Ternary heterogeneous Z-scheme photocatalyst $TiO_2/CuInS_2$/OCN incorporated with carbon quantum dots (CQD) for enhanced photocatalytic degradation efficiency of reactive yellow 145 dye in water

Manh B. Nguyen[a,b#], Pham Thi Lan[c#], Nguyen Tuan Anh[c], Nguyen Ngoc Tung[d], Shaoliang Guan[e,f], Valeska P. Ting[g,h], T.-Thanh-Bao Nguyen[i], Huan V. Doan[g], Mai Thanh Tung, and Tran Dai Lam[c*]

[a]Institute of Chemistry (ICH), Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet street, Cau Giay, Hanoi, Vietnam.

[b]Graduate University of Science and Technology (GUST), Vietnam Academy of Science and Technology. 18 Hoang Quoc Viet Street, Cau Giay, Hanoi, Vietnam.

[c]Institute for Tropical Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam.

[d]Center for Research and Technology Transfer, Vietnam Academy of Science and Technology (VAST), 18 Hoang Quoc Viet Street, Cau Giay, Ha Noi, Vietnam.

[e]School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK.

[f]HarwellXPS, Research Complex at Harwell, Rutherford Appleton Laboratory, Didcot OX11 0FA, UK.

[g]Research School of Chemistry, The Australian National University, AT 2601, Canberra, Australia.

[h]College of Engineering, Computing and Cybernetics, The Australian National University, ACT 2601, Canberra, Australia.

[f]Institute of Physics, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Viet Nam

[i]Hanoi University of science and technology, 1 Dai Co Viet, Bach Khoa, Hai Ba Trung, Hanoi, Vietnam

# The authors contributed equally to this work

†Corresponding author: trandailam@gmail.com (Tran Dai Lam)

1. Chemicals

Titanium isopropoxide (TIP, 97%, Sigma-Aldrich), indium(III) chloride tetrahydrate ($InCl_3.4H_2O$, 97%, Sigma-Aldrich), Copper(II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$, 99%, Sigma-Aldrich), thioacetamide (C_2H_5NS, 98%, Sigma-Aldrich), sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$, 98%, China), hydroperoxide (H_2O_2, 30%, China), ammonium chloride (NH_4Cl, 98%, China), ethylene glycol (EG, 98%, China), acid acetic (CH_3COOH, 98%, China), ethanol (C_2H_5OH, 98%, Vietnam) were all purchased and used without further purification.

