Electronic Supplementary Information

Catalysis of Solar Hydrogen Production by Iron Atoms on the Surface of Fe-doped Silicon Carbide

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1. Experimental

Materials

All chemicals, including nanosized silicon dioxide (SiO_2), silicon (Si), iron(II) oxalate dihydrate ($FeC_2O_4{\cdot}2H_2O$) and hydrofluoric acid (HF, 40%), were obtained from Aldrich and used as received. Multiwalled carbon nanotubes (MWCNT) were supplied by Shenzhen Nanotech Port Ltd. Co.

Caution: HF is highly corrosive and a contact poison. It should be handled with extreme caution.

Synthesis of photocatalysts

SiC:Fe/Fe_{surf}···Si-OH nanowires: A mixture of MWCNTs (0.48 g), SiO_2 (0.6 g), Si (0.28 g) and $FeC_2O_4{\cdot}2H_2O$ (0.36 g) was milled for 1 h then transferred to an alumina boat and placed in a furnace. The furnace was ramped to 1400 ºC at a rate of 5 ºC/min and held for 2 h under a constant flow of argon. After calcining at 700 ºC for 7 h to burn off the unreacted carbon, the material was immersed in hydrofluoric acid for 60 minutes at room temperature to remove the silica shell coating, as confirmed by TEM[1]. Care was taken not to exceed the 60 minute contact time because extended treatment leads to removal of surface Fe atoms. The product was washed overnight with 0.1 M NaOH to remove fluoride, then dried thoroughly in an oven at 80 ºC. Removal of F^- ions was confirmed by XPS analysis through the absence of a peak at 685.5 eV.

SiC:Fe/Si-OH nanowires: A 100 mg sample of SiC:Fe/Fe_{surf}···Si-OH nanowires was stirred in 60 mL hydrofluoric acid at room temperature. After etching for 6 h, the suspension was centrifuged and washed with 0.1 M NaOH. Finally, the product was dried overnight in an oven at 80 ºC. Complete removal of F^- ions was confirmed by XPS analysis.

SiC/Si-OH nanowires: The preparation of SiC/Si-OH nanowires was the same as for SiC:Fe/Fe_{surf}···Si-OH nanowires except that $FeC_2O_4 \cdot 2H_2O$ was omitted from the starting mixture. The detailed morphology of SiC nanowires has been reported previously[1].

Characterizations

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker AXS D5000 diffractometer. Transmission electron microscope (TEM) images were obtained using a Tecnai G2 F30 electron microscope under an accelerating voltage of 300 keV. Transmission electron microscopy (TEM) samples were prepared by dropping a diluted suspension onto amorphous carbon-coated copper grids and drying in the air. An energy-dispersive X-ray (EDX) spectrometer was attached to the electron microscope to provide *in situ* determination of the sample composition. X-ray photoelectron spectra were obtained using a PHI 5700 X-ray photoelectron spectrometer equipped with a monochromatic Al Kα X-ray source. UV-vis diffuse reflection spectra were recorded with a SOLID 3700 UV-vis spectrometer. The BET surface areas of samples were determined from nitrogen adsorption-desorption isotherms at 77K measured using a Micrometrics ASAP 2020 V3.00 H system. Impedance measurements were performed using an Ivium Technologies COMPACTSTAT.e portable electrochemical interface and impedance analyzer, controlled by IviumSoft software.

Photocatalytic H_2 production

Photocatalytic activity tests were carried out using a slide projector light source (Kodak Carousel S-AV 1010) featuring a 100 W tungsten halogen lamp equipped with a UV cut-off filter (λ > 420 nm). Light intensity over the illuminated area of 3.5 cm^{-2} was determined using a Melles Griot Broadband Power/Energy Meter 13PEM001. The photocatalyst suspension was gently stirred and purged with 2% CH_4 in N_2 for 15 min. The reaction vessel was maintained at 25 °C using a thermostatted water circulator. The

H_2 product was quantified using an Agilent 7890A Series gas chromatograph equipped with a thermal conductivity detector, with CH_4 as internal standard[2].

