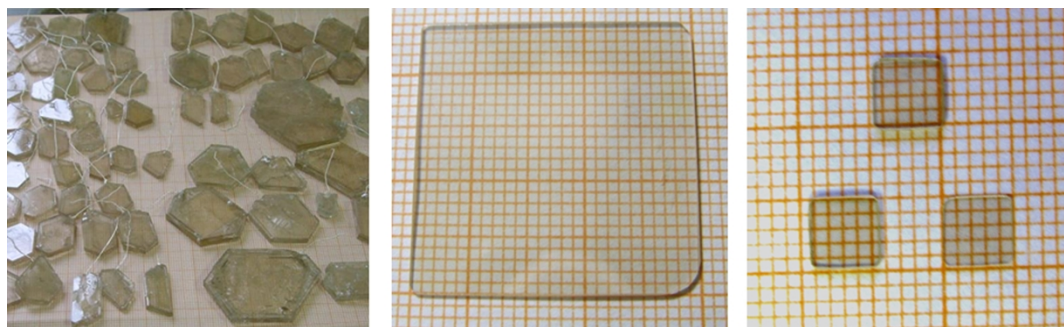


## Supplementary information

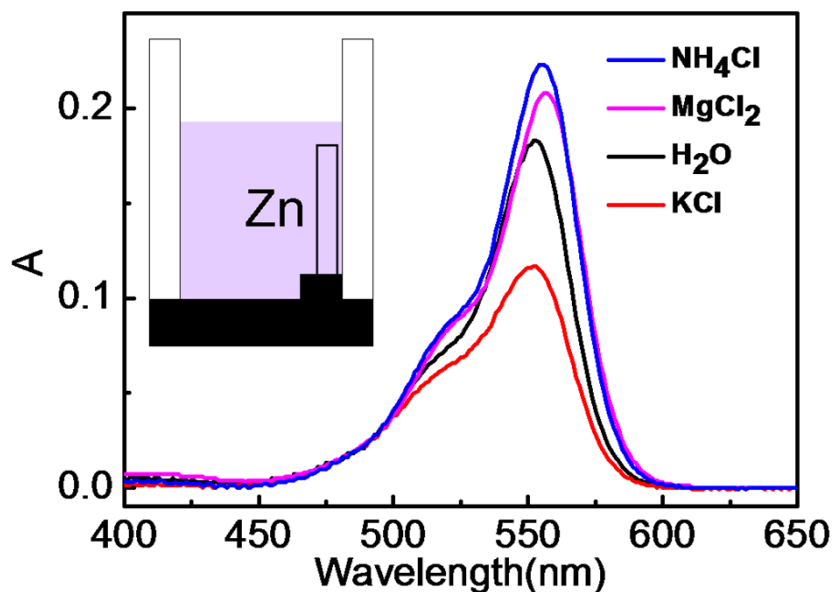
### Experimental Section

Preparation of new type of photocatalytic system. Firstly, ZnO single crystal was embedded into a PTFE sheet and sealed with silicone adhesive; Secondly, the PTFE was inserted into a quartz cuvette and sealed with silicone adhesive, as shown in Figure S5 (see supplementary information). In this condition, every single polar surface of ZnO contacts only one compartment of RhB solution. The photogenerated electrons and holes can be injected into RhB solution through the interface of Zn-polar-surface/RhB-solution or O-polar-surface/RhB-solution while ion exchange and radical diffusion between two compartments of new system was forbidden.

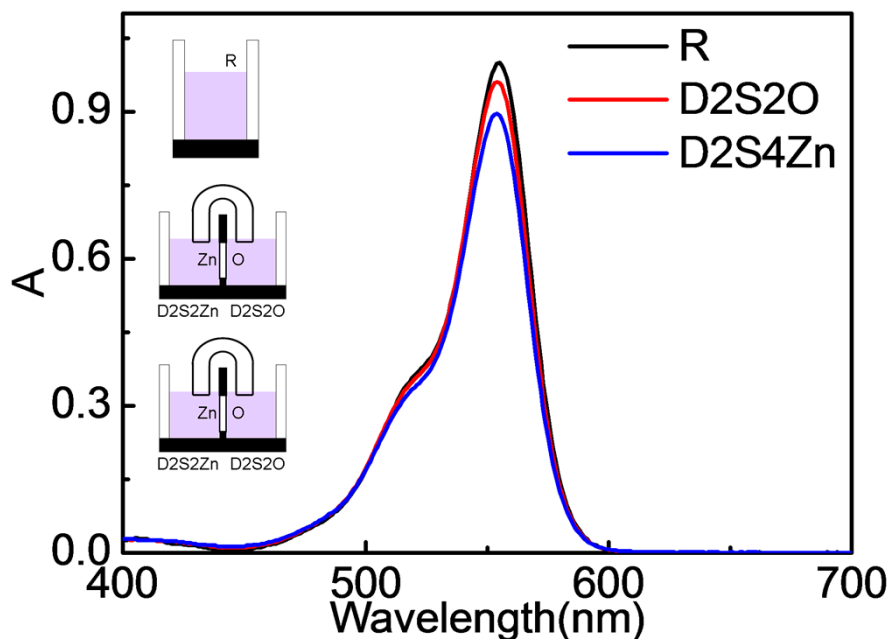
Calibration the relative concentration of  $Zn^{2+}$ . 2.5ml deionized water was trickled into four compartments of sample 2 and 4 and irradiated by UV for 2.5h. After irradiation, the 2.5ml deionized water was mixed with 2ml chloroform solution of dithizone with concentration of  $4 \times 10^{-3} \text{g/L}$  and shook violently for several minutes. The  $Zn^{2+}$  was extracted to the chloroform solution of dithizone. Then the extract solution was used to detect the UV-vis spectrum after complete standing.