2. Additional figures

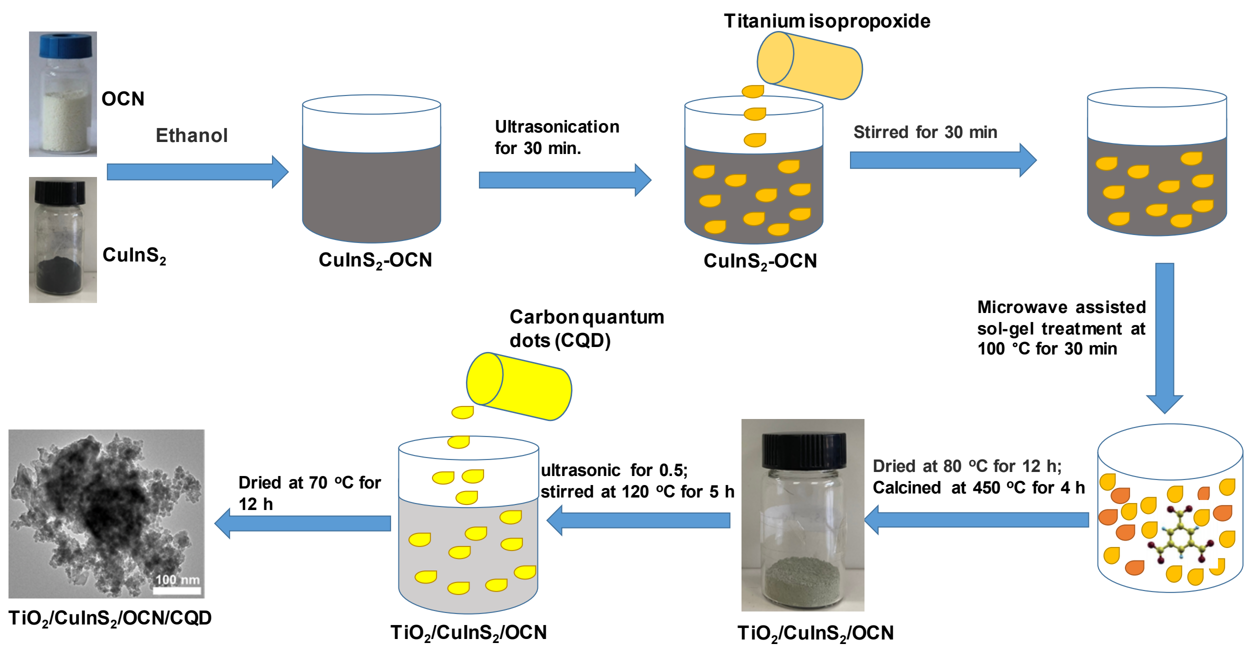


Figure S1. Schematic diagram of the synthesis process of $TiO_2/CuInS_2/OCN/CQD$ material

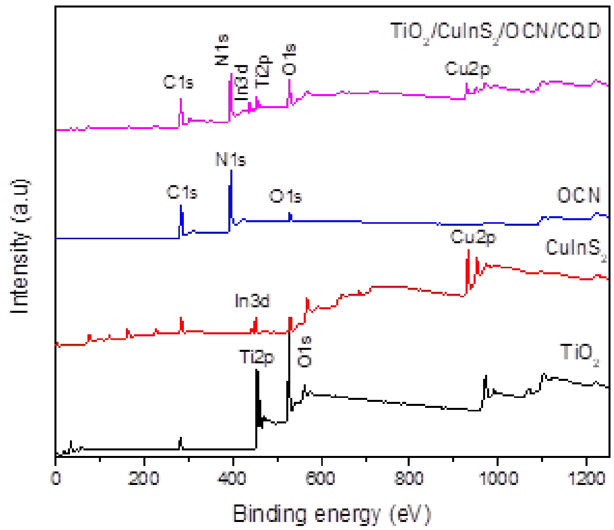


Figure S2. Survey XPS spectra of the $CuInS_2$, OCN, TiO_2, and $TiO_2/CuInS_2/OCN/CQD$ samples.

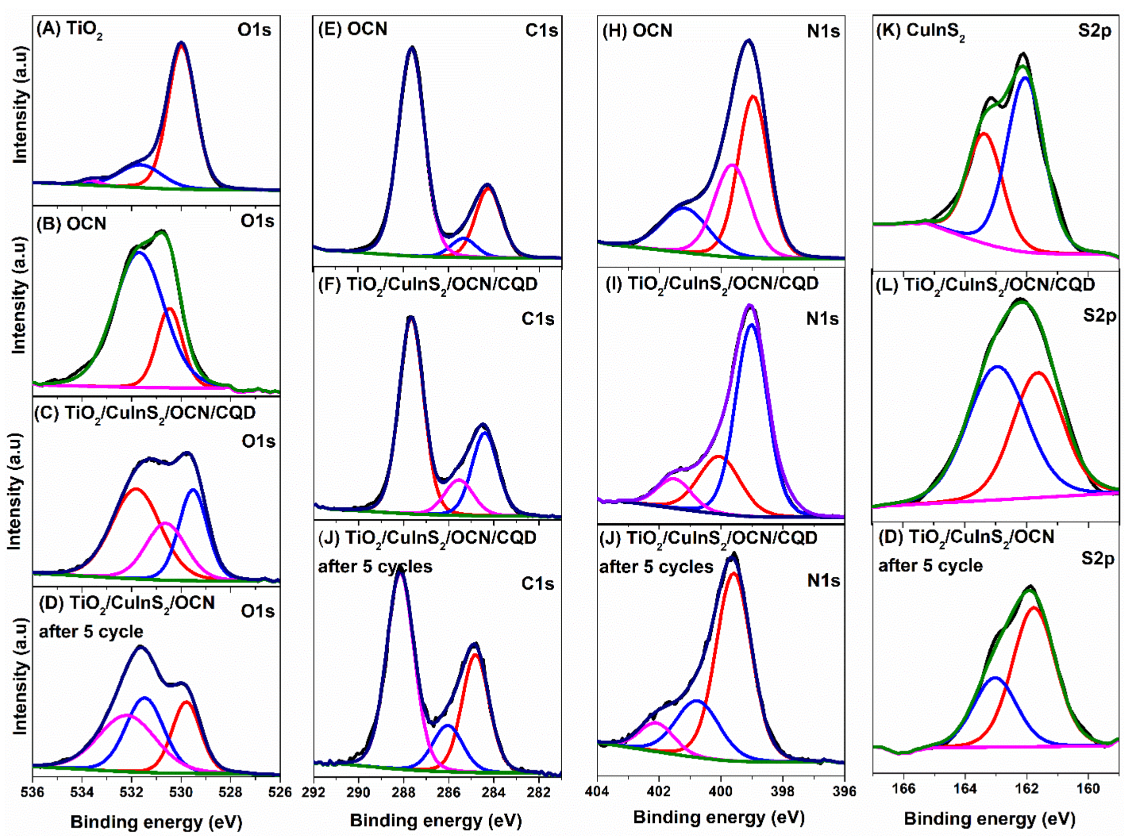


Figure S3. High-resolution O 1s, C 1s, N 1s and S 2p XPS spectra of $CuInS_2$, OCN, TiO_2, $TiO_2/CuInS_2$/OCN/CQD samples

