

1 **Supplementary Information**

2
3 **Pivotal role of starch in restoring the photocatalytic performance of**
4 **chitosan films for eliminating water pollutants**

5 Aman Chauhan,^a Archana Negi,^a Kirti,^a Moondeep Chauhan,^b Ajeet Kaushik,^c Ganga Ram
6 Chaudhary^{*a,d}

7 ^a. Department of Chemistry, Centre of Advanced Studies in Chemistry, Panjab University,
8 Chandigarh 160014, India.

9 ^b. Department of Environmental Studies, Amity University, 140306 Mohali, Punjab, India.

10 ^c. NanoBioTech Laboratory, Department of Environmental Engineering, Florida Polytechnic
11 University, Lakeland 33805, FL, USA.

12 ^d. SAIF/CIL, Panjab University, Chandigarh 160014, India.

13 Email: grc22@pu.ac.in

14
15 **Table of Contents**

16 **1. Methods.....S2**

17 **2. Preparation procedure for catalytic films.....S3**

18 **3. XRD analysis.....S4**

19 **4. FT-IR analysis.....S4**

20 **5. XPS analysis.....S5**

21 **6. Supporting tables and figures.....S6**

22 **7. References.....S10**

23

24

25

26 **1. Methods**

27 **Materials**

28 Glacial acetic acid ($\geq 99.7\%$) and dimethyl sulfoxide (DMSO) were bought from Thermo Fisher
29 Scientific. Cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) ($\geq 98\%$), copper (II) chloride
30 dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), sodium sulphide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) ($\geq 98\%$), L-ascorbic acid
31 (99%), para-benzoquinone (PBQ), chitosan and ciprofloxacin were procured from Sigma
32 Aldrich. Starch powder, sodium hydroxide pellets and methanol (99.5%) were provided by
33 Fisher Scientific. Thiourea ($\text{CH}_4\text{N}_2\text{S}$) (99%) was supplied by Alfa Aesar. Polyvinylpyrrolidone
34 (PVP K-30) was bought from SRL. All the reagents have been employed without any further
35 purification.

36 **Instrumentation**

37 The XRD analysis for crystal structure elucidation of powdered particles and catalytic films
38 was performed using XRD PANalytical Xpert Pro diffractometer. Fourier Transform Infrared
39 (FT-IR) spectra of samples were obtained from Perkin Elmer - Spectrum RX-1 FT-IR
40 instrument. For morphological investigations, FE-SEM Hitachi SU8010 was employed which
41 was equipped with EDS instrument for elemental analysis of the samples. For gaining deeper
42 insights of morphology and ultrastructure, High Resolution Transmission Electron Microscopy
43 (HR-TEM) was carried out using JEOL JEM 2100 Plus instrument. The experiments pertaining
44 to Zeta potential estimation were performed on Anton Paar Litesizer 500 instrument. The
45 Brunauer-Emmett-Teller (BET) surface area of the particles was estimated by nitrogen
46 adsorption-desorption process using BET Quanta Chrome; NOVA 2000e analyzer. UV- DRS
47 spectrophotometer (Jasco V-760 DR-81) was used to record UV-Vis diffuse reflectance
48 spectra for estimating the band gaps of the particles and the films. Mott-Schottky experiments
49 for estimation of conduction band edge potential were carried out on Auto lab-203, Metro ohm
50 electrochemical workstation using 0.1M Na_2SO_4 solutions.

51 **Photocatalytic activity experiments**

52 The photocatalytic experiments were carried out in glass made cylindrical reactor consisting of
53 300 W Xenon lamp as visible light source. For each degradation cycle, 40 mL of CP solutions
54 were used. In order to adequately compare the degradation performance, the amount chosen
55 for powdered $\text{CdS}@\text{CuS}$ photocatalyst was kept similar to that of its loading amount in 4×4
56 sections of catalytic films. Before exposing to visible light source, CP solutions were placed in
57 dark for 1 hour to establish adsorption-desorption equilibrium. In irradiated phase, samples

58 were extracted after adequate intervals to ascertain kinetic aspects of CP degradation process.
59 For recyclability experiments, films were properly washed under visible light source and
60 adequately dried after every cycle. The degradation analysis was carried out using UV-Visible
61 spectroscopic measurements wherein, alleviation in the intensity of absorption of maxima of
62 CP was taken as a measure of degradation efficiency.

