cr₂O₃ barrier layer coated on Rh/SrTiO₃[†]

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Dual-functional photocatalysis for H₂ evolution with the simultaneous mineralization of 4-chlorophenol was achieved under de-aerated conditions using a Cr₂O₃/Rh/SrTiO₃ photocatalyst which has Rh nanoparticles covered with a thin Cr₂O₃ 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.^{1–4} In particular, photocatalytic water splitting is widely studied as a promising technology to produce hydrogen using solar light.^{5–7} Another important application of photocatalysis is the degradation of organic compounds for the remediation of polluted water and air.^{8–12} In photocatalytic H₂ production, organic electron donors are commonly used as sacrificial agents to scavenge photogenerated holes.^{13–17} However, the intentional addition of organic electron donors (e.g., alcohols, organic acids, amines) for H₂ production is not practically acceptable since the electron donors themselves are another energy resource (often more expensive than H₂). 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 H₂ along with the simultaneous degradation of organic pollutants.^{18–20} Recently, Kim *et al.* demonstrated that the simultaneous H₂ production with the anoxic photocatalytic degradation of organic compounds can be achieved by using TiO₂ modified by both surface fluorination and Pt deposition (F-TiO₂/Pt).^{19,20}

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-TiO₂/Pt, because dioxygen was needed for mineralization. Meeting the optimal condition for dual-purpose photocatalysis is contradictory because the H₂ evolution requires anoxic conditions whereas the mineralization of organic compounds needs dioxygen.

In this study, a selective dual-purpose photocatalysis that achieves H₂ production and TOC removal simultaneously under anoxic conditions is reported. Instead of using the combination of TiO₂ (as a base photocatalyst) and Pt (as a cocatalyst for H₂ evolution), SrTiO₃ (base photocatalyst) and Rh@Cr₂O₃ core-shell nanostructure (cocatalyst) were employed in this work. The photocatalytic activities of the composite materials of Cr₂O₃/Pt/SrTiO₃ and other Rh@Cr₂O₃ (core-shell) loaded metal oxides have been previously demonstrated for the overall water splitting.^{21,22} In this work, we demonstrate that Cr₂O₃/Rh/SrTiO₃ can be a promising dual-purpose photocatalyst that can produce H₂ 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.

Cr₂O₃/Rh/SrTiO₃ photocatalyst was prepared by step-wise photo-deposition of Rh nanoparticles on the SrTiO₃ surface as a core and then the Cr₂O₃ nano-shell on the Rh core.²² The loading amount of Rh and Cr₂O₃ was 0.5 wt% and 0.75 wt%, respectively. Fig. S1 (ESI[†]) shows the HRTEM images of Cr₂O₃/Rh/SrTiO₃ and Rh/SrTiO₃ photocatalysts. Rh nanoparticles of 2–4 nm diameter were observed to be deposited on the surface of both photocatalysts and the Cr₂O₃ shell was seen around the Rh core of the Cr₂O₃/Rh/SrTiO₃ catalyst. Rh/SrTiO₃ and Cr₂O₃/Rh/SrTiO₃ were compared for the photocatalytic degradation of 4-CP under de-aerated conditions as shown in Fig. 1. Cr₂O₃/Rh/SrTiO₃ exhibited a much higher activity than Rh/SrTiO₃ in both the removal of 4-CP and the concurrent production of chloride (Fig. 1a). The TOC removal was also highly enhanced with Cr₂O₃/Rh/SrTiO₃ (Fig. 1b). These results clearly indicate that the removal of 4-CP in the suspension of Cr₂O₃/Rh/SrTiO₃ proceeded along with the mineralization

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[†] Electronic supplementary information (ESI) available: Experimental details of the synthesis of Rh/SrTiO₃, Cr₂O₃/Rh/SrTiO₃ and F-TiO₂/Pt, experimental details of photocatalytic reaction and photoelectrochemical tests, and Fig. S1–S7. See DOI: 10.1039/c6cc04260k

