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Supporting Information

Exploration of irradiation intensity dependent external in-band quantum yield for ZnO and CuO/ZnO photocatalysts

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1. Experimental section

1.1 Method for conventional photocatalytic RhB degradation experiments

The photocatalytic degradation properties of the samples were explored by considering the degradation of rhodamine B (RhB) under simulated sunlight, UV and visible light illumination. Initial absorbance (A_0) scanning of the dye (4 mg·L^{-1}) solution was performed at the characteristic wavelength of 554 nm. Typically, 50 mg of sample was dispersed in 100 mL RhB solution in a beaker. After 10 min of ultrasonic oscillation, the sample-dye suspension was left in a dark environment and stood for 20 min to satisfy the adsorption–desorption equilibrium. The solution with photocatalyst was then irradiated by using a high-pressure mercury lamp and xenon lamp, respectively. A total of 5 mL of the residual contamination solution was taken out at regular intervals and was then centrifuged at a speed of 6000 $r\cdot min^{-1}$ using a centrifugal machine, the supernatant was collected and the absorbance (A_t) was measured by spectrophotometer.

The photocatalytic degradation rate can be calculated by Eq. (1):

$$R = C_0/C_t = A_0/A_t \qquad (1)$$

1.2 Method for cycling experiments

Cycling photocatalytic experiments are conducted to investigate the stability of the nano-photocatalyst. After each run of dye degradation, the sample was recycled by a series of procedures, including filtration, washing and drying, and applied for the next run.

1.3 Quenching agents experiments

A total of 0.2 mmoL Benzoquinone (BQ), 0.5 mmoL edta-disodium (EDTA-2Na) and 0.5 mmoL isopropyl alcohol (IPA) were added in the experiment of degradation of RhB as trapping agents to trap superoxide radical ($\cdot O_2^-$), hole (h^+) and hydroxyl radical ($\cdot OH$), respectively.

2 The physical significance on the application of the transmittance parameter

The conventional testing method for the degradation percentage constitutes centrifuging the indicator/sample suspension and measuring the absorbance (A). The degradation rate is calculated by the relation (1) or:

$$R = (C_0-C_t)/C_0 = (A_0-A_t)/A_0, \qquad (2)$$

This method can always conveniently acquire degradation rate due to the elimination of the influence of sample. However, In conventional methods, at each sampling interval, the degree of sample dispersity is totally different. Therefore, after sampling, the ratio between the amount of photocatalyst and pollutant are changing for the further experiments, this introduces an error in pollutant degradation rate extrapolation. Therefore, it is highly encouraged to direct measure the reference T curve from sample/pollutant suspension at each degree of particle dispersity, where the sampled solution could be added back to remain the constant ratio between photocatalyst and pollutant for further experiments.

In sample/pollutant suspension reference T curve measurement, the Bouguer's law should be first considered, the transmission light intensity I_{trans} can be described as equation (3):

$$I_{trans} = I_0 \exp[(\mu_a + \mu_s)l] \qquad (3)$$

Where I_0 is the excitation intensity (here the excitation wavelength is 554 nm, corresponding to RhB absorption wavelength), μ_a and μ_s are the absorption coefficient and scattering coefficient, respectively. For the sample/pollutant suspension, μ_a and μ_s should be rewrite as equation (4).

$$\mu_a = \mu_{a\,sample} + \mu_{a\,pollu\tan t}, \\ \mu_s = \mu_{s\,sample} + \mu_{s\,pollu\tan t} \qquad (4)$$

Where the $\mu_{a\ sample}$ and $\mu_{a\ pollutant}$ parameters demonstrate the absorption coefficients of sample and pollutant respectively, while the scattering coefficient for sample and pollutant are denoted as $\mu_{s\ sample}$ and $\mu_{s\ pollutant}$. During the sample precipitation, the photon scattered from sample can be utilized by pollutant. Similarly, the photon scattered by pollutant might be also absorbed by sample (554 nm can be absorbed by CuO). Therefore, the determination of μ_a and μ_s as a function of time are extremely complicated, leaving the accurately quantification of the pollutant concentration to be problem. To solve this problem, first of all, we should fix the pollutant concentration as a constant, where the $\mu_{a\ pollutant}$ and $\mu_{s\ pollutant}$ remain constant during the entire sample precipitation period. Only the $\mu_{a\ sample}$ and $\mu_{s\ sample}$ are matters for determining the pollutant concentration through T, and since the sample was kept in the total dark environment, the $\mu_{a\ sample}$ can be also neglected, so at each degree of sample dispersity induced photon-particle scattering coefficient could be properly estimated. Therefore, by repeating this experiment for different pollutant concentration, the degradation curve contains $\mu_{s\ sample}$, $\mu_{a\ pollutant}$ and $\mu_{s\ pollutant}$, which serves as a reference data for further analysis, by subtracting this curve from experimental data. Due to the *T* parameter in our experiment includes scattering coefficient, if the *T* varies according to the different degree of sample dispersity, the external in-band quantum yield attributed to $\mu_{a\ sample}$ can be properly extrapolated. In our case, we conducted the pertinent experiments mentioned above and found that there was negligible effect of the precipitation on the *T* measurement from the two samples, so the sample scattering and absorption coefficient were negligible in pollutant concentration determination through *T* value measurement.

