Supplementary

Non-Noble Metallic Cu with Three Different Roles in Cu doped ZnO/Cu/g-C_3N_4 Heterostructure for Enhanced Z-Scheme Photocatalytic Activity

Mohammed Abdullah Bajiri[1], Abdo Hezam[2], K. Namratha[3], Basheer M. Al-Maswari[4]

H .S.BhojyaNaik*[,1], K. Byrappa[5], Nabil Al-Zaqri[6], Ali Alsalme[6], Fahad A. Alharthi[6]

[1]Department of Studies and Research in Industrial Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta-577 451, India

[2]Department of Physics, Ibb University, Ibb, Yemen

[3] DOS in Earth Science, University of Mysore, Mysore-570006, India

[4]Department of Chemistry, Yuvaraja'sCollege(Autonomous), University of Mysore, India

[5]Adichunchanagiri University, N.H. 75, B. G. Nagara, Mandya, 571448, India

[6]Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh, 11451, Saudi Arabia.

*Corresponding author:hsb_naik@redimail.com

1. XRD calculation data

Table S1:The lattice parameters, crystal size, and micro-strain.

Samples	2θ	θradians	FWHM (β)	FWHM(radians)	Cosθ	Sinθ	d=λ/2sinθ
ZnO	36.2249	0.316122	0.2728	0.004761258	0.950448	0.310883	2.476816
ZnOCugc200	36.1718	0.315659	0.3552	0.00619941	0.950592	0.310443	2.48033
ZnOCugc300	36.234	0.316201	0.4337	0.007569493	0.950424	0.310958	2.476215
ZnOCugc100	36.2176	0.316058	0.3398	0.005930629	0.950468	0.310822	2.477299
ZnOCu	36.7001	0.320269	0.2857	0.004986406	0.949151	0.314822	2.445829

SIZE	Micro-strain (ε)	Micro-strain (ε) 10^{-3}	d-spacing [Å]	a=b	c	c/a Ratio
30.63755	0.00113133	1.13133	2.47777	3.2543	5.2067	1.599945
23.52663	0.00147328	1.47328	2.48129	3.2638	5.2128	1.597157
19.27171	0.00179856	1.79856	2.47717	3.2582	5.2052	1.597569
24.59608	0.00140922	1.40922	2.47826	3.2534	5.2085	1.600941
29.29418	0.00118321	1.18321	2.48758	3.2659	5.2278	1.600723

2θ values ((θ) is Bragg's diffraction angle) were taken from the XRD data. The (hkl) of XRD data represents (101). The θ and the full width at half maximum of XRD (FWHM (β)) were converted to FWHM in radian (radian = 180π degrees).

d value calculated by using the formula:

$$d=\lambda/2\sin\theta \qquad (1)$$

λ is the wavelength of X-ray (1.54 Å).

The average crystal size (nm) of the particles can have been calculated by the formula:

The average size of the crystal =(0.9λ)/(FWHM *cosθ) (2)

FWHM radian and cosθ have been calculated earlier.

Micro-strain (ε) 10^{-3} was calculated by the represent formula:

Micro-strain (ε) 10^{-3} = (FWHM radian *cosθ / 4) 10^{-3} (3)

The calculation of lattice constants a, b, c was done by using this formula:

$$d = \frac{1}{\sqrt{4/3(h^2 + hk + k^2)/a^2 + l^2/c^2}} \quad (4)$$

d represents the d-spacing in angstrom [Å] which will be collected from the XRD data, and (hkl) represented (101).

2. Roles of Cu in Cu doped ZnO/Cu/g-C_3N_4

To further prove the roles of Cu, Cu doped ZnO/g-C_3N_4 and ZnO/g-C_3N_4 heterostructures were prepared. The photocatalytic performance of ZnO/g-C_3N_4 and ZnO/gC_3N_4 were compared with that of Cu doped/Cu/gC_3N_4.