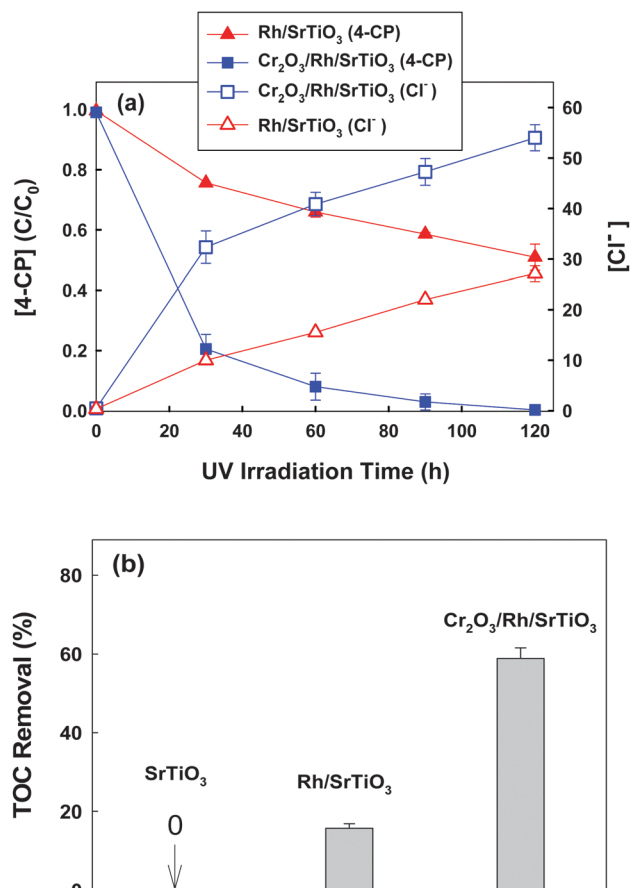


Fig. 1 (a) Photocatalytic degradation of 4-CP and the concurrent production of chloride in a de-aerated catalyst suspension. (b) Comparison of TOC removal efficiencies after 2 h photocatalytic reaction. Experimental conditions: [catalyst] = 0.5 g L⁻¹, [4-CP]₀ = 100 μM, pH₀ = 7, λ > 320 nm, air-tight, and initially Ar-purged for 1 h before UV irradiation.

(i.e., TOC removal) even under the de-aerated conditions, where the initial dissolved O₂ was measured to be less than 0.1 ppm using a dissolved O₂ meter. In the absence of O₂ 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 Cr₂O₃ changes the photocatalytic reaction mechanism.

H₂ evolution was also monitored during the anoxic degradation of 4-CP. As seen in Fig. 2a, markedly increased H₂ production was observed with the Cr₂O₃/Rh/SrTiO₃ photocatalyst compared with Rh/SrTiO₃. The initial rate of H₂ production on Cr₂O₃/Rh/SrTiO₃ was around 12 μmol h⁻¹. The apparent photonic efficiency of H₂ 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 O₂ evolution was also observed in the case of Cr₂O₃/Rh/SrTiO₃, whereas no O₂ production was observed with Rh/SrTiO₃. Such a difference can be ascribed to the fact that the Cr₂O₃ layer over Rh can suppress the back reaction of H₂ with O₂ to produce H₂O.²³ The fact that O₂ was evolved along with the degradation of 4-CP on Cr₂O₃/Rh/SrTiO₃ indicates that holes react with both 4-CP and water molecules. The *in situ* generated O₂ should be subsequently consumed during the

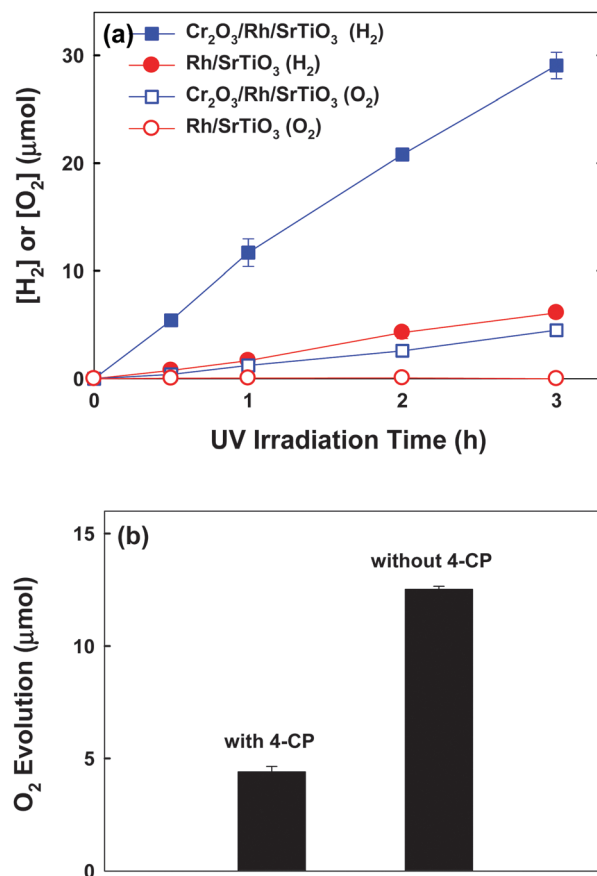
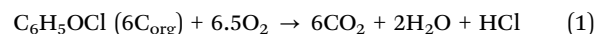