63 **2. Preparation procedure for catalytic films**

64 **Synthesis of CdS@CuS photocatalyst**

65 For preparing CuS nanoparticles (NPs), 1.704 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2 g PVP were dissolved in
66 180 mL of distilled water. After complete dissolution, 5 mL of 2M NaOH was added dropwise,
67 followed by the addition of 10 mL of 1M L-Ascorbic acid solution. Then, the solution
68 temperature was elevated to 60 °C and 20 mL of 1M $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ solution was added into it.
69 As-prepared solution was allowed to heat for 3 hours at 60 °C under vigorous magnetic stirring.
70 Thereafter, the solution was centrifuged and CuS NPs were separated and adequately washed
71 5-6 times by distilled water and ethanol. As-synthesized CuS NPs were dried in a vacuum oven
72 and were preserved for further steps. For synthesizing CdS NPs, 1.3 g of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$
73 and 760 mg of thiourea were dissolved in 100 ml of distilled water under vigorous stirring.
74 This mixture was then added to a 250 mL autoclave and heated at 180 °C for 15 hours. After
75 reaction, CdS NPs were separated, washed and preserved for further steps. To synthesize
76 CdS@CuS, CdS:CuS (2:1) was allowed to react hydrothermally at 65 °C for 5 hours in a hot
77 air oven. Thereafter, as-prepared composite CdS@CuS photocatalyst was collected and
78 adequately washed before drying.

79 **Synthesis of SH/CH films**

80 To prepare SH/CH films, 2% (w/v) chitosan was added to 25 mL of 2% acetic acid solution
81 under vigorous mechanical stirring until a thick slurry was formed. To this slurry, starch
82 powder (2% (w/v)) was added in small proportions to form homogeneous SH/CH gel. As
83 formed gel was casted onto a glass plate and subjected to drying at 50 °C for 3 hours. After
84 drying, the films were neutralized with 5% (w/v) NaOH solution. Thereafter, the films were
85 kept in water bath for 60 seconds to remove excess NaOH from surface of the films. Finally,
86 the films were dried at 40 °C for 2 hours and preserved for further steps. Meanwhile for
87 preparing pure CH film, all the steps were kept same barring SH addition step, which was
88 excluded.

89 **Synthesis of SH/CH-CdS@CuS films**

90 To synthesize SH/CH-CdS@CuS catalytic films, 165 mg of CdS@CuS photocatalyst were
91 added to 25 mL of 2% acetic acid solution alongside 2% (w/v) chitosan in the initial step.
92 Except this, all the steps from the preparation of SH/CH films were followed exactly. However,
93 while preparing CH-CdS@CuS films (devoid of starch), starch addition step was excluded.

94 **3. XRD analysis**

95 The XRD patterns obtained for powdered particles and catalytic films have been shown in Fig.
96 S1a. In the diffraction pattern of CuS, peaks observed at 28.01°, 29.60°, 32.44°, 48.3°, 52.8°
97 and 59.3° represent the (101), (102), (103), (110), (108) and (116) planes of hexagonal lattice,
98 respectively (JCPDS - 06-0464).¹ Meanwhile for CdS, peaks observed at 25.1°, 26.6°, 28.3°,
99 36.75°, 43.8°, 48.0°, 52.0°, 53.1°, and 53.05° were assigned to the (100), (002), (101), (102),
100 (110), (103), (200), (112), and (201) planes of hexagonal lattice, respectively (JCPDS - 02-
101 0549).² In the diffraction pattern of CdS@CuS, peaks of both CdS and CuS were retained
102 indicating the successful formation of composite.

103 The diffraction pattern of bare CH film shows the emergence of peaks at 10.05° and 20.2°,
104 which is characteristic of chitosan.³ It may be noted that diffraction peaks of both starch and
105 chitosan appear at almost same values, due to this reason no extra peak was observed in the
106 diffraction pattern of SH/CH film.⁴ At last, diffraction pattern of both the catalyst blended
107 films, i.e., CH-CdS@CuS and SH/CH-CdS@CuS retained all the peaks of catalysts and
108 biopolymeric components, confirming their formation and successful association.