The apparent quantum efficiency (QE) at λ = 420 nm (±20 nm) was calculated from the following equation:[3]

$$QE\ (\%) = 2 \times \frac{\text{number of evolved H2 molecules}}{\text{number of incident photons}} \times 100\% \qquad \text{(S1)}$$

2. Assessing the cost of producing the catalyst.

Based on retail prices, the following raw materials costs were estimated as follows: MWCNT (0.48 g, 0.46 GBP), SiO_2 (0.6 g, 0.48 GBP), Si (0.28 g, 0.09 GBP) and $FeC_2O_4 \cdot 2H_2O$ (0.36 g, 0.04 GBP). This mixture produces 0.75 g of SiC:Fe/Fe_{surf}⋯Si-OH Based on the above figures, the cost for 1 g SiC:Fe/Fe_{surf}⋯Si-OH is in the region of 1.4 GBP.

3. Supporting Figures and Tables

Figure S1. FT-IR spectrum of SiC:Fe/Fe_{surf}⋯Si-OH.

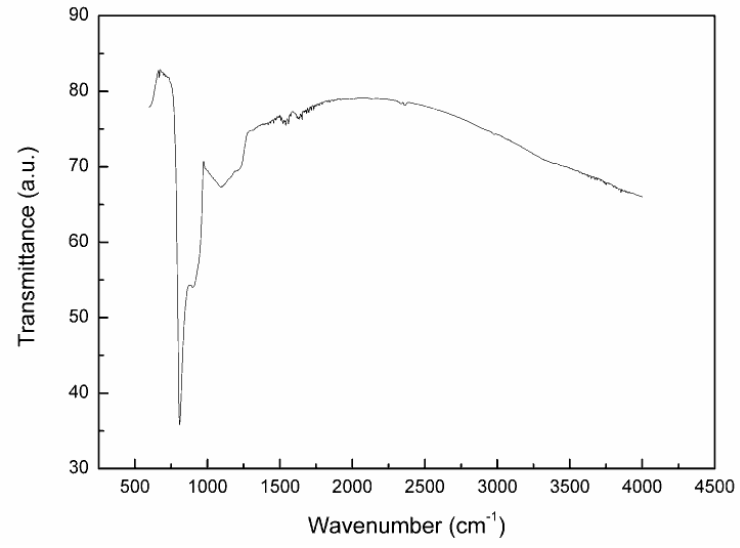


Figure S2. The XPS Si 2p spectra of SiC:Fe/Fe_{surf}···Si-OH (a1) and SiC:Fe/Si-OH (a2), O 1s spectra of SiC:Fe/Fe_{surf}···Si-OH (b1) and SiC:Fe/Si-OH (b2), C 1s spectra of SiC:Fe/Fe_{surf}···Si-OH (c1) and SiC:Fe/Si-OH (c2).