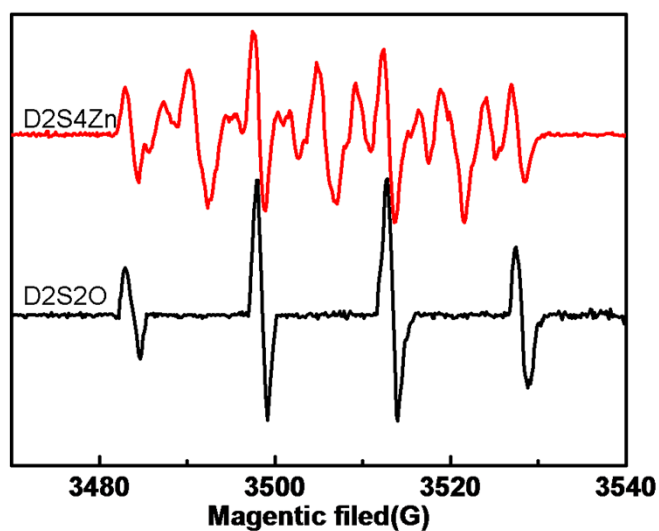
ZnO single crystals were grown by a hydrothermal method developed in our group. Several 8mm\*8mm asgrown ZnO were used in this study.



**Figure S1.** The absorption spectrum of residual RhB solution mixed with different electrolyte after being degraded by D1S1Zn. To study the impact of different electrolyte on photocatalytic activity of ZnO single crystal, 1ml RhB solution with concentration of  $1 \times 10^{-5}$  mol/L was mixed with 1ml deionized water,  $\text{NH}_4\text{Cl}$ ,  $\text{MgCl}_2$  and  $\text{KCl}$  saturated solution, and then trickled into device 1 and degraded for 1 h under irradiation, respectively. Compared to deionized water,  $\text{KCl}$  solution increases, while  $\text{MgCl}_2$  and  $\text{NH}_4\text{Cl}$  decrease the photocatalytic activity of ZnO single crystal. According to the result, the existing of  $\text{NH}_4\text{Cl}$  in the salt bridge in device 2 will reduce the photocatalytic activity of D2S2Zn or D2S4O. However, in our experiment, the photocatalytic activity of D2S2Zn and D2S4O increases to almost double compare to D1S1Zn and D1S3O, respectively. It is obviously that device 2 improves the photocatalytic activity of ZnO single crystal.



**Figure S2.** The absorption spectrum of residual RhB solution after being degraded by UV, D2S2O and D2S4Zn. It is observed that although no UV irradiation, D2S2O and D2S4Zn present observable photocatalytic activity.



**Figure S3.** DMPO spin-trap ESR spectra of D2S4Zn and D2S2O in aqueous solution in device 2 under irradiation for 10 min. For  $\cdot\text{OH}$  in aqueous solution, it has been confirmed undoubtedly by DMPO spin-trap ESR spectra with the 1:2:2:1 quartet pattern, as  $\cdot\text{OH}$  is rather stable and can react rapidly with DMPO (rate  $k = 10^8 - 10^{10} \text{ M}^{-1}\text{s}^{-1}$ ).<sup>[1-4]</sup> But for  $\cdot\text{O}_2^-/\text{HO}_2\cdot$  in aqueous solution, there are rare evidence from ESR method.<sup>[1-3,5]</sup> It is possible that they are unstable and react slowly with DMPO ( $k = 10$

and  $6.6 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ , respectively).<sup>[3]</sup> As shown in the figure, the ESR signal of D2S2O are the same to the characteristic signals of DMPO-•OH adduct with the 1:2:2:1 quartet pattern, which means there is only holes injected into solution in D2S2O. While the ESR signal of D2S4Zn is completely different from the characteristic signals of DMPO-•OH adduct. Except for the signal of DMPO-•OH adduct, there are still have signal maybe from DMPO-•H DMPO-•O<sub>2</sub>⁻/HO<sub>2</sub>•.<sup>[1,3,6]</sup>