109 **4. FT-IR analysis**

110 The results of FT-IR analysis have been shown in Fig. S1b. In the spectrum of CuS, the peak
111 observed around 550 cm⁻¹ was assigned to Cu-S bond.⁵ In case of CdS, a broad peak between
112 850-1140 cm⁻¹ marked the presence of Cd-S bond.⁶ For CdS@CuS, peaks of both the
113 components were observed, which confirmed the formation of composite. Besides, other peaks
114 due to precursors were also observed at 1089 cm⁻¹, 1367 cm⁻¹, 1818 cm⁻¹ and 3012 cm⁻¹ which
115 were assigned to C=S stretching of thiourea; C-H bending, C=O stretching and C-H stretching
116 of L-ascorbic acid.⁷ The FT-IR spectrum of CH film and SH/CH film was almost similar,
117 perhaps due to overlapping of peaks. The spectra of both these films contained absorption peaks
118 corresponding to stretching vibrations of C-O, C-N, C=O, C-H and N-H groups at 1035 cm⁻¹,
119 1383 cm⁻¹, 1614 cm⁻¹, 2909 cm⁻¹ and 3317 cm⁻¹, respectively.⁸ At last, the retention of

120 CdS@CuS peaks was observed in both CH-CdS@CuS and SH/CH-CdS@CuS film, which
121 suggested the successful formation of catalytic films and strong adhesion of catalysts with
122 biopolymer surface.

123 **5. XPS analysis**

124 The results of XPS experiments are shown in Fig. S2. The XPS scans of CuS are presented in
125 Fig. S2a-c. The Cu 2p scan ranged between 930 eV to 955 eV shows the characteristic pattern
126 of divalent Cu (Fig. S2b). Meanwhile, XPS scan of S 2p resembled with the peculiar pattern of
127 S²⁻, confirming the formation of CuS.⁵ In the XPS scans for CdS (Fig. S2d-f), S followed the
128 similar pattern as observed in case of CuS (Fig. S2f). The Cd 3d scan, was comprised of two
129 fitted peaks at 405 eV and 411 eV, which corresponded to its 3d_{5/2} and 3d_{3/2} states.⁶ In the XPS
130 scan of CdS@CuS photocatalyst (Fig. S2g-j), the scans of Cd, Cu and S did not show any
131 significant deviation from their individual scans. The scans of SH/CH-CdS@CuS film shown
132 in Fig. S2k-p, reveal the appearance of peaks of all the catalyst components with no significant
133 deviation from their bare forms. Besides, the XPS scan of C, N and O was also in accordance
134 with the usually observed scans of chitosan and starch.⁷

135

136

137

138

139

140

141

142

143

144

145

146

147 **6. Supporting tables and figures**

148 **Table S1.** Textural analysis of powdered catalysts.

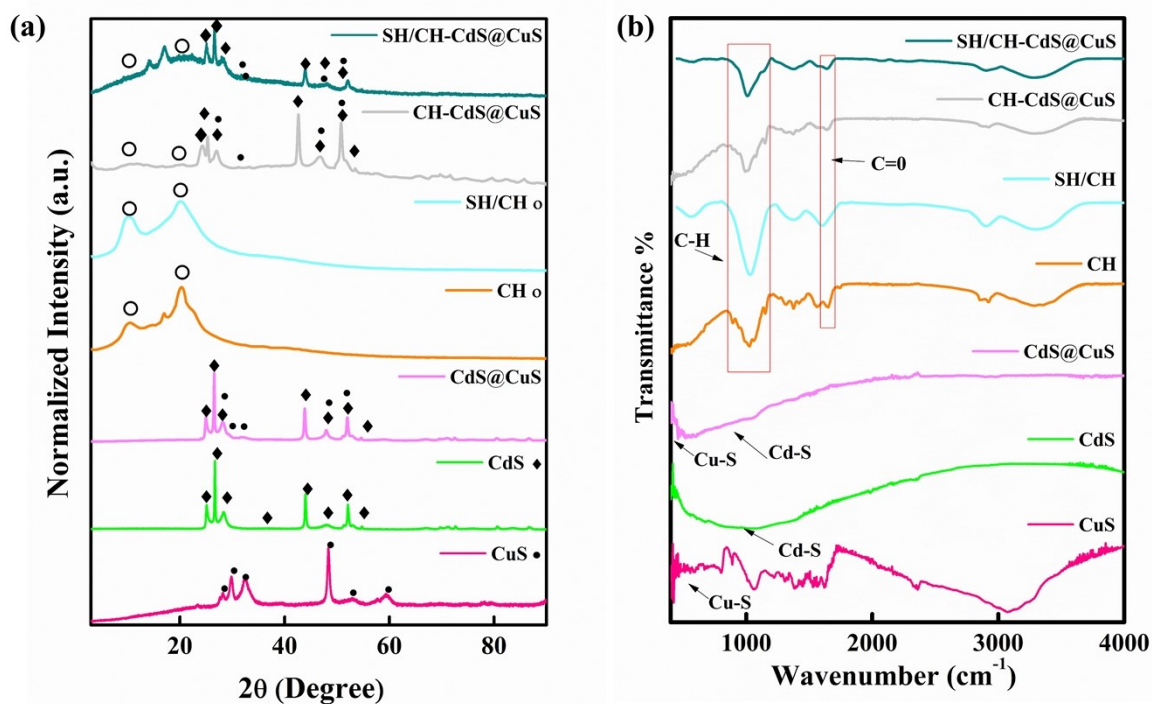
Catalysts	Surface Area (m ² /g)	Pore Volume (cc/g)	Pore diameter (nm)
CuS	27.289	0.244	1.812
CdS	0.790	0.003	1.799
CdS@CuS	8.477	0.079	1.806