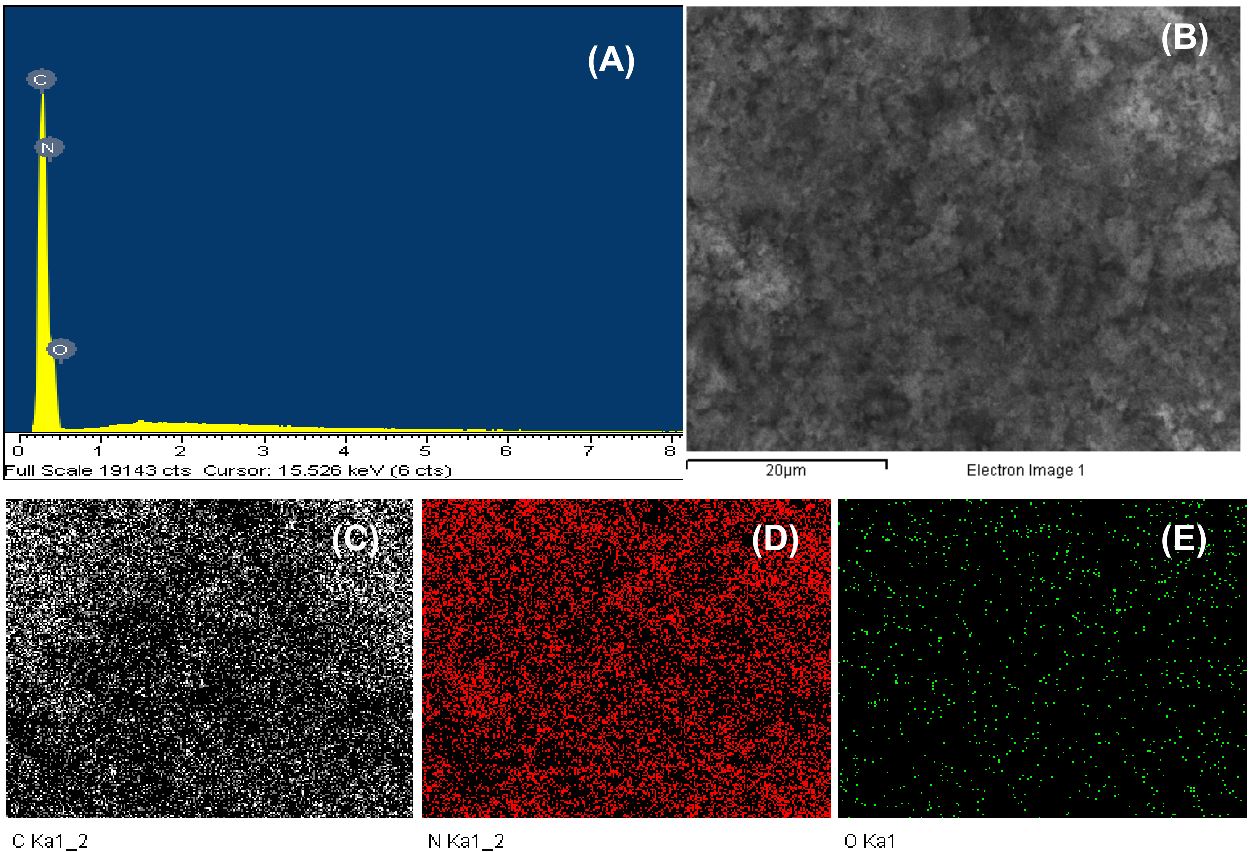


Figure S4. (A) EDS spectrum and (B) EDS-mapping image of OCN sample; EDS elemental mapping images of C (C), N (D) and O (E) in the sample

