Electronic Supplementary Information

Photogenerated Electron Reservoir in Hetero-P-N CuO-ZnO Nanocomposite

for Visible-Light-Driven Photocatalytic Reduction of Aqueous Cr(VI)

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Figure S1. SEM of the as-synthesized ZnO nanorods.



Figure S2. Variation of $(\alpha h\nu)^2$ versus the photon energy $(h\nu)$ of ZnO nanorods.

The optical band gap (E_g) of ZnO was determined based on the equation $(\alpha hv)^2 = D(hv - E_g).^{1,2}$ And the variation of $(\alpha hv)^2$ versus the photon energy (hv) of ZnO nanorods is plotted in Figure S2, from which the band gap of sample can be estimated to be about 3.14 eV.



Figure S3. Absorption spectra and corresponding photos (inset) of Cr(VI) aqueous solutions catalyzed by different catalysts for 80 min.



Figure S4. Absorption spectra of Cr(VI) aqueous solutions catalyzed by CuO-ZnO foil with the presnece of RhB for different time under visible light irradiation. The inset is the corresponding photos of Cr(VI) aqueous solutions catalyzed by CuO-ZnO foil with the presnece of RhB under visible light irradiation for 0, 60, 120, 180 and 240 min. Note that the initial absorbance of RhB aqueous solution at 554 nm and 352 nm as well as Cr(VI) aqueous solution at 352 nm is 4.205, 0.665 and 0.239, respectively. Therefore, based on the aborption spectra in Figure S4, the actual absorbances of the RhB solution and the Cr(VI) solution

at 352 nm at different irradiation time can be calculated as shown in Supplementary Table 1.

Supplementary Table 1. Absorbances (A) and percentage (P) of RhB and Cr(VI) in the RhB and Cr(VI) mixed solution at 554 nm and 352 nm at different irradiation time.

Wavelengt									
h	554 nm		352 nm						
Time (min)	A(RhB)	Р	A(F	P(RhB)	P(Cr)				
0	4.205	100%	0.904=0.665+0.239	0.665*100%+0.239*100%	100%	100%			
20	3.831	91.2%	0.727	0.665*91.2%+0.239*50.5%	91.2%	50.5%			
40	3.174	75.6%	0.543	0.665*75.6%+0.239*17.0%	75.6%	17.0%			
60	2.530	60.3%	0.403	0.665*60.3%+0.239*0.90%	60.3%	0.9%			
120	1.318	31.4%	0.209	0.665*31.4%+0.239*0	31.4%	0			
180	0.638	15.2%	0.101	0.665*15.2%+0.239*0	15.2%	0			
240	0.021	0.5%	0.003	0.665*0.5%+0.239*0	0.5%	0			



Figure S5. (a) XRD pattern and (b) SEM image of the recycled CuO-ZnO foil.



Figure S6. PL spectra of pure ZnO nanorods, CuO foil and CuO-ZnO composite excited at 325 nm.



Figure S7. Time-resolved PL decay measurements.

To support the pathway of the interfacial charge transfer in the CuO-ZnO, we performed the timeresolved PL decay measurements of ZnO nanorods and CuO-ZnO sample, as shown in Figure S7. A picosecond pulsed diode laser driver (PicoQuant, PDL 800-B) and head (PicoQuant, LDH Series) were used to get the wavelength of 405 nm with a repetition of 5-MHz. For the time-resolved PL decay measurements, the laser beam was focused on the sample surface with a diameter of ~50 μ m at an incident angle of ~45° relative to the surface normal direction. The sample PL was collected by a ×50 microscope objective and sent to an avalanche photodiode in the time-correlated single photon-counting system with a time resolution of ~8 ps. All the measurements were performed at room temperature.³

The multiexponential decay curves were fitted using a nonlinear least-squares method with a multicomponent decay law⁴ given by $I(t) = a_1 exp(-t/\tau_1) + a_2 exp(-t/\tau_2) + ... + a_n exp(-t/\tau_n)$. The average lifetime $\langle \tau_{PL} \rangle$ was then determined using the equation: $\langle \tau_{PL} \rangle = \sum_{i=1}^{i=n} a_i \tau_i^2 / \sum_{i=1}^{i=n} a_i \tau_i$ and listed in Supplementary Table 2.

Sample	a_1	$\boldsymbol{\tau}_1(ps)$	<i>a</i> ₂	$\boldsymbol{\tau}_2(ps)$	<i>a</i> ₃	$\boldsymbol{\tau}_3(ps)$	$\langle \tau_{\rm PL} \rangle$ (ps)	$\langle \tau_{\rm PL} \rangle$ (ns)
ZnO	52.29	1.41×10^{30}	53.77	1.17×10^{102}	7465.81	704.6	1.17×10^{102}	1.17×10 ⁹⁹
						1		
CuO-ZnO	18119.	785.27	18119.3	785.27	18119.3	785.2	785.27	0.79
	33		3		3	7		

Supplementary Table 2. Kinetic Parameters of the Emission Decay of Samples

The intensity-weighted average lifetime $\langle \tau_{PL}^{ZnO} \rangle$ for ZnO was about 1.17×10^{99} ns. After it was combined with CuO, however, the PL of CuO-ZnO was strongly quenched and $\langle \tau_{PL}^{CuO-ZnO} \rangle$ and the lifetime reduced to about 0.79 ns. This demonstrates the interfacial transfer of photogenerated electron from CuO to ZnO in the CuO-ZnO.⁴



Figure S8. Theoretical band structures of CuO-ZnO p-n heterojunction in the state of (a) pre-equilibrium and (b) equilibrium in dark.

Based on the work functions of CuO (-4.07 eV) and ZnO (-4.35 eV) as well as their band gaps (CuO, 1.4 eV; ZnO, 3.37 eV),⁵⁻⁶ detailed theoretical band structures of CuO-ZnO p-n junction in the state of preequilibrium and equilibrium in dark are shown in Figure S8, respectively. Fermi level (dotted line) is the chemical potential of thermodynamic equilibrium, CuO and ZnO semiconductors normally have different positions of the Fermi levels when they are separated or pre-equilibrium as shown in Figure S8a. When CuO and ZnO semiconductors form p-n heterojunction in dark, electrons (e⁻) will move from the CB of n-ZnO to p-CuO because of the higher Fermi level of n-type semiconductor, and the holes (h⁺) flow in an opposite direction (see Figure S8b). The flowing of charge carriers (electrons and holes) can generate a depletion layer (positively charged region) in the ZnO side, and an accumulation layer (negatively charged region) in the CuO side of CuO-ZnO p-n juction. Finally, the depletion and accumulation layers lead to a built-in potential from ZnO to CuO. After the charge equilibrium being built, both CuO and ZnO semiconductors have the same Fermi level. In other words, they have same chemical potential. So no degradation will happen in dark.⁷⁻⁸

However, when they are exposed to suitable illumination, the photogenerated carriers will break the thermodynamic equilibrium, and generate quasi-Fermi levels (quasi-static equilibrium) for each semiconductor (Figure 7a and b). Because of the built-in potential in the CuO-ZnO p-n juctions, the photogenerated electrons in the accumulation layer of CuO side will drift to the depletion layer of ZnO side, and result in the anodic shift of quasi-Fermi level of ZnO, whereas the drifting of photogenerated holes lead to the cathodic shift of quasi-Fermi level of CuO.⁸⁻¹⁰

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