149

150 **Table S2.** Rate constant values of different catalysts.

Catalysts	Rate constant (min ⁻¹)
CuS	7.06×10^{-3}
CdS	5.52×10^{-3}
CdS@CuS	2.618×10^{-2}
CH	1.9496×10^{-4}
SH/CH	1.77206×10^{-4}
CH-CdS@CuS	8.23×10^{-3}
SH/CH-CdS@CuS	2.358×10^{-2}

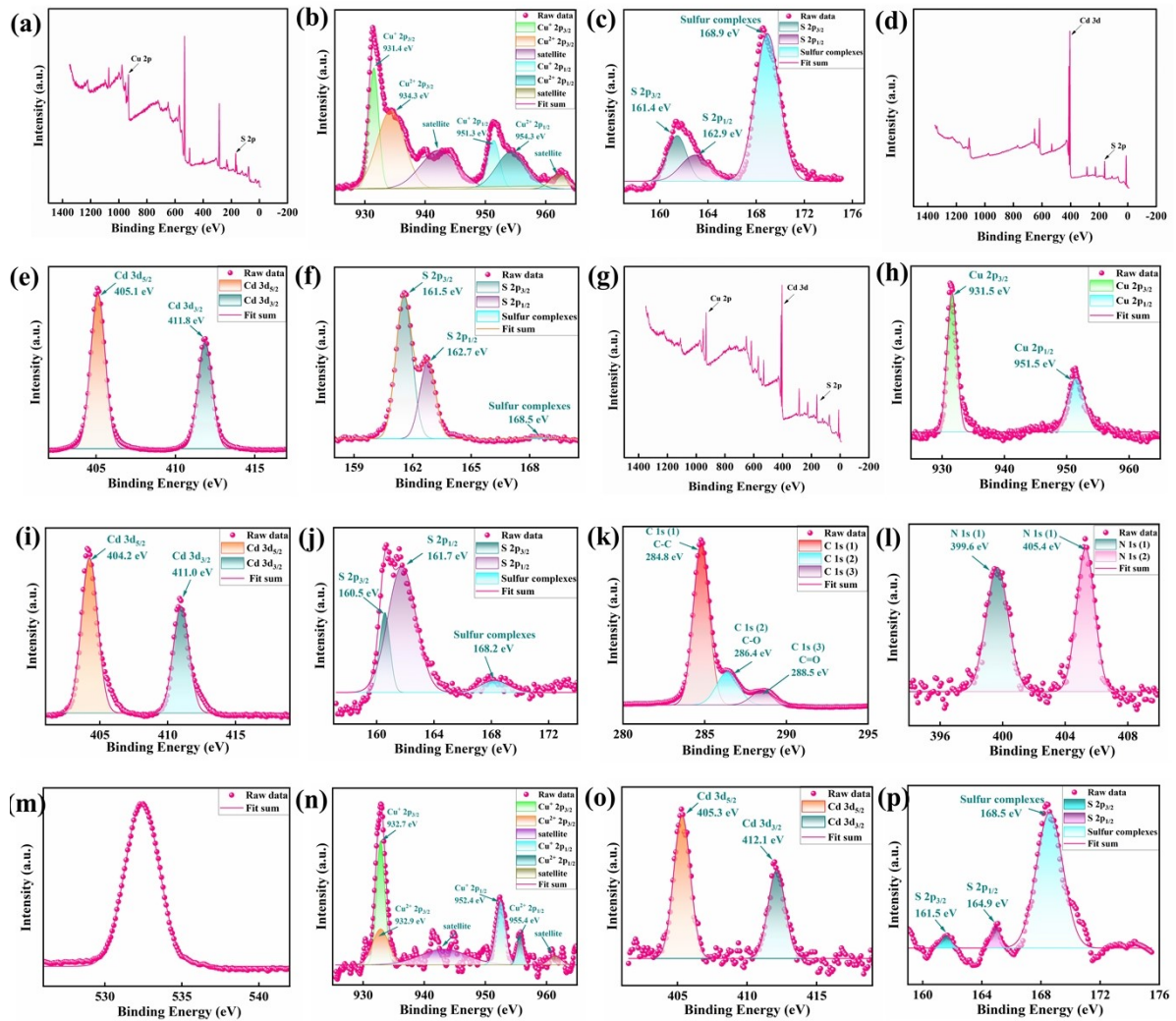