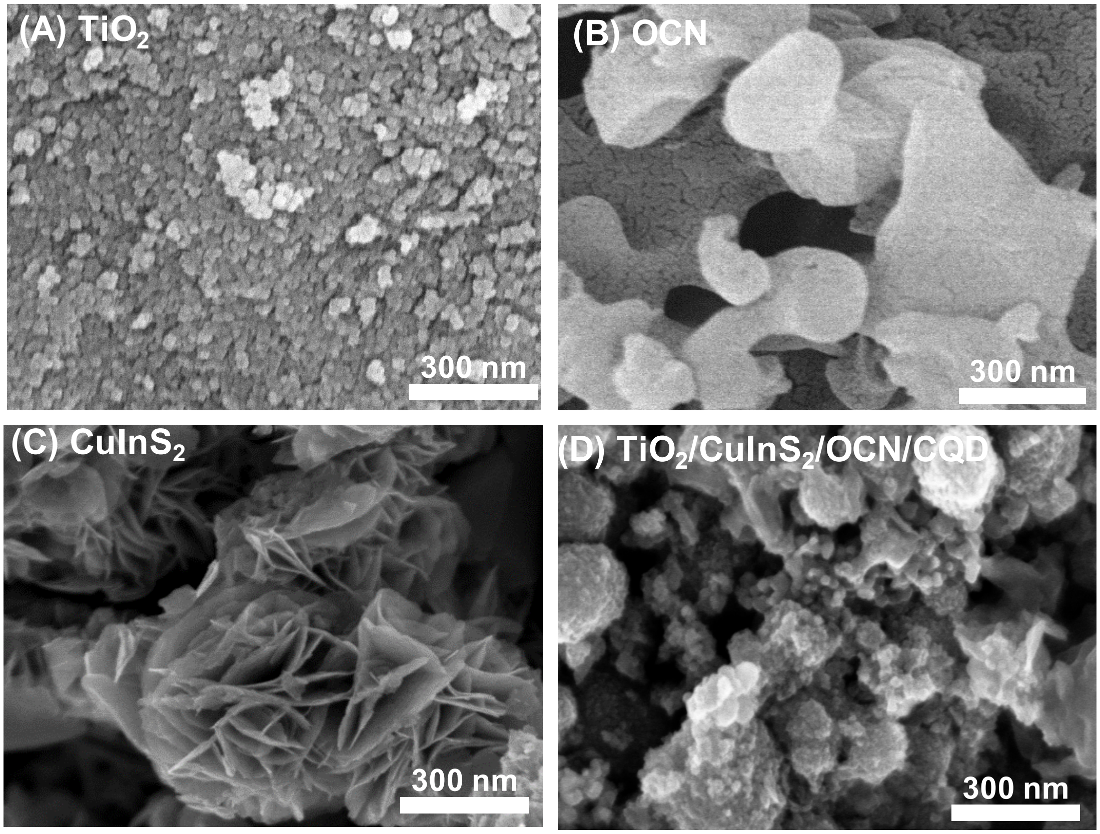


Figure S5. SEM images of $CuInS_2$, TiO_2, OCN and TiO_2/$CuInS_2$/OCN/CQD samples

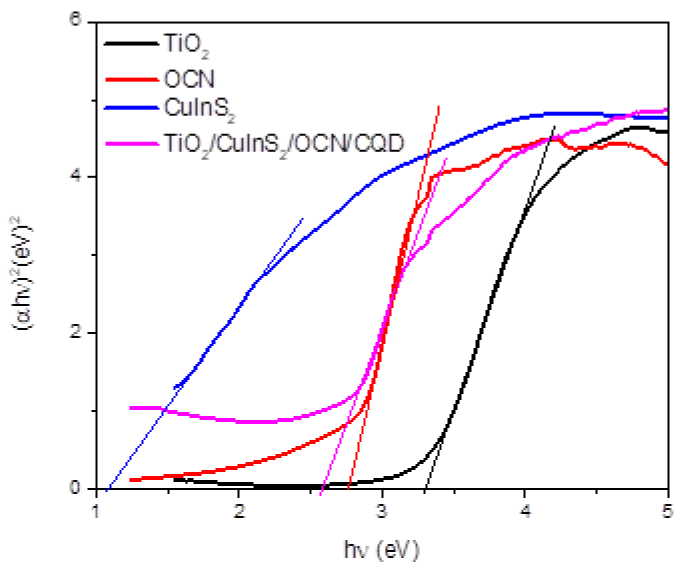


Figure S6. Chart for calculating band gap energy of TiO_2, $CuInS_2$, OCN and TiO_2/$CuInS_2$/ OCN samples.

