

1 **Counterion Chemistry of 5-Halo (X: Cl, Br, I)-Uracil Derived Carbon**
2 **Nitride: Unlocking Enhanced Photocatalytic Performance**

3 Toshali Bhoyar, B. Moses Abraham, Akanksha Gupta, Dong Jin Kim, Nilesh R. Manwar,

4 Kedhareswara Sairam Pasupuleti, Devthade Vidyasagar,* Suresh S. Umare*

5

6

7 The Supporting information contains 22 Figures, 4 Tables, References.

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34 **Table of contents**

| | |
|--|------------|
| Section S1. Characterization details | S4 |
| Figure S1. Fourier transform infrared spectra of PCN and XUCN catalyst. | S5 |
| Figure S2. (A) Cross polarized magic angle spinning (CP-MAS) ^{13}C nuclear magnetic resonance (NMR) spectra of PCN and BUCN catalyst, (B) optimized structure of 5-bromouracil doped PCN catalyst highlighting the different carbon atoms in the structure, and (C) high resolution CP-MAS ^{13}C NMR spectra of PCN and BUCN. | S6 |
| Figure S3. (A) UV-vis DRS spectra, and (B) Tauc plot (with mid-gap states energy as the inset) of PCN and XUCN catalyst. | S7 |
| Figure S4. High resolution deconvoluted N1s X-ray photoelectron spectra for PCN and XUCN catalyst. | S8 |
| Figure S5. SEM image of PCN | S9 |
| Figure S6. TEM image of PCN | S10 |
| Figure S7. Energy dispersive X-ray (EDX) mapping for C, N, O, and Cl and EDX spectrum of CUCN. | S11 |
| Figure S8. Energy dispersive X-ray (EDX) mapping for C, N, O, and Br and EDX spectrum of BUCN. | S12 |
| Figure S9. Energy dispersive X-ray (EDX) mapping for C, N, O, and I and EDX spectrum of IUCN. | S13 |
| Figure S10. Electron spin resonance (ESR) spectra of PCN and XUCN catalysts. | S14 |
| Figure S11. Cyclic photocatalytic H_2O_2 generation over BUCN catalyst to check durability for five cycles. | S15 |
| Figure S12. (A) XRD, (B) FTIR, (C) UV-DRS spectra, and (D) KM plot of freshly prepared BUCN (Fresh) and recycled BUCN (Recycled) catalyst after fifth cycle of H_2O_2 generation. | S16 |
| Figure S13. Cr (VI) reduction rate constant calculated by pseudo first order kinetic fitting. | S17 |
| Figure S14. UV-Visible absorption spectra for Cr (VI) reaction mixture on light irradiation with time. | S18 |
| Figure S15. Photocatalytic activity evaluation of BUCN catalyst for increased Cr (VI) concentration up-to 50 mg L ⁻¹ . | S19 |

| | |
|---|-----|
| Figure S16. Photocatalytic Cr (VI) reduction performance evaluated by varying BUCN catalyst's dosage. | S20 |
| Figure S17. Effect of pH on Cr (VI) reduction activity by BUCN catalyst. | S21 |
| Figure S18. Rhodamine B rate constant values for PCN and XUCN catalysts calculated by pseudo first order kinetic fit model. | S22 |
| Figure S19. Density of states of calculated for PCN, BU, and BUCN. | S23 |
| Figure S20. The photocatalytic H ₂ O ₂ generation rates of BUCN under different reaction gases or different sacrificial agents. | S24 |
| Figure S21. Percentage Photocatalytic RhB degradation by BUCN catalyst in presence of scavenging agents. | S25 |
| Figure S22. Electron spin resonance spectra of (a) DMPO-·OH adduct and (b) DMPO-·O ₂ ⁻ adduct in DMSO of PCN and XUCN catalysts. | S26 |
| Table S1. Elemental analysis of PCN and XUCN catalysts. | S27 |
| Table S2. Summary of BET surface area and BJH pore radius and pore volume of the PCN and XUCN catalysts. | S28 |
| Table S3. Summary of the photoluminescence decay time of the PCN and XUCN catalyst. | S29 |
| Table S4. Summary of the photoluminescence decay time of the PCN and XUCN catalyst. | S30 |
| References | S32 |