151



152

153

Fig. S1 (a) X-ray diffraction pattern and (b) FT-IR spectra of catalysts.

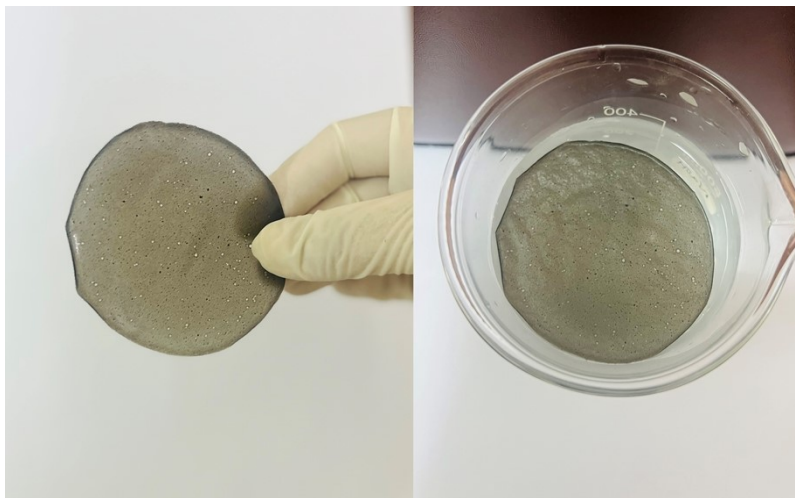


155

156 **Fig. S2** XPS scans of (a-c) CuS, (d-f) CdS, (g-j) CdS@CuS and (k-p) SH/CH-CdS@CuS

157

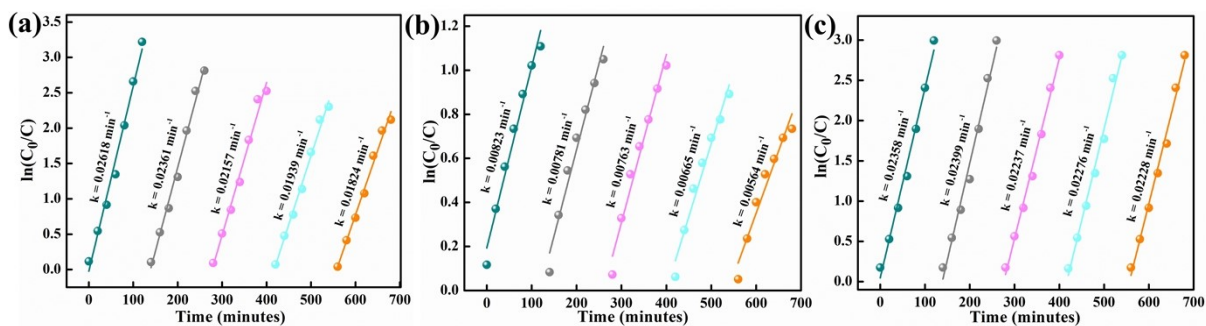
film.