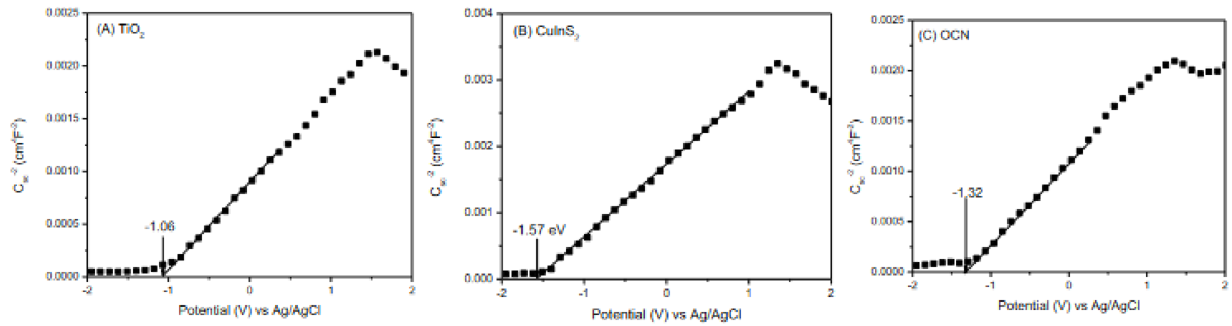


Figure S7. Mott-Schottky characteristics of TiO_2, $CuInS_2$ and OCN samples

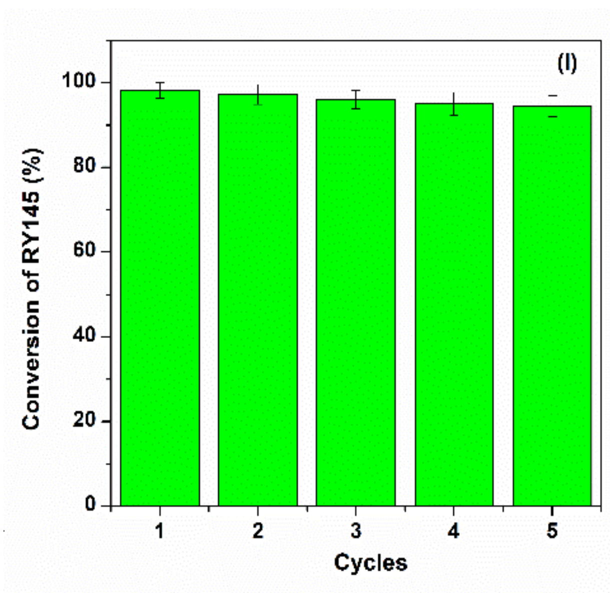


Figure S8. Conversion of RY145 after 5 reaction cycles on TiO_2/$CuInS_2$/OCN/CQD photocatalyst

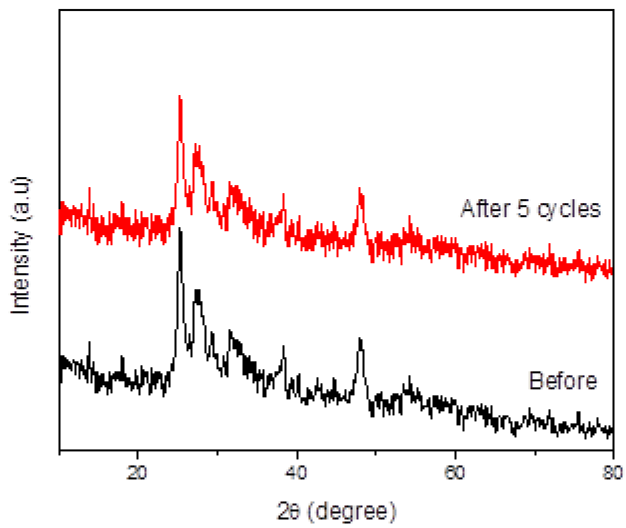


Figure S9. XRD patterns of $TiO_2/CuInS_2$/OCN/CQD before and after 5 reaction cycles