3 Figures S1-S6

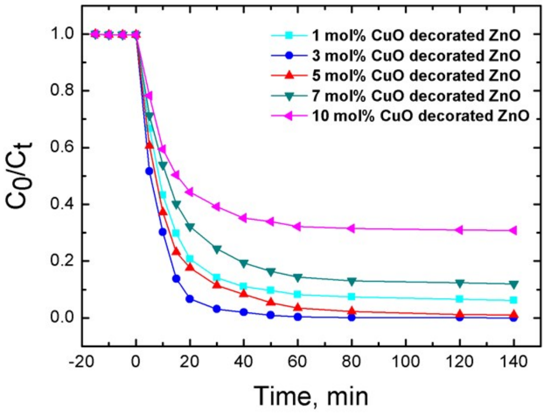

Fig. S1 The photocatalytic degradation of RhB solution under simulated sunlight with different CuO-decorated ZnO samples.

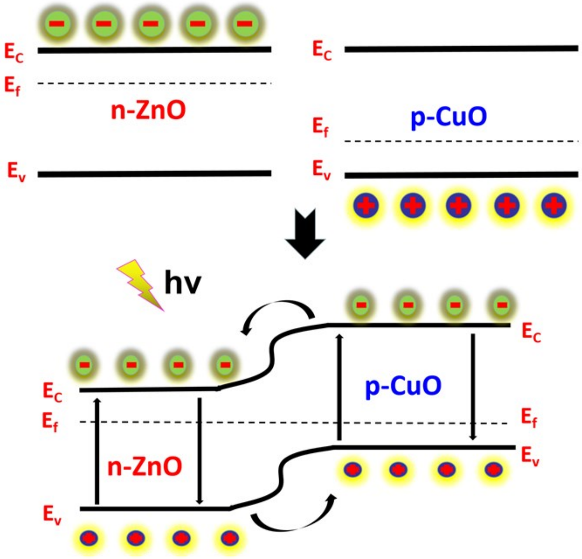

Fig. S2 The band alignment of p-n type CuO/ZnO heterostructure.

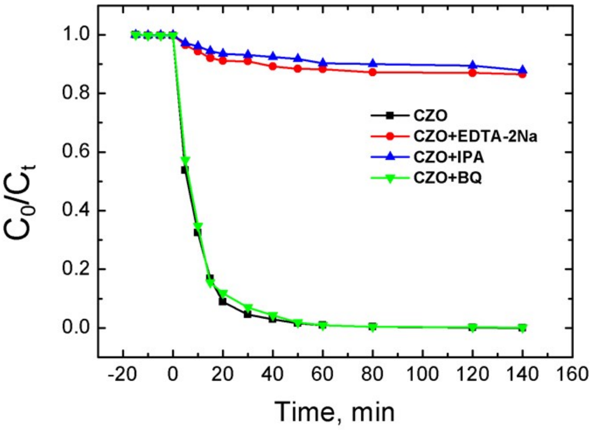

Fig. S3 The photocatalytic degradation of RhB with the addition of quenching agents (EDTA-2Na, IPA, BQ) under simulated sunlight irradiation.

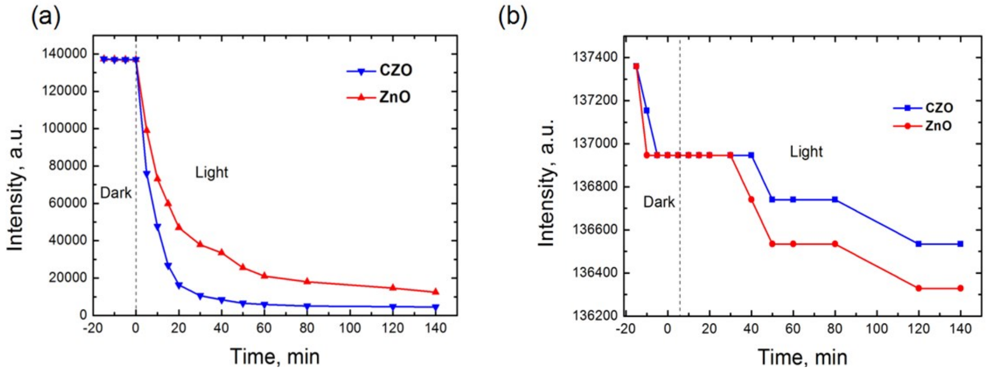

Fig. S4 The photoluminesence (PL) intensity decay curves of RhB during the photocatalytic degradation under (a) UV light irradiation and (b) visible light irradiation.