158

159

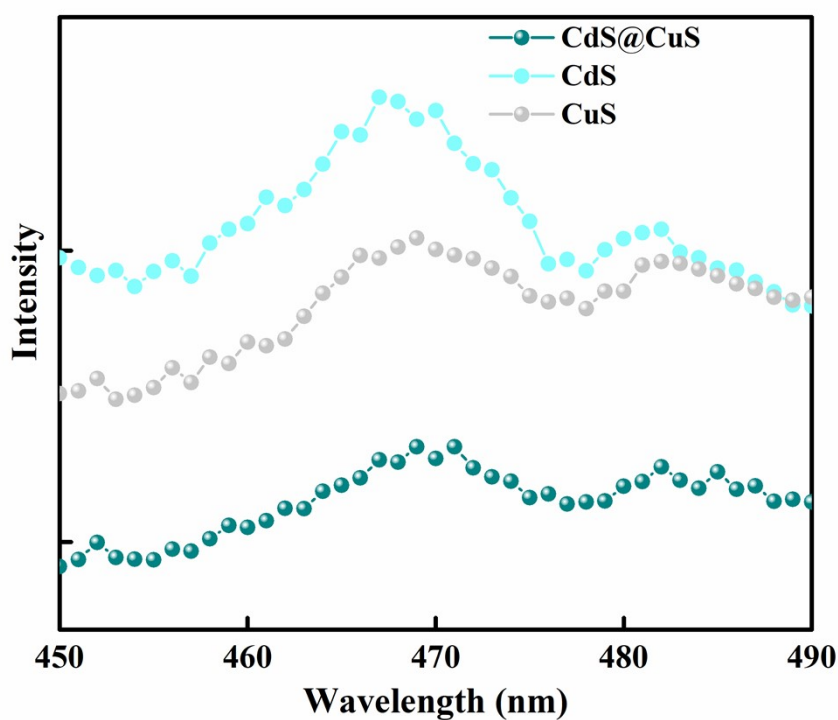
Fig. S3 Digital pictures of SH/CH-CdS@CuS film.



160

161 **Fig. S4** First-order fitting for reusability profiles of (a) CdS@CuS, CH-CdS@CuS film and

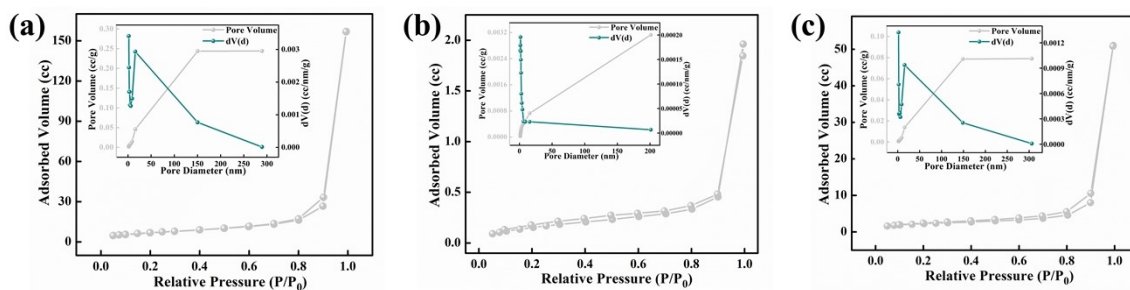
162 (c) SH/CH-CdS@CuS film.