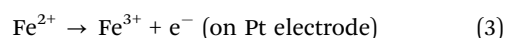
Fig. 2 (a) Time-profiled production of H₂ and O₂ in the suspension of Cr₂O₃/Rh/SrTiO₃ and Rh/SrTiO₃ with 4-CP (300 μM) in the initially de-aerated suspension. (b) Comparison of photocatalytic O₂ evolution in the suspension of Cr₂O₃/Rh/SrTiO₃ (after 3 h reaction) in the presence and absence of 4-CP.

mineralization of 4-CP,^{19,24,25} which explains why the degradation of 4-CP was possible under de-aerated conditions. As a result, the *in situ* O₂ 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 H₂ and O₂ evolution were determined to be around 12 μmol h⁻¹ and 1.2 μmol h⁻¹, respectively. The O₂ evolution rate is much lower than the expected stoichiometric rate (6 μmol h⁻¹) in the dual-purpose photocatalysis, which should be ascribed to the *in situ* consumption of O₂ in the mineralization (as mentioned above). In this case, the average TOC removal rate was 5.0 μmol h⁻¹, which corresponds to 5.4 μmol h⁻¹ of the O₂ consumption rate (according to eqn (1)). Therefore, the sum of the apparent O₂ evolution (1.2 μmol h⁻¹) and the *in situ* consumption of O₂ (5.4 μmol h⁻¹) is 6.6 μmol h⁻¹, which is close to the stoichiometric O₂ evolution rate of 6.0 μmol h⁻¹. Incidentally, from a practical point of view, dual-functional photocatalysts working under air-saturated conditions would be desirable. Therefore, H₂ evolution in an aerated suspension of Cr₂O₃/Rh/SrTiO₃ was

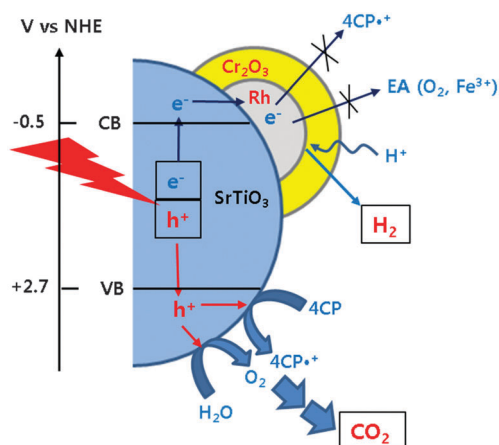
To investigate the role of the Cr₂O₃ shell on the Rh core and its effects on the interfacial electron transfer on Cr₂O₃/Rh/SrTiO₃ and Rh/SrTiO₃, the Fe^{3+/2+} redox couple-mediated photocurrent was collected (*via* reactions (2) and (3)) in the UV-irradiated suspension of each catalyst.²⁷



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

Our recent studies demonstrated that the 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 H_2 and degradation of 4-CP.^{19,20} In Fig. 3, the 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 O_2 and other electron acceptors (EA) is hindered because the Cr_2O_3 barrier layer is selectively permeable only to protons. On the other hand, VB holes are utilized to oxidize both H_2O (to O_2) and 4-CP (organic pollutants) simultaneously and the *in situ* generated O_2 is immediately consumed for the mineralization of the organic pollutants.^{19,24,28} The reaction mechanisms described above are schematically illustrated in Scheme 1. In the absence of the Cr_2O_3 layer, the CB electrons can be consumed by not only protons but also *in situ* generated 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.^{29,30} To further investigate the effect of organic compounds in this dual functional photocatalysis, the evolution of H_2 and O_2 was simultaneously measured with repeated photocatalysis cycles. In this case, 100 μM 4-CP was initially added but not replenished in the subsequent cycles. Fig. S7 (ESI[†]) shows that H_2 production was higher in the first cycle than in the subsequent cycles: the difference in 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 H_2 production. At the same time, O_2 evolved in the first cycle is immediately consumed for the mineralization of 4-CP. As a result, the ratio of H_2 to 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 H_2 production over a $\text{Cr}_2\text{O}_3/\text{Rh}/\text{SrTiO}_3$ photocatalyst. The present study showed the highest H_2 evolution efficiency in dual-purpose photocatalysis to our knowledge. It is proposed that the Cr_2O_3 shell on the Rh nanoparticle core markedly enhances the 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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References