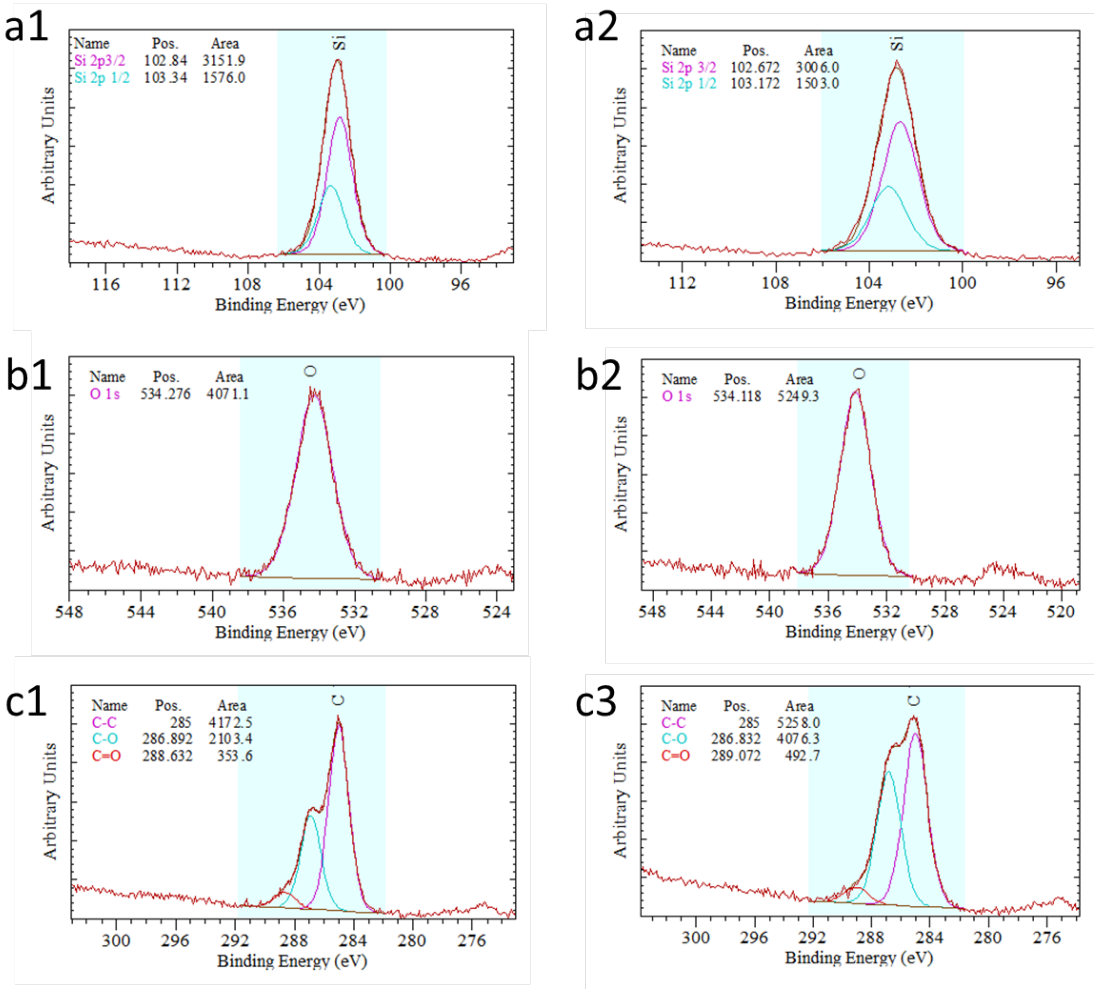


Figure S3. TEM image (a) and EDX spectrum (b) of a sample of SiC:Fe/Si-OH nanowires (depleted of surface Fe).

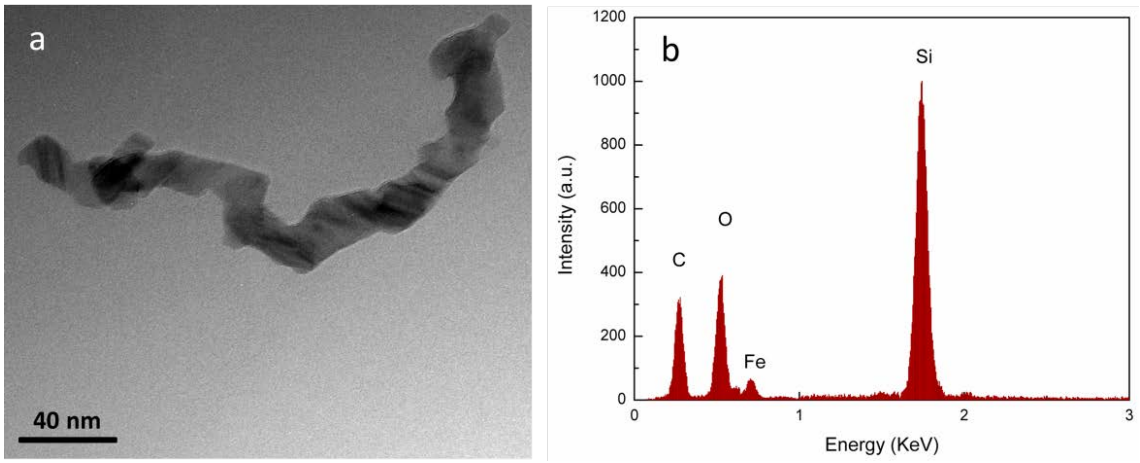


Figure S4. XRD patterns of samples of SiC:Fe/Fe_{surf}···Si-OH and SiC:Fe/Si-OH.