35

36

37

38

39

40

41

42

43

44 **Section S1. Characterization details**

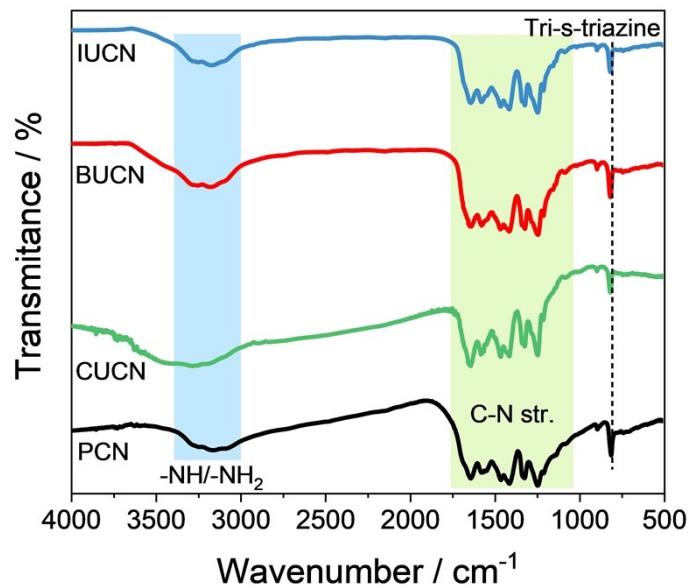
45 Powder X-ray diffraction (XRD) pattern of the as-prepared catalysts was recorded using Bruker
46 D8 Advance diffractometer operated at voltage = 40 kV and current = 25 mA with
47 monochromatic Cu K α radiation ($\lambda=0.15418$ nm). Fourier transform infrared (FT-IR) analysis
48 of was recorded using a Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific, MA, USA)
49 in the range 4000-400 cm $^{-1}$. The optical absorption property of the catalysts was analysed by
50 ultraviolet diffuse reflectance spectrophotometer (UV-DRS, UV-2600, Shimadzu, Japan). For
51 the elemental analysis, X-ray photoelectron spectroscopy (XPS), Thermo Scientific Nexa
52 spectrometer, UHV was used. The Brunner Emmette Teller (BET) surface area analysis was
53 done using nova touch surface area analyser NT1-1 (Quantachrome, FL, USA). Magellan 400L
54 FEI High-resolution scanning electron microscope (HR-SEM, Hillsboro, Oregon) was used to
55 analyse the surface topography and obtain elemental mapping. The TEM and HRTEM images
56 were recorded using JEM 2100 transmission electron microscope (TEM) and High-resolution
57 transmission electron microscope (HR-TEM) equipped with a Gatan USC 4000 4x4k camera,
58 at an accelerating voltage of 200 kV. Steady-state photoluminescence (PL) emission spectra
59 were recorded on a spectrofluorometer FL-1039/40 (Horiba Jobin Yvon, NJ, USA) at an
60 excitation wavelength of 320 nm. The time-resolved photoluminescence (TRPL) measurement
61 was done on the Fluorocube-Life Time system JOBINYON M/S (NJ, USA). The X-band
62 electron paramagnetic resonance (EPR) was recorded on the EPR spectrophotometer Bruker
63 ELEXSYR500CW (MA, USA). The absorbance of the liquid samples was measured by an
64 ultraviolet-visible (UV-Vis) spectrophotometer (UV-1800, Shimadzu, Japan).

65

66

67

68



69

70 **Figure S1.** Fourier transform infrared spectra of PCN and XUCN catalyst.

