

## Electronic Supplementary information

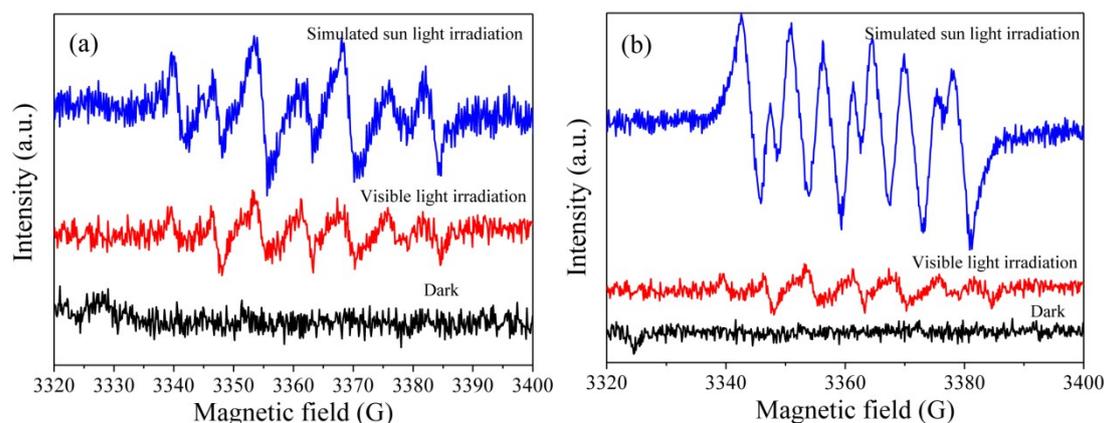


Fig. 1 DMPO spin-trapping EPR spectra of  $Zn_{0.5}Mg_{0.5}Fe_2O_4/TiO_2$  NTs under dark, visible light and simulated sun light trapped in aqueous dispersion:(a) DMPO-•OH and (b) DMPO-•O<sub>2</sub><sup>-</sup>.

ESR technique was conducted to detect the active species such as hydroxyl radical and superoxide radical species. As shown in Fig. 1a, Four characteristic peaks (1:2:2:1) due to DMPO-•OH can be observed after irradiating the  $Zn_{0.5}Mg_{0.5}Fe_2O_4/TiO_2$  composite electrode with simulated sun light, while weak peaks could be detected for  $Zn_{0.5}Mg_{0.5}Fe_2O_4/TiO_2$  irradiated by visible light and no such signals under dark conditions. Similarly, it could be observed from Fig. 1b, the six characteristic peaks of the DMPO-•O<sub>2</sub><sup>-</sup> adducts are also detected under simulated sun light irradiation in methanol dispersions of  $Zn_{0.5}Mg_{0.5}Fe_2O_4/TiO_2$  composite electrode, while feeble six peaks can be observed with the composite electrode illuminated by visible light. It also could be found that no such signals for the doped electrode under dark conditions. ESR results indicate that simulated sun light irradiation is crucial to the generation of •OH radical and •O<sub>2</sub><sup>-</sup> radical species, and it is confirmed that both

•OH and •O<sub>2</sub><sup>-</sup> are produced on the surface of Zn<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> electrode and these species with strong oxidation capability act as the predominant species in PEC reaction.

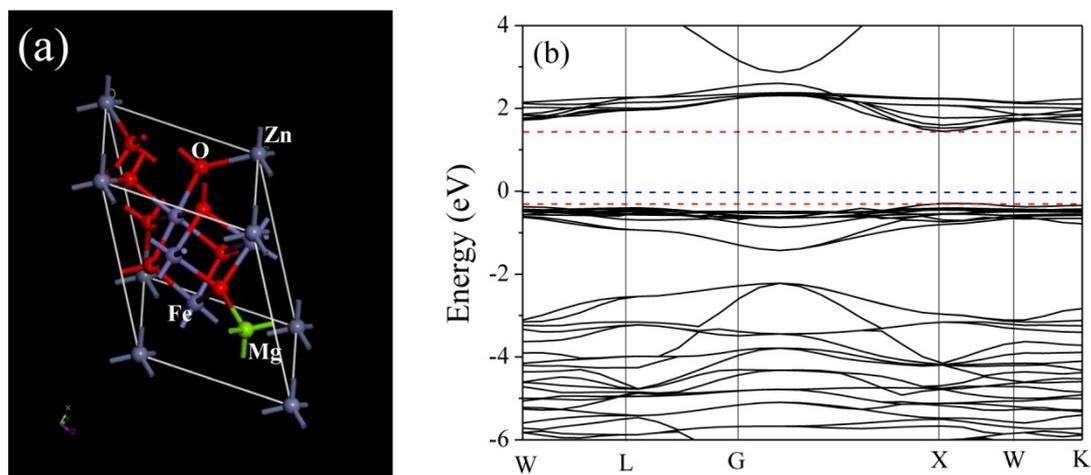


Fig. 2 (a) Structure of primitive cell Zn<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>; (b) Conduction band and valence band structure of Zn<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>, the position of Fermi level is set to be 0 eV.

To calculate the band structures of Zn<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub>, periodic density functional calculations (DFT) computations were performed using a plane-wave method implemented in the Cambridge Sequential Total Energy Package (CASTEP) code. The ultrasoft pseudopotential was used to describe the exchange-correlation effects and electron-ion interactions, respectively. A 340 eV cutoff for the plane-wave basis set was adopted in the computations. The self-consistent convergence accuracy was set at  $1 \times 10^{-6}$  eV atom<sup>-1</sup>. The optimized lattice parameters for Zn<sub>0.5</sub>Mg<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> were

found to be  $a \times b \times c = 8.441 \text{ \AA} \times 8.441 \text{ \AA} \times 8.441 \text{ \AA} \langle 90^\circ \times 90^\circ \times 90^\circ \rangle$ , herein the fractional coordinates of Zn atom was (0, 0, 0), Fe atom was (0.625, 0.625, 0.625) and O atom was (0.38672, 0.38672, 0.38672). Firstly, Materials Studio 7.0 in CASTEP module was run on a server. Then, the doping atom will replace the original cell in a position green. Seen from Fig. 2 a, spinel  $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4$  primitive cell structure was constructed. From Fig. 2 b, it can be obtained that the band gap of  $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4$  is approximately 1.9 eV, in good agreement with DRS experimental values 2.0 eV. In addition, we can estimate that the valence band and conduction band position of  $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4$  are  $-0.4$  eV and  $1.5$  eV, respectively. Herein, the position of Fermi level is set to be 0 eV. Since the oxidation potential position of  $\text{H}_2\text{O}-\text{O}_2$  located at  $1.23$  eV (vs. NHE), which was more negative than the valence band of  $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4$ , the composites could oxidize the water theoretically.