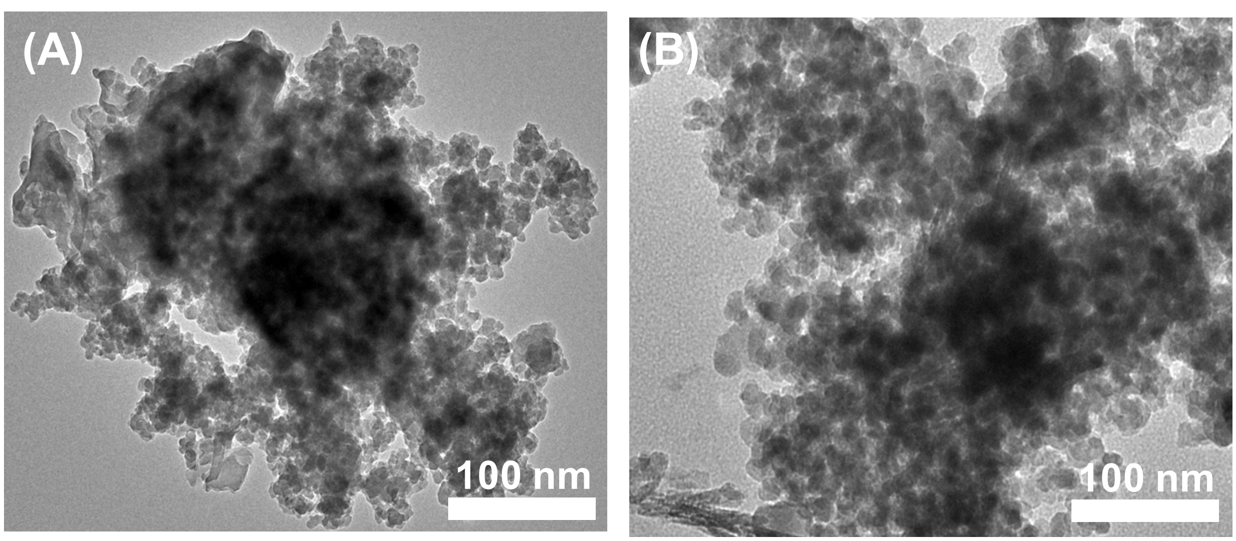
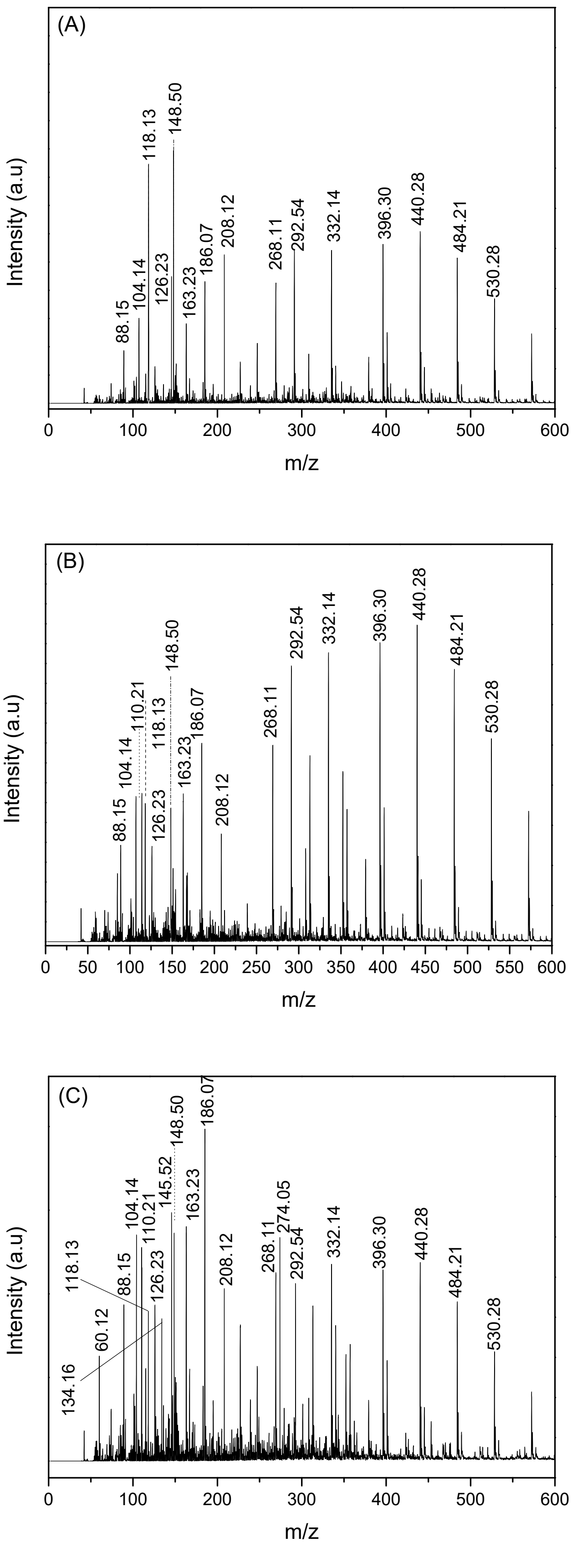


Figure S10. TEM images of $TiO_2/CuInS_2$/OCN/CQD before (A) and after 5 reaction cycles (B)