71

72

73

74

75

76

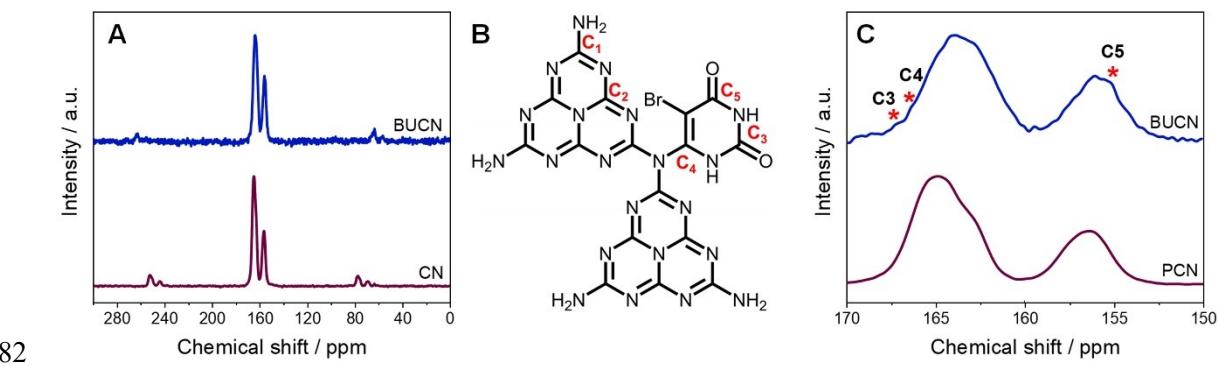
77

78

79

80

81



83 **Figure S2.** (A) Cross polarized magic angle spinning (CP-MAS) ^{13}C nuclear magnetic
 84 resonance (NMR) spectra of PCN and BUCN catalyst, (B) optimized structure of 5-
 85 bromouracil doped PCN catalyst highlighting the different carbon atoms in the structure, and
 86 (C) high resolution CP-MAS ^{13}C NMR spectra of PCN and BUCN.