2.1 Synthesis of ZnO/g-C_3N_4

$ZnCl_2$ was dissolved in deionized water. Then 1.34 g NaOH and the prepared 0.02 g-C_3N_4 were added to the $ZnCl_2$ (0.67 M, in 10 ml) aqueous solution. The mixture was transferred to autoclave and heated at 80 ^{O}C for 24h in an air oven. The obtained samples were washed several times with ultrapure water and ethanol and dried at 80 ^{o}C for 12 h.

2.2 Synthesis of Cu doped ZnO/gC_3N_4

About 20 mg of the prepared g-C_3N_4 was added to a beaker that contains 50 ml ethanol and 20 ml distilled water. The solution was maintained at 6 pH by H_2SO_4 and a suitable amount of the 100 mg of Cu doped ZnO was added. The mixture was sonicated for 1 h, followed by stirring for 24 h. The product was collected by centrifugation, followed by washing with distilled water several times, and dried at 80 °C on a hot plate. In the end, fine powder of Cu doped ZnO/gC_3N_4 was obtained.

2.3 Photocatalytic performance comparison

Photocatalytic degradation of MB on ZnO/g-C_3N, Cu doped ZnO/g-C_3N_4, Cu doped ZnO/Cu/g-C_3N_4 are after 60 min sunlight irradiation is compared in Figure S1. 98%, 76%, and 61% of MB were degraded on ZnO/g-C_3N, Cu doped ZnO/g-C_3N_4, and Cu doped ZnO/Cu/g-$C_3N_{4,}$ respectively. Obviously, ZnO/g-C_3N_4 exhibited the lowest photocatalytic performance. After doping the ZnO with Cu, the MB degradation performance increased from 61% to 76% on Cu doped ZnO/g-C_3N_4. Cu doped ZnO/Cu/g-C_3N_4 showed the highest degradation performance. Doping of ZnO with Cu enhanced the light absorption in the visible area therefore Cu doped ZnO/g-C_3N_4 shows higher activity than ZnO/g-C_3N_4. The dramatic increase in the MB degradation on Cu doped ZnO/Cu/g-C_3N_4 is due to (1) the enhanced charge transport from CB of ZnO to VB of Cu induced by the electron mediator Cu (2) Cu plays also as co-catalyst leading to further improvement in the MB degradation performance.

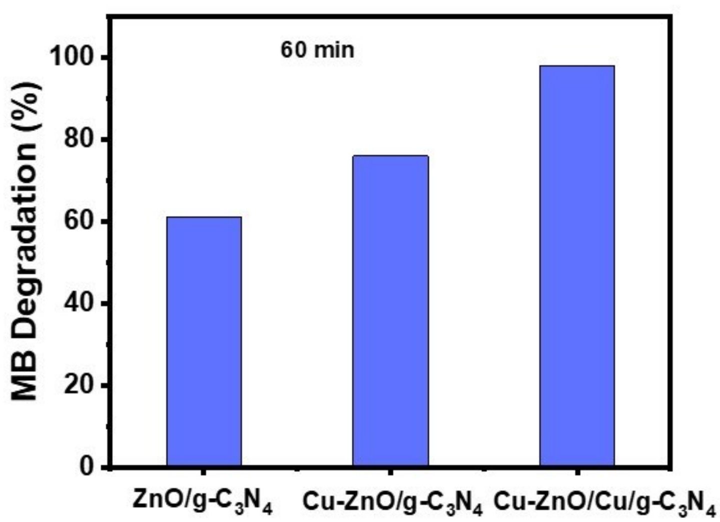

Figure S1. MB degradation on ZnO/g-C_3N, Cu doped ZnO/g-C_3N_4, Cu doped ZnO/Cu/g-C_3N_4 are after 60 min sunlight irradiation

XPS analysis confirmed the presence of both Cu^0 and Cu^{2+} that Cu which clearly supports the assumption of different roles of Cu in Cu doped ZnO/Cu/g-C_3N_4 including dopant (Cu^{2+}), electrons mediator (Cu^0), and co-catalyst (Cu^0). DRS results showed that the bandgap of Cu-ZnO is 2.75 which is much lower than that of pure ZnO (3.37 eV). This decrease in the bandgap could enhance the absorption of the visible light which in turn enhances photocatalytic activity.