(A)
Intensity (a.u)
88.15
104.14
118.13
126.23
148.50
163.23
186.07
208.12
268.11
292.54
332.14
396.30
440.28
484.21
530.28
m/z
(B)
Intensity (a.u)
88.15
104.14
110.21
118.13
126.23
148.50
163.23
186.07
208.12
268.11
292.54
332.14
396.30
440.28
484.21
530.28
m/z
(C)
Intensity (a.u)
60.12
118.13
134.16
88.15
104.14
110.21
126.23
145.52
148.50
163.23
186.07
208.12
268.11
274.05
292.54
332.14
396.30
440.28
484.21
530.28
m/z

Figure S11. LC-MS spectra of RY145 degraded by $TiO_2/CuInS_2$/OCN/CQD photocatalyst at different reaction times

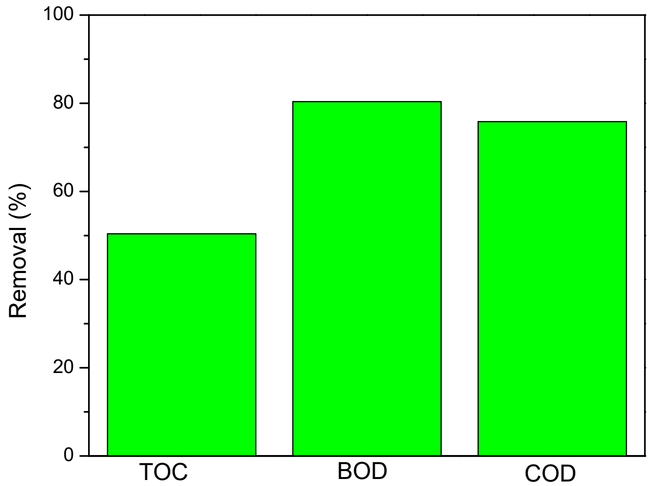


Figure S12. COD, BOD, TOC removal efficiency of RY145 after 60 minutes of visible light irradiation

3. Additional tables

Table S1. Binding energies of the bonds in the $CuInS_2$, TiO_2, OCN and $TiO_2/CuInS_2$/OCN/CQD samples

Element		$CuInS_2$	TiO_2	OCN	$TiO_2/CuInS_2$/OCN/CQD	$TiO_2/CuInS_2$/OCN/CQD after 5 cycles
Cu2p	Cu^o	929.52	-	-	-	-
		949.22	-	-	-	-
	Cu^+	932.13	-	-	931.94	932.50
		952.01	-	-	951.74	952.40
	Cu^{2+}	933.42	-	-	933.19	934.92
		953.78	-	-	953.78	954.98

In	In^{2+}	446.14	-	-	444.67	444.75
		453.64	-	-	452.73	452.80
	In^{3+}	448.37	-	-	446.25	446.42
		455.84	-	-	453.62	453.75
S	S^{2-}	162.04	-	-	161.64	161.77
		163.36	-	-	162.95	163.03
Ti2p	Ti^{4+}	-	458.80	-	458.99	459.16
		-	464.56	-	464.71	464.12
C1s	sp^2 C–C	-	-	284.24	284.40	284.81
	C–O	-	-	285.34	285.55	286.05
	N–C=N	-	-	287.64	287.66	288.15
N1s	C–N=C	-	-	398.97	399.01	399.59
	sp^3N	-	-	399.64	400.05	400.76
	C_2–NH	-	-	401.18	401.31	402.08
O1s	N–C–O	-	-	530.47	529.52	529.79
	Ti-O	-	529.98	-	530.62	531.47
	–OH groups	-	531.94	531.69	531.81	532.18