87

88

89

90

91

92

93

94

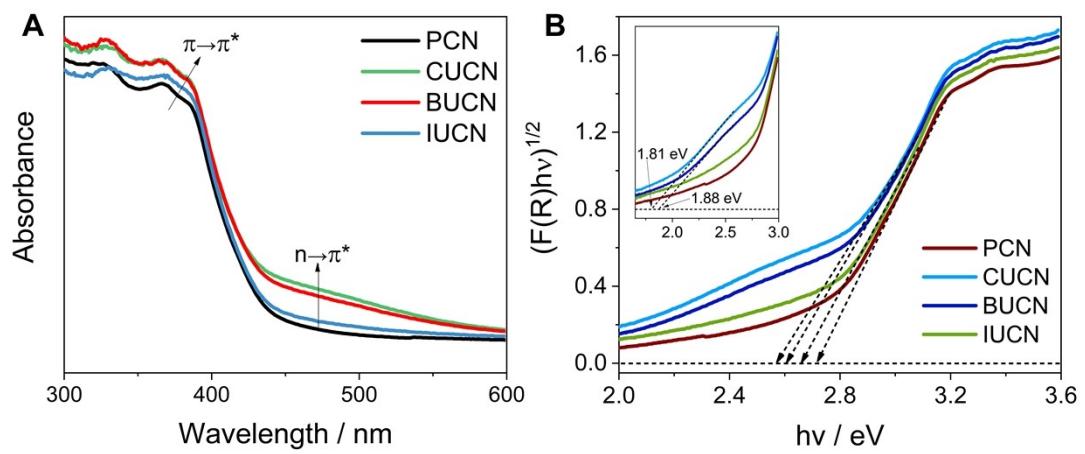
95

96

97

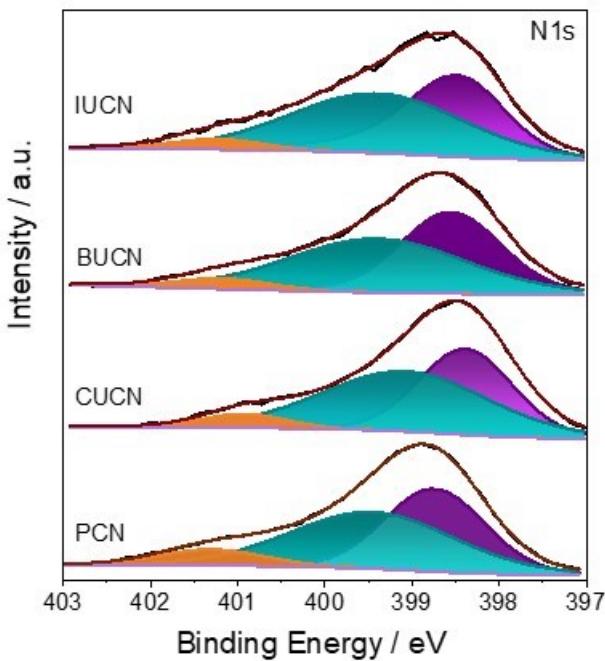
98

99



100
101 **Figure S3.** (a) UV-vis DRS spectra, and (b) Tauc plot (with mid-gap states energy as the inset)
102 of PCN and XUCN catalyst.

103
104
105
106
107
108
109
110



111

112 **Figure S4.** High resolution deconvoluted N1s X-ray photoelectron spectra for PCN and XUCN
113 catalyst.