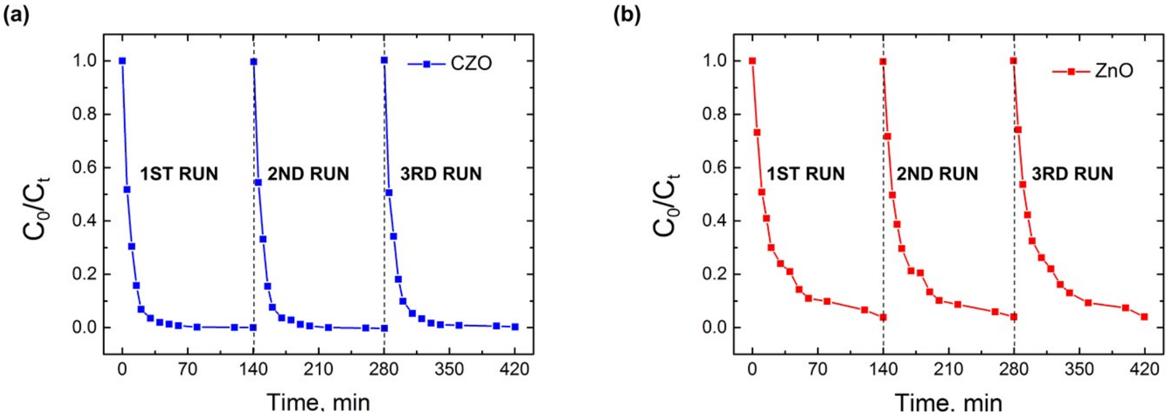

Fig. S5 The cycling experiments of RhB degradation by (a) CZO and (b) ZnO samples.

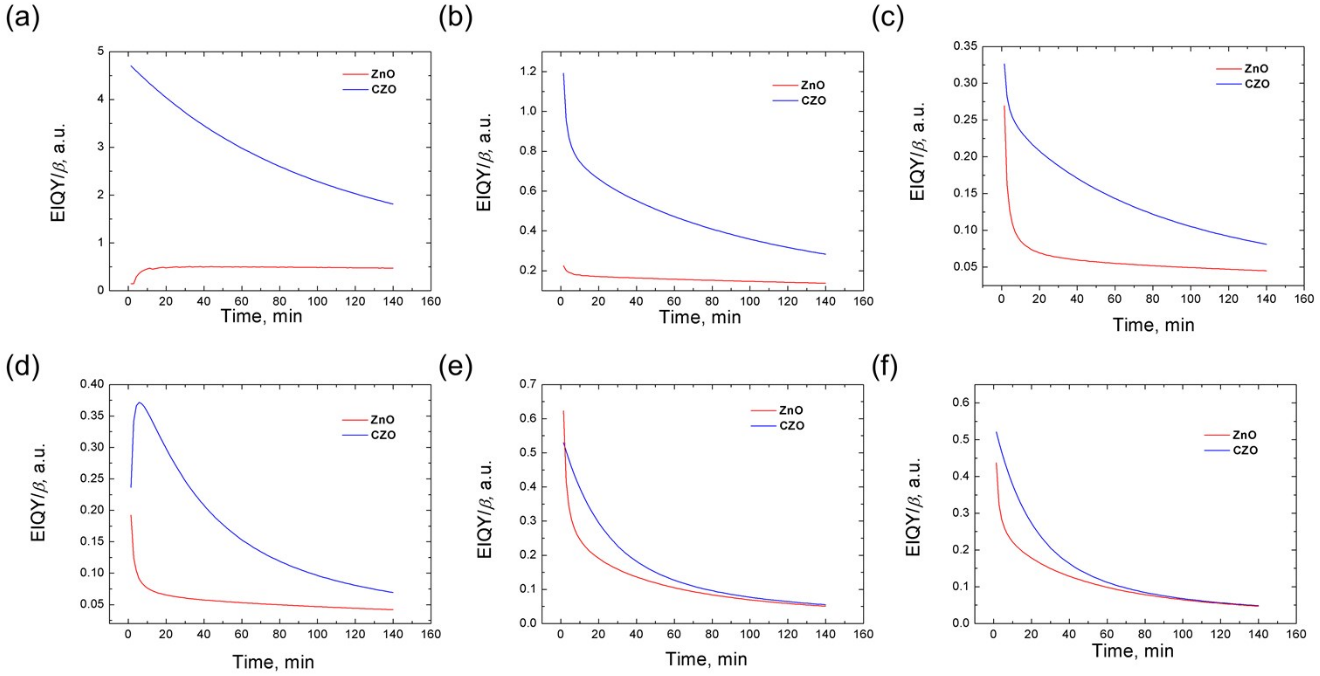

Fig. S6 The calculated *EIQY/β* value for CZO and ZnO samples under (a) 0.3 cm aperture, (b) 0.5 cm aperture, (c) 0.7 cm aperture, (d) 1.0 cm aperture, (e) 1.5 cm aperture and (e) 2.0 cm aperture.