- G. Zhang, C. Ni, X. Huang, A. Welgamage, L. A. Lawton, P. K. J. Robertson and J. T. S. Irvine, *Chem. Commun.*, 2016, **52**, 1673.
- M. Ni, D. Y. C. Leung and M. K. H. Leung, *Int. J. Hydrogen Energy*, 2007, **32**, 3238–3247.
- F. Sastre, M. Oteri, A. Corma and H. Garcia, *Energy Environ. Sci.*, 2013, **6**, 2211.
- Y. Tachibana, L. Vayssieres and J. R. Durrant, *Nat. Photonics*, 2012, **6**, 511.
- A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253.
- Y. Ma, X. Wang, Y. Jia, X. Chen, H. Han and C. Li, *Chem. Rev.*, 2014, **114**, 9987.
- T. Hisatomi, J. Kubota and K. Domen, *Chem. Soc. Rev.*, 2014, **43**, 7520.
- H. Park, Y. Park, W. Kim and W. Choi, *J. Photochem. Photobiol., C*, 2013, **15**, 1.
- M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69.
- Q. Xiang, J. Yu and M. Jaroniec, *Chem. Soc. Rev.*, 2012, **41**, 782.
- J. Yang, R. Hu, W. Meng and Y. Du, *Chem. Commun.*, 2016, **52**, 2620.
- H. Park, H.-i. Kim, G.-h. Moon and W. Choi, *Energy Environ. Sci.*, 2016, **9**, 411.
- X.-Y. Zhang, H.-P. Li, X.-L. Cui and Y. Lin, *J. Mater. Chem.*, 2010, **20**, 2801.
- M.-C. Wu, J. Hiltunen, A. Sápi, A. Avila, W. Larsson, H.-C. Liao, M. Huuhtanen, G. Tóth, A. Shchukarev, N. Laufer, A. Kukovecz, Z. Kónya, J.-P. Mikkola, R. Keiski, W.-F. Su, Y.-F. Chen, H. Jantunen, P. M. Ajayan, R. Vajtai and K. Kordás, *ACS Nano*, 2011, **5**, 5025.
- P. Gomathisankar, K. Hachisuka, H. Katsumata, T. Suzuki, K. Funasaka and S. Kaneco, *Int. J. Hydrogen Energy*, 2013, **38**, 11840.
- W. Zhang, Y. Wang, Z. Wang, Z. Zhong and R. Xu, *Chem. Commun.*, 2010, **46**, 7631.
- M. Wen, Y. Kuwahara, K. Mori, D. Zhang, H. Li and H. Yamashita, *J. Mater. Chem. A*, 2015, **3**, 14134.
- Y.-J. Cho, H.-i. Kim, S. Lee and W. Choi, *J. Catal.*, 2015, **330**, 387.
- J. Kim and W. Choi, *Energy Environ. Sci.*, 2010, **3**, 1042.
- J. Kim, D. Monllor-Satoca and W. Choi, *Energy Environ. Sci.*, 2012, **5**, 7647.
- K. Maeda, A. Xiong, T. Yoshinaga, T. Ikeda, N. Sakamoto, T. Hisatomi, M. Takashima, D. Lu, M. Kanehara, T. Setoyama, T. Teranishi and K. Domen, *Angew. Chem., Int. Ed.*, 2010, **49**, 4096.
- K. Maeda, K. Teramura, D. Lu, N. Saito, Y. Inoue and K. Domen, *Angew. Chem., Int. Ed.*, 2006, **45**, 7806.
- M. Yoshida, K. Takanabe, K. Maeda, A. Ishikawa, J. Kubota, Y. Sakata, Y. Ikezawa and K. Domen, *J. Phys. Chem. C*, 2009, **113**, 10151.
- D. Hufschmidt, D. Bahnemann, J. J. Testa, C. A. Emilio and M. I. Litter, *J. Photochem. Photobiol., A*, 2002, **148**, 223.
- J. Kim, J. Lee and W. Choi, *Chem. Commun.*, 2008, 756.
- C. Minero, G. Mariella, V. Maurino, D. Vione and E. Pelizzetti, *Langmuir*, 2000, **16**, 8964.
- H. Park and W. Choi, *J. Phys. Chem. B*, 2003, **107**, 3885.
- J. Theurich, M. Lindner and D. W. Bahnemann, *Langmuir*, 1996, **12**, 6368.
- M. I. Franch, J. Peral, X. Domenech and J. A. Ayllon, *Chem. Commun.*, 2005, 1851.
- S. Weon and W. Choi, *Environ. Sci. Technol.*, 2016, **50**, 2556.