114

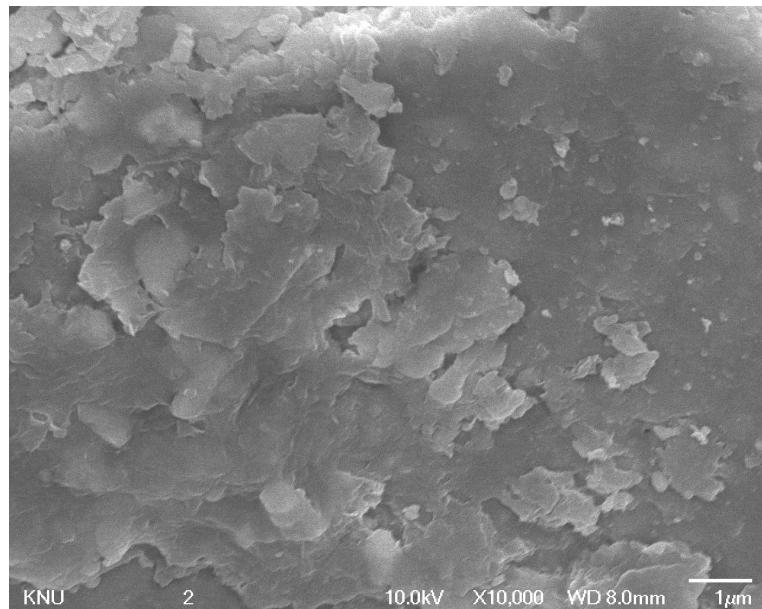
115

116

117

118

119



KNU

2

10.0kV X10,000 WD 8.0mm

1μm

120 **Figure S5.** SEM image of PCN

121

122

123

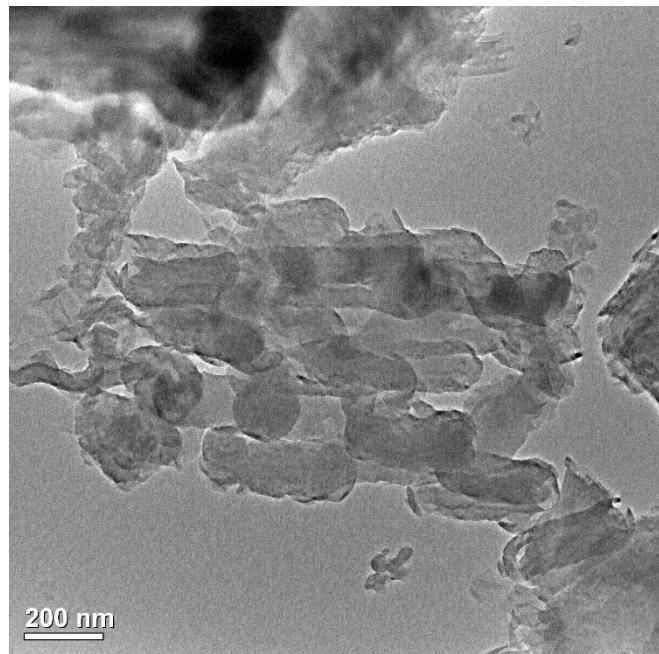
124

125

126

127

128



129 **Figure S6.** TEM image of PCN