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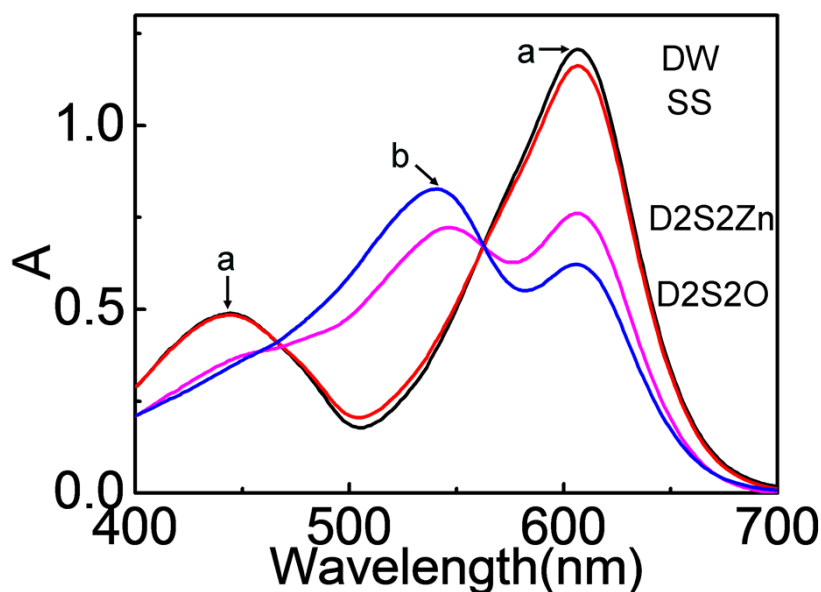
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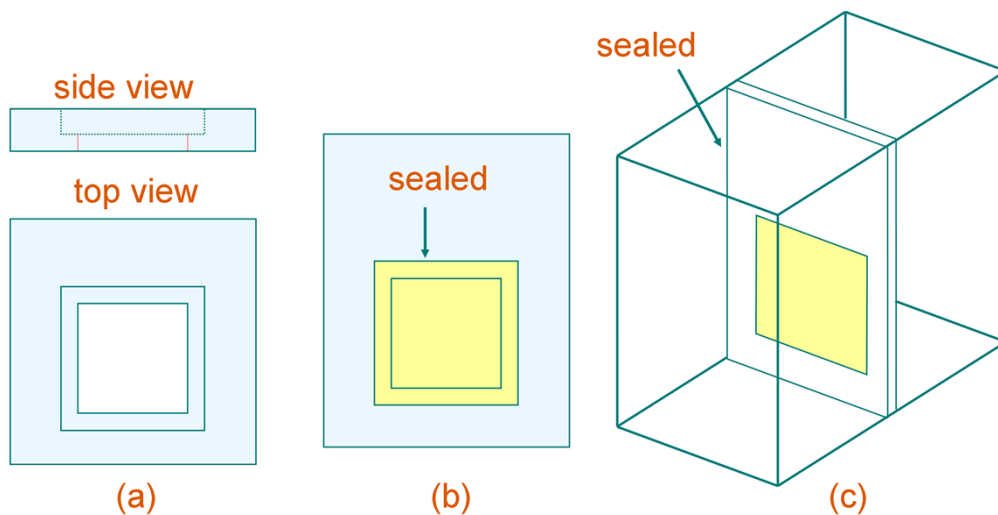
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**Figure S4.** UV-vis spectrum of the complex of dithizone with  $\text{Zn}^{2+}$  in water in left compartment of device 2. Compared to the ZnO saturated solution, both of the concentration of  $\text{Zn}^{2+}$  in D2S2Zn and D2S4O increased obviously. Both of electrons and holes were injected into deionized water from D2S2Zn and D2S2O, however, electrons were more than holes in D2S2Zn while on the contrary in D2S2O, which means D2S2O was photocorroded more deeper than D2S2Zn.

**Figure S5** SEM images of D2S4Zn before (a) and after (c), and D2S2O before (b) and after (d) reaction for 5h. The scale bar is 1 $\mu$ m. We can see that after 5h reaction time, D2S4Zn has no significant changes, while D2S2O has been photocorroded seriously.



**Figure S6.** Preparation of new type of photocatalytic system. (a) Drill a square hole in a PTFE sheet; (b) ZnO single crystal was embedded into PTFE sheet and sealed with silicone adhesive; (c) The PTFE was inserted into a quartz cuvette and sealed with silicone adhesive.