3. Mass spectroscopy of the LC-MS

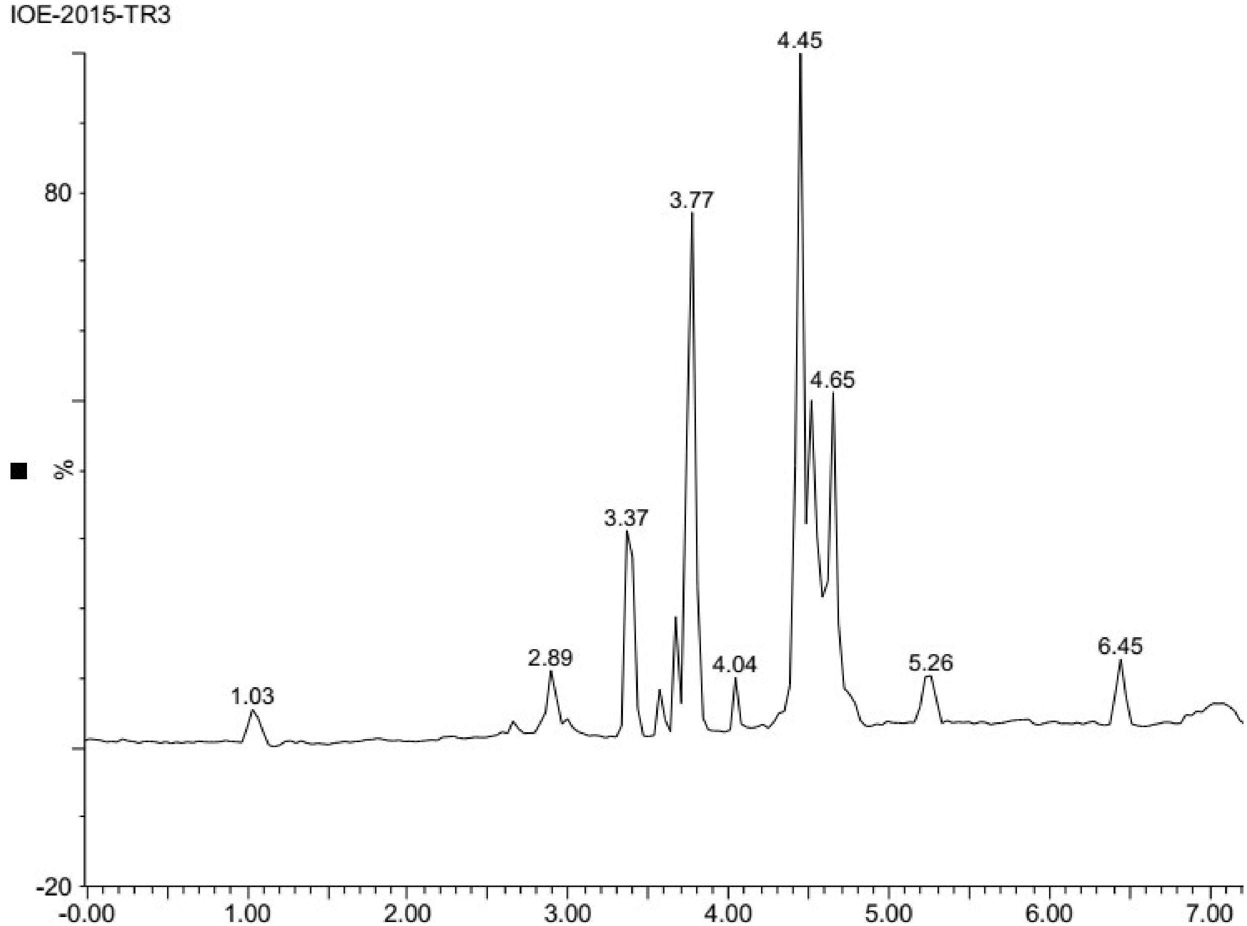

Figure S2. Liquid chromatography spectrum of intermediate product for the degradation of RhB.