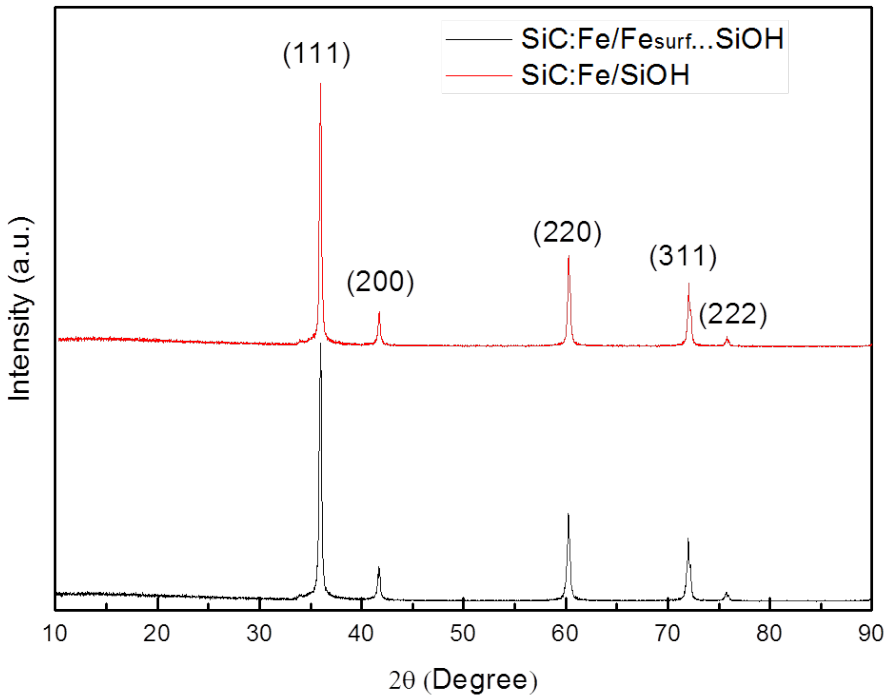


Figure S5. UV-vis adsorption spectra of SiC:Fe/Fe_{surf}···Si-OH and SiC:Fe/Si-OH photocatalysts.

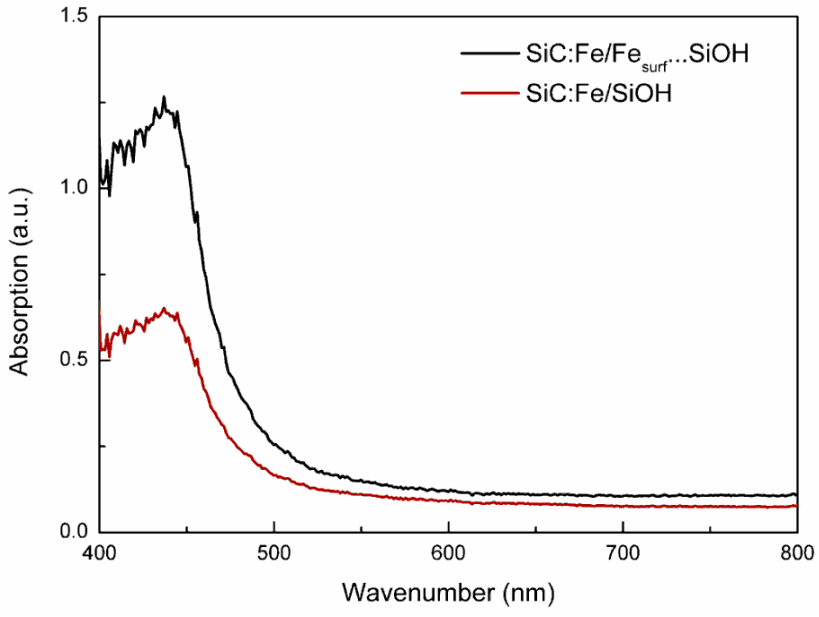


Figure S6. (a) Plot of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for SiC/Si-OH nanowires. The intersection value is the band gap, being 2.56 eV, which is wider than that of SiC:Fe/Si-OH nanowires. (b) The photocatalytic activity of SiC/Si-OH nanowires, compared to SiC:Fe/Si-OH (surface Fe-depleted). The H_2 evolution rate catalyzed by SiC/Si-OH nanowires was 0.09 μmol h^{-1} g^{-1}, which is lower than that observed for SiC:Fe/Si-OH (surface-Fe depleted) nanowires.