163

164

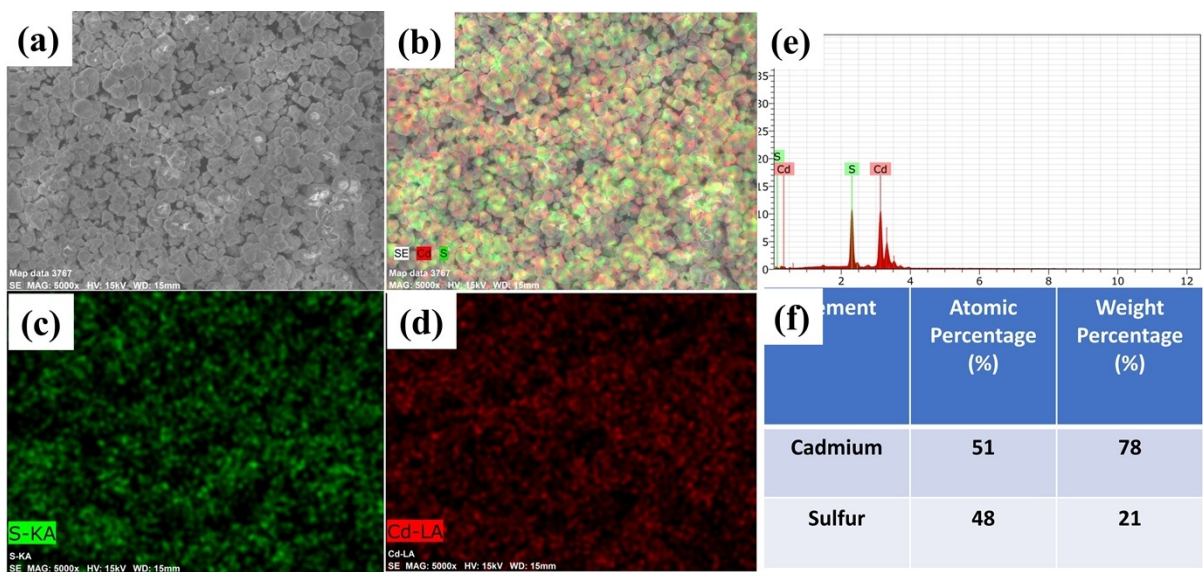
Fig. S5 Photoluminescence spectra of powdered catalysts.



165

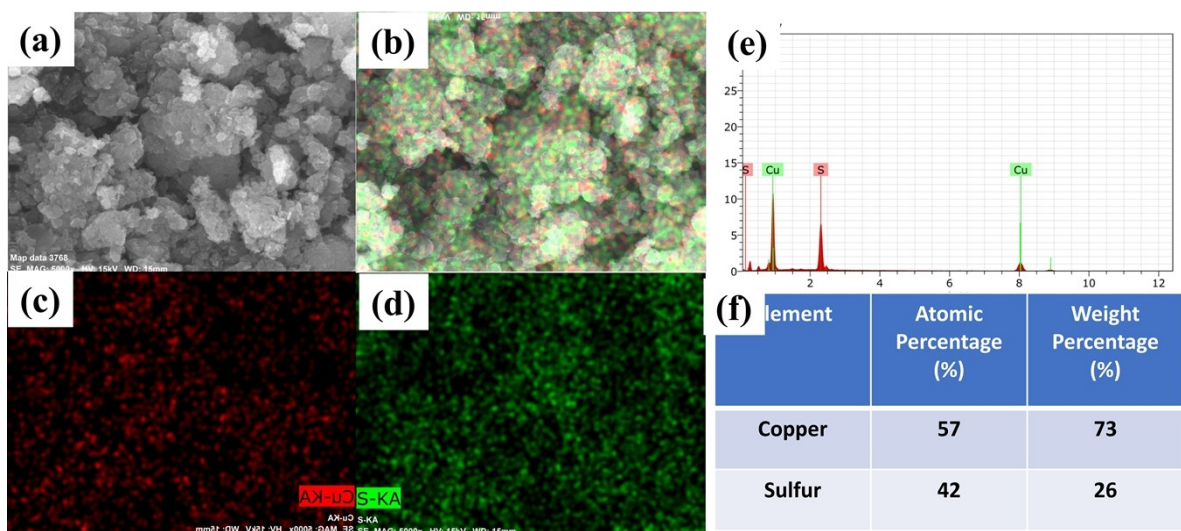
166

Fig. S6 BET profiles of (a) CuS, (b) CdS and (c) CdS@CuS catalyst.