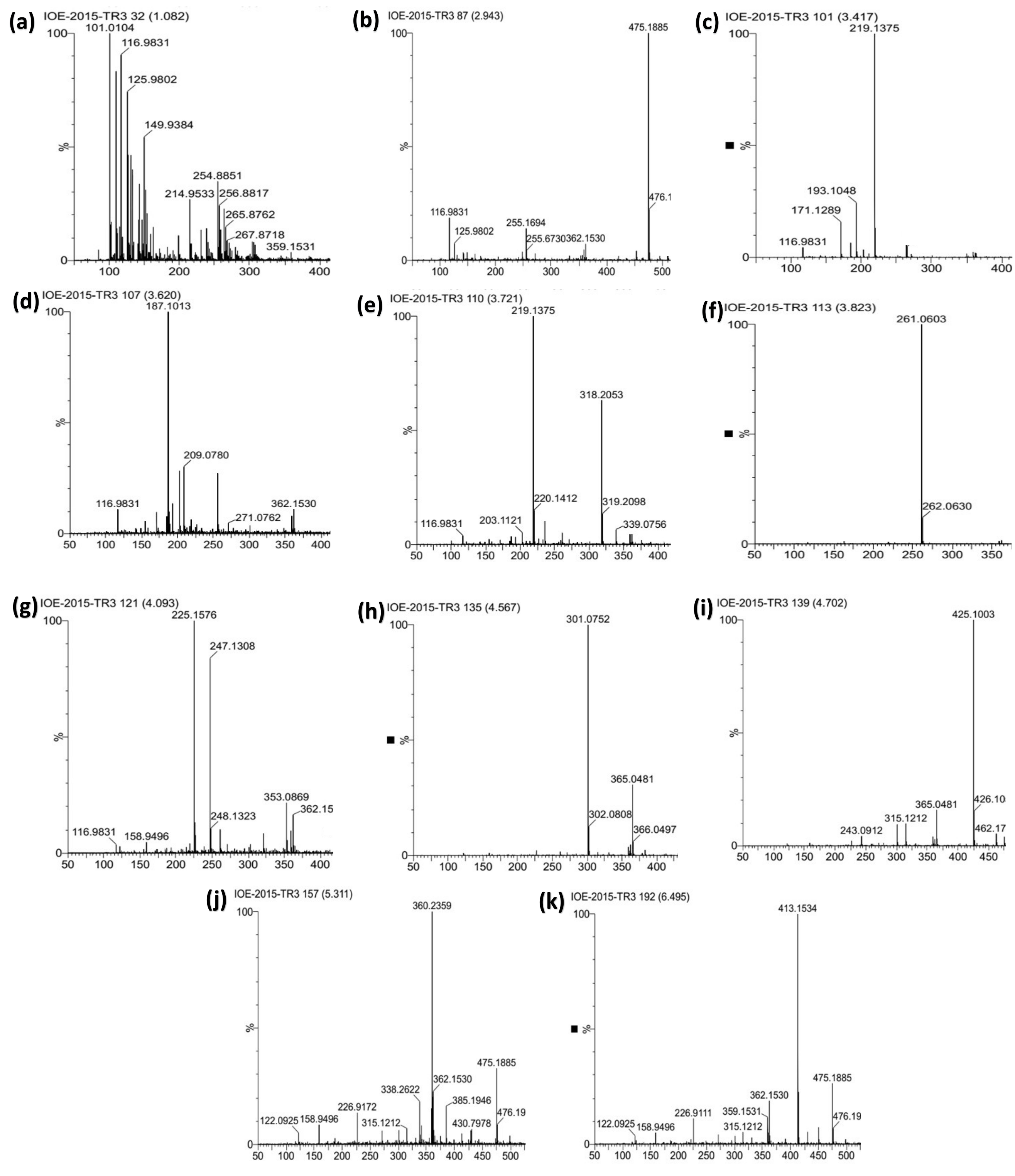

Figure S3. MS spectra of intermediate product for the degradation of RhB.