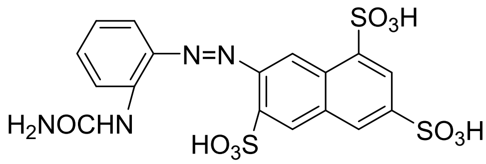
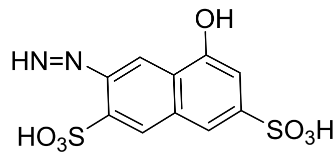
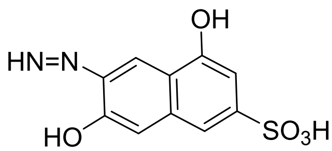
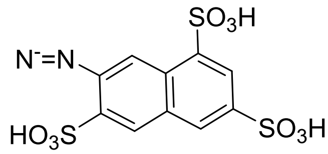
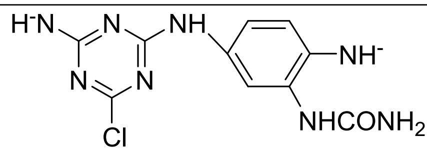
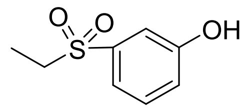
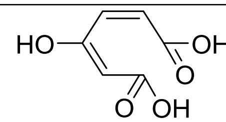
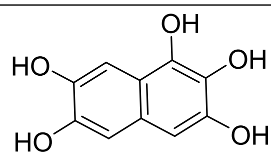
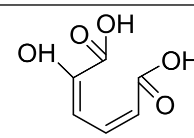
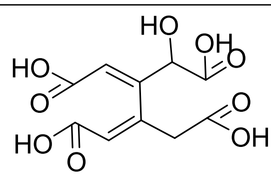
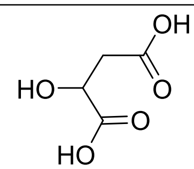
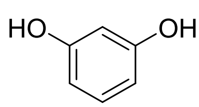
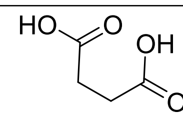
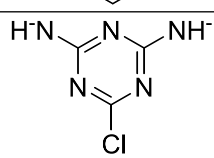
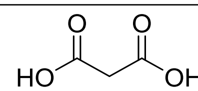
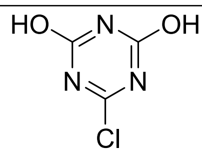
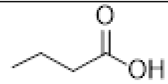
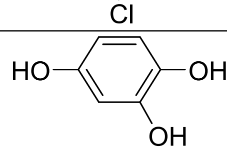
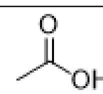
Table S2. Chemical composition (wt%) of elements in samples TiO_2, $CuInS_2$, OCN and TiO_2/$CuInS_2$/OCN/CQD samples

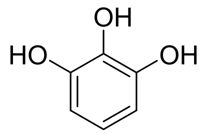
Samples	C	N	O	Ti	Cu	In	S	Total
OCN	44	52.32	3.68	-	-	-	-	100
$CuInS_2$	-	-	-	-	29.57	40.18	30.25	100
TiO_2	-	-	42.47	57.53	-	-	-	100
TiO_2/$CuInS_2$/OCN/CQD	23.47	28.75	17.62	13.71	4.65	6.88	4.92	100

Table S3. Comparative results of RY145 dye pollutants removal by various heterogeneous materials

Samples	Reaction conditions	Removal efficiency (%)	Reaction time (min)	Ref.
$TiO_2/CuInS_2$/OCN/CQD	[RY145] = 50 mg/L [Catalyst] = 0.4 g/L Lamp: 15W pH = 5.5	98.2	60	This work
Cu-NiO/ZnO	RY145] = 30 mg/L [Catalyst] = 6 g/L	99	70	[1]
TiO_2/CQD	RY145] = 30 mg/L [Catalyst] = 1 g/L Lamp: intensity: 30,798 lux; Wavelength: 400–700 nm	55	30	[2]
ZnO	RY145] = 5 mg/L [Catalyst] = 1 g/L	99	320	[3]
g-C_3N_4-BiOBr	[RY145] = 50 mg/L [Catalyst] = 1 g/L Lamp: Wonfram 500 W	93	60	[4]
Cu –ZnO	[RY145] = 40 mg/L [Catalyst] = 1 g/L Lamp: Solar light irradiation	80	100	[5]
α-Al_2O_3 NPs	[RY145] = 60 mg/L [Catalyst] = 0.6 mg/L pH = 6.5 Fluorescent lamp (80W)	95	60	[6]
$MTiO_3$ (M = Sr, Ca, Ba, Pb	[RY145]= 50 mg/L [Catalyst] = 0.5 g/L pH = 6.5 Lamp: 8 W	78	120	[7]
g-C_3N_4-$SrTiO_3$	[RY145]= 50 mg/L [Catalyst] = 1 g/L Lamp: 500 W tungsten	100	90	[8]
TiO_2/Activated carbon	[RY145]= 50 mg/L [Catalyst] = 50 mg/L [H_2O_2] = 2 mL/L pH =3 Lamp: Low-pressure mercury	93	240	[9]

Table S4. Reactive yellow 145 dye (RY145) degradation under irradiation of visible light intermediates as detected by LC-MS analysis

m/z	Probable structure	m/z	Probable structure
530.28		332.14	
268.11		396.30	
292.54		186.07	
163.23		158.22	
208.12		158.22	
274.05		134.16	
110.21		118.13	
145.52		104.14	
148.5		88.15	
126.23		60.12	

126.23			

4. References

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