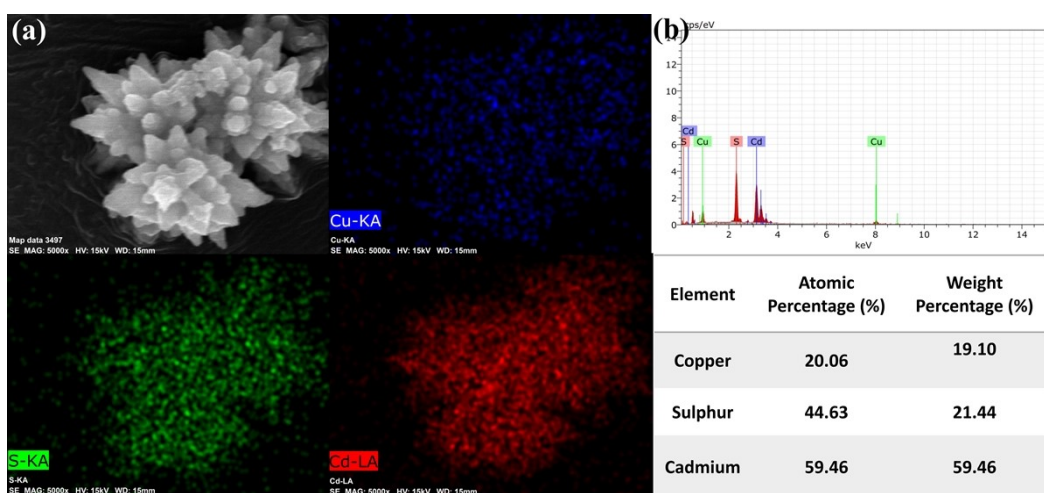
167
168

Fig. S7 (a-d) Elemental mapping and (e, f) EDS of CdS.



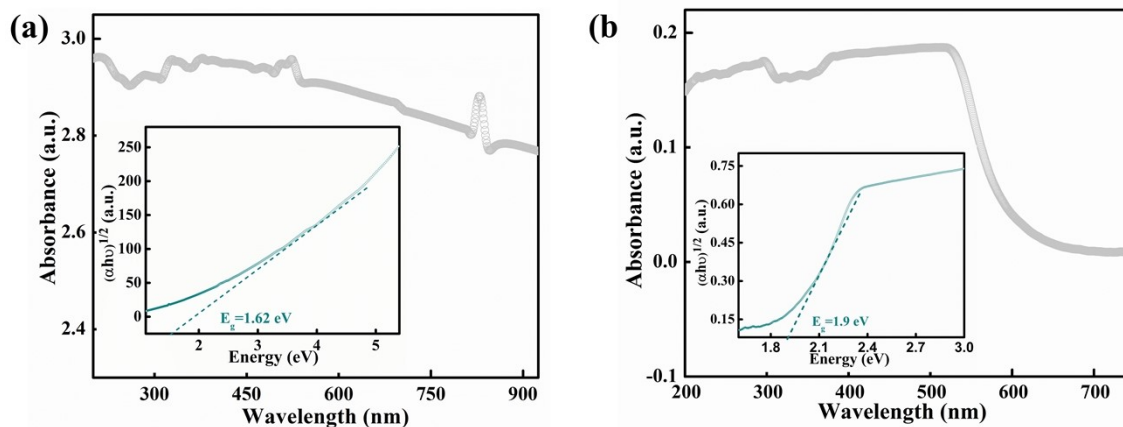
169
170

Fig. S8 (a-d) Elemental mapping and (e, f) EDS of CuS.



171
172

Fig. S9 (a) Elemental mapping and (b) EDS of CdS@CuS.



173

174

Fig. S10 UV-DRS spectrum and tauc plot (inset) of (a) CuS and (b) CdS.

175 7. References

176 1. J. Shen, Y. Zhang, D. Chen, X. Li, Z. Chen, S.A. Cao, T. Li and F. Xu, *J. Mater. Chem. A*,
 177 2019, **7**, 21410.

178 2. S. Zhang, H. Yang, H. Gao, R. Cao, J. Huang and X. Xu, *ACS Appl. Mater. Interfaces*,
 179 2017, **9**, 23635.

180 3. B. Zhang, F. Liu, C. Nie, Y. Hou and M. Tong, *J. Hazard. Mater.*, 2022, **435**, 128966.

181 4. F. L. G. de Menezes, R. H. de Lima Leite, F. K. G. dos Santos, A. I. Aria and E. M. M.
 182 Aroucha, *Colloids Surf. A: Physicochem. Eng. Asp.*, 2021, **630**, 127661.

183 5. S. Umasankari and R. Anitha, *Int. J. Adv. Technol. Eng. Sci.*, 2017, **5**, 184.

184 6. S. Kumar and J. K. Sharma, *Mater. Sci. Pol.*, 2016, **34**, 368.

185 7. B. Shen, S. Sun, L. Zhu, J. Yu and L. Jiang, *Food Packag. Shelf Life*, 2023, **37**, 101083.

186 8. N. Zhang, C. Gao, L. Meng and X. Tang, *Carbohydr. Polym.*, 2023, **319**, 121224.