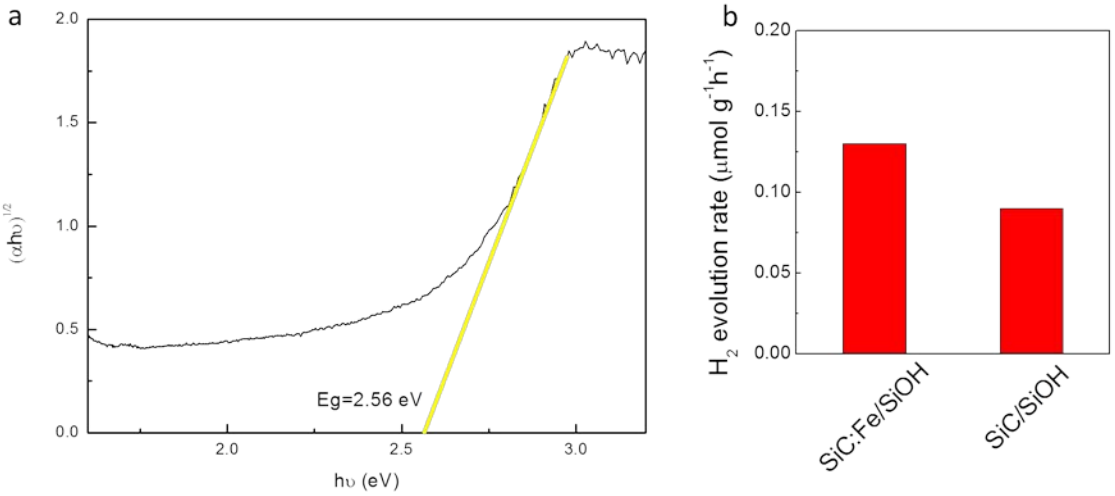


Figure S7. The variation of H_2 production rate with the molar ratio of Fe:Si used in synthesis of the photocatalyst.

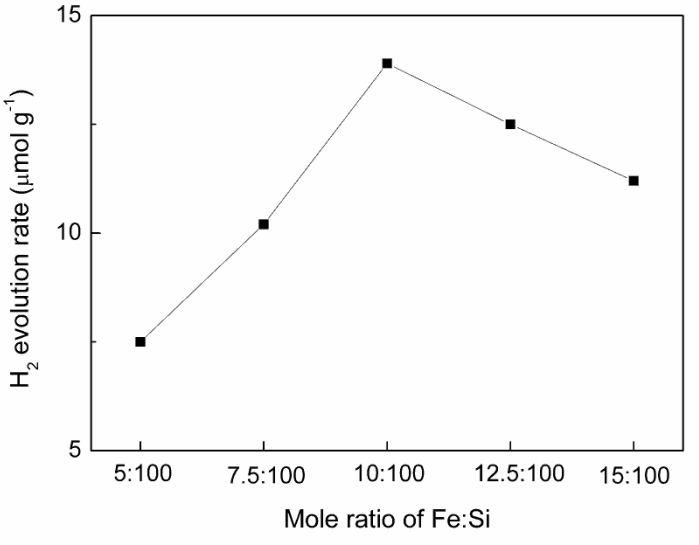
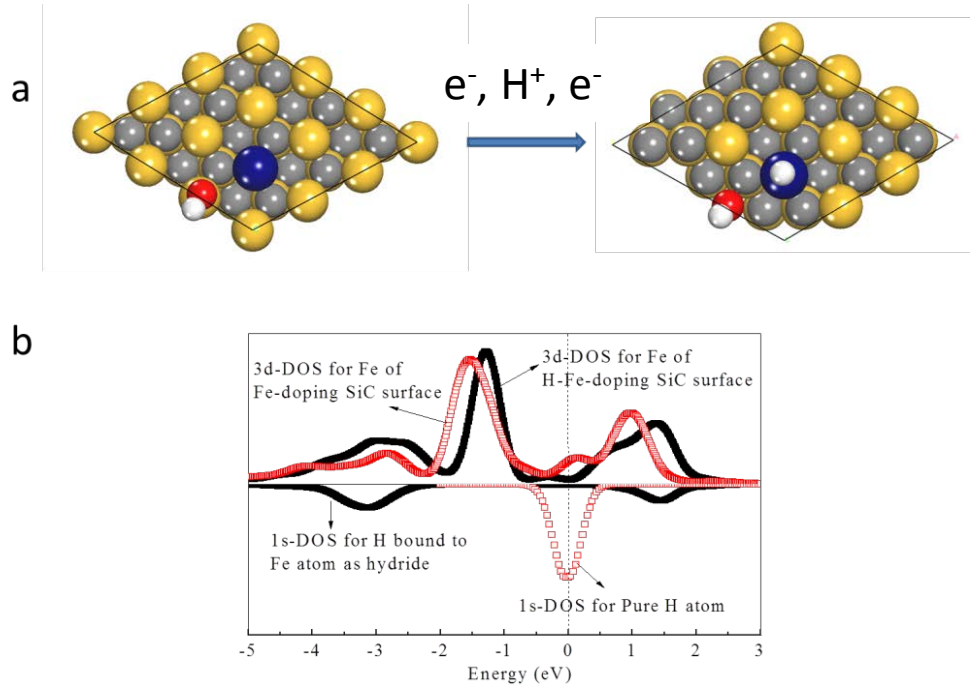


Figure S8. Summary of DFT calculations to examine hydride formation on SiC:Fe/Fe_{surf}···Si-OH.



All calculations were performed on the basis of spin-polarized DFT as implemented with the Cambridge Sequential Total Energy Package (CASTEP) program package. The one-electron Kohn–Sham orbitals were developed by using a plane wave basis set and the electron exchange correlation energy was described by the Perdew-Burke-Ernzerhof (PBE) functional at Generalized Gradient Approximation (GGA) level, which also accounted for dispersion interactions. The ionic core was described by the ultrasoft pseudopotential. Brillouin-zone integrations were performed with a mesh of 4 × 4 × 1 *k* points generated by following the scheme of Monkhorst and Packin. The self-consistency cycle was terminated when the total energies in the next step only changed by less than 10^{-6} eV per cell. The ionic relaxation energies were converged to 10^{-4} eV. During calculation, all atoms were fully relaxed. In (a) initial and final states for hydride formation are shown, red sphere is O, yellow spheres are Si, grey spheres are C, white spheres are H and blue sphere is Fe.

Partial densities of states (PDOS) variation for the H atom and Fe atom were calculated. Panel (b) compares the 1s-DOS of the pure H atom and that of the Fe-H hydride on the surface, and the 3d-DOS of Fe atom on the surface before and after formation of hydride to the Fe site. The bonding energy calculation indicates that after the input of electrons into the SiC:Fe/Fe_{surf}···Si-OH, $E_{Fe\text{-}H}$ is -2.54 eV which implies that the bonding of H to Fe is an exothermic process. The stabilization is large enough to assign the interaction to chemical adsorption. The 1s-DOS of the pure H atom shows a semi-filled peak locating around the Fermi level (0 eV), while the 1s-DOS of Fe-H on the surface splits into two peaks at the energy around -3 eV and 1.5 eV, respectively, which correspond to the bonding molecular orbit and antibonding molecular orbit of the new formed H-Fe hydride bond.

Table S1. Specific surface areas of SiC:Fe/Fe_{surf}···Si-OH and SiC:Fe/Si-OH nanowires.

Samples	BET surface area (m^2 g^{-1})
SiC:Fe/Fe_{surf}···Si-OH	87
SiC:Fe/Si-OH	86

Table S2. Elemental composition of the SiC:Fe/Fe_{surf}···Si-OH and SiC:Fe/Si-OH nanowires.

Surface elements	O (Atomic%)	C (Atomic%)	Si (Atomic%)	Fe (Atomic%)
SiC:Fe/Fe_{surf}···Si-OH	14.8	39.5	41.1	4.6
SiC:Fe/Si-OH	16.2	41.4	40.6	1.8

References

1. H. Zhang, Y. Xu, J. Zhou, J. Jiao, Y. Chen, H. Wang, C. Liu, Z. Jiang and Z. Wang, *Journal of Materials Chemistry C*, 2015, **3**, 4416-4423.
2. E. Reisner, D. J. Powell, C. Cavazza, J. C. Fontecilla-Camps and F. A. Armstrong, *Journal of the American Chemical Society*, 2009, **131**, 18457-18466.
3. A. Kudo and Y. Miseki, *Chemical Society Reviews*, 2009, **38**, 253-278.