130

131

132

133

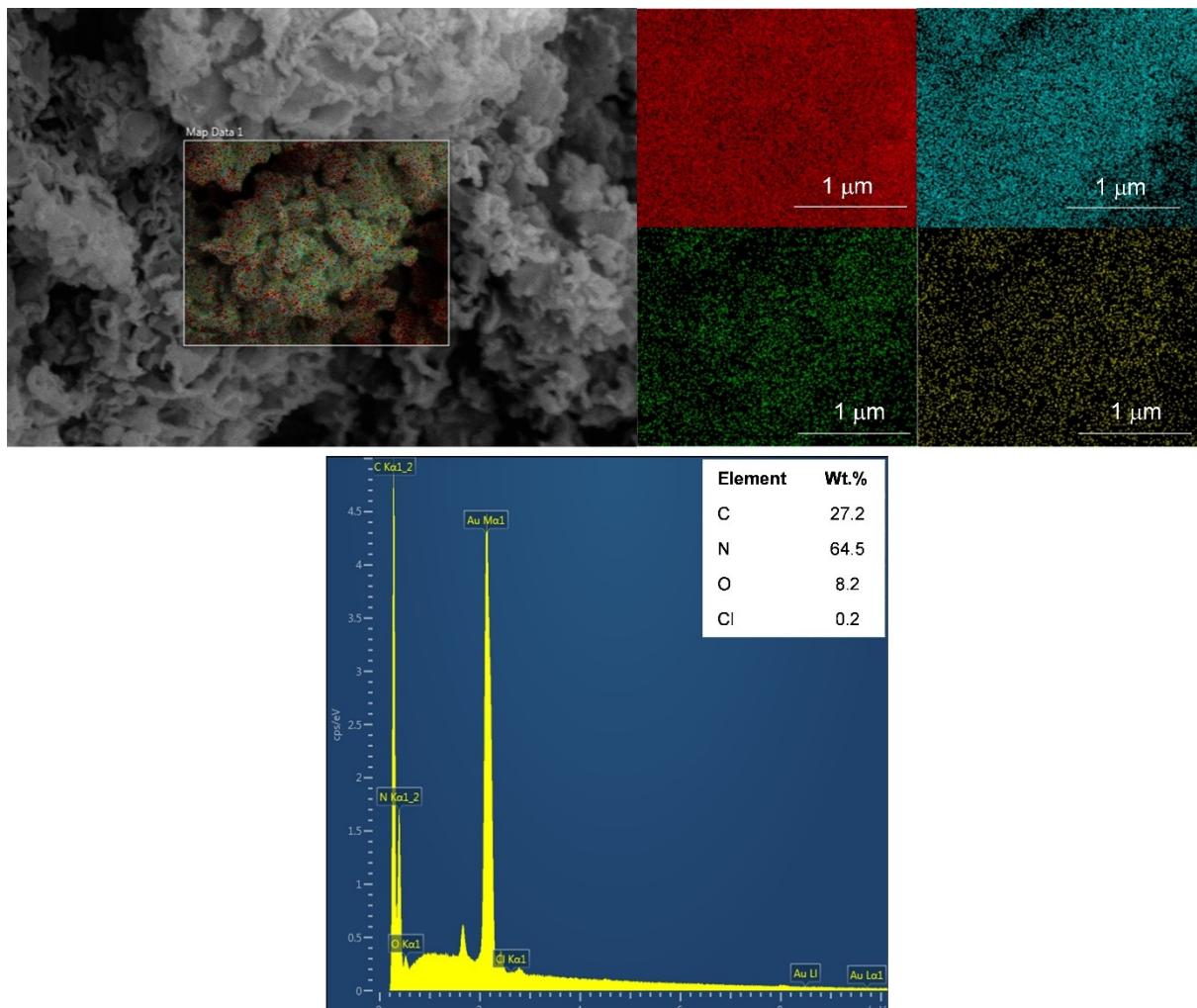
134

135

136

137

138



139

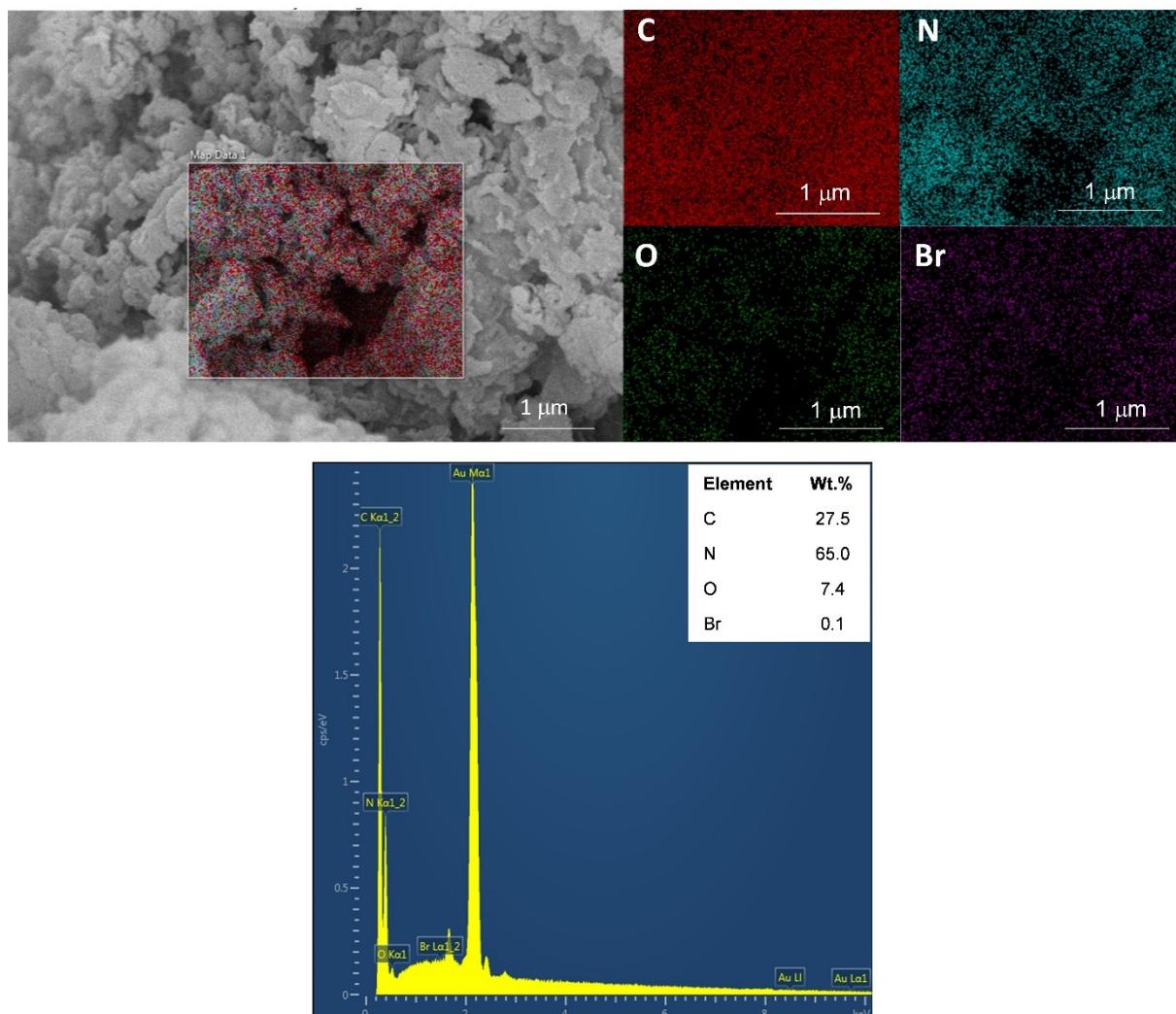
140 **Figure S7.** Energy dispersive X-ray (EDX) mapping for C, N, O, and Cl, and EDX spectrum
 141 of CUCN.

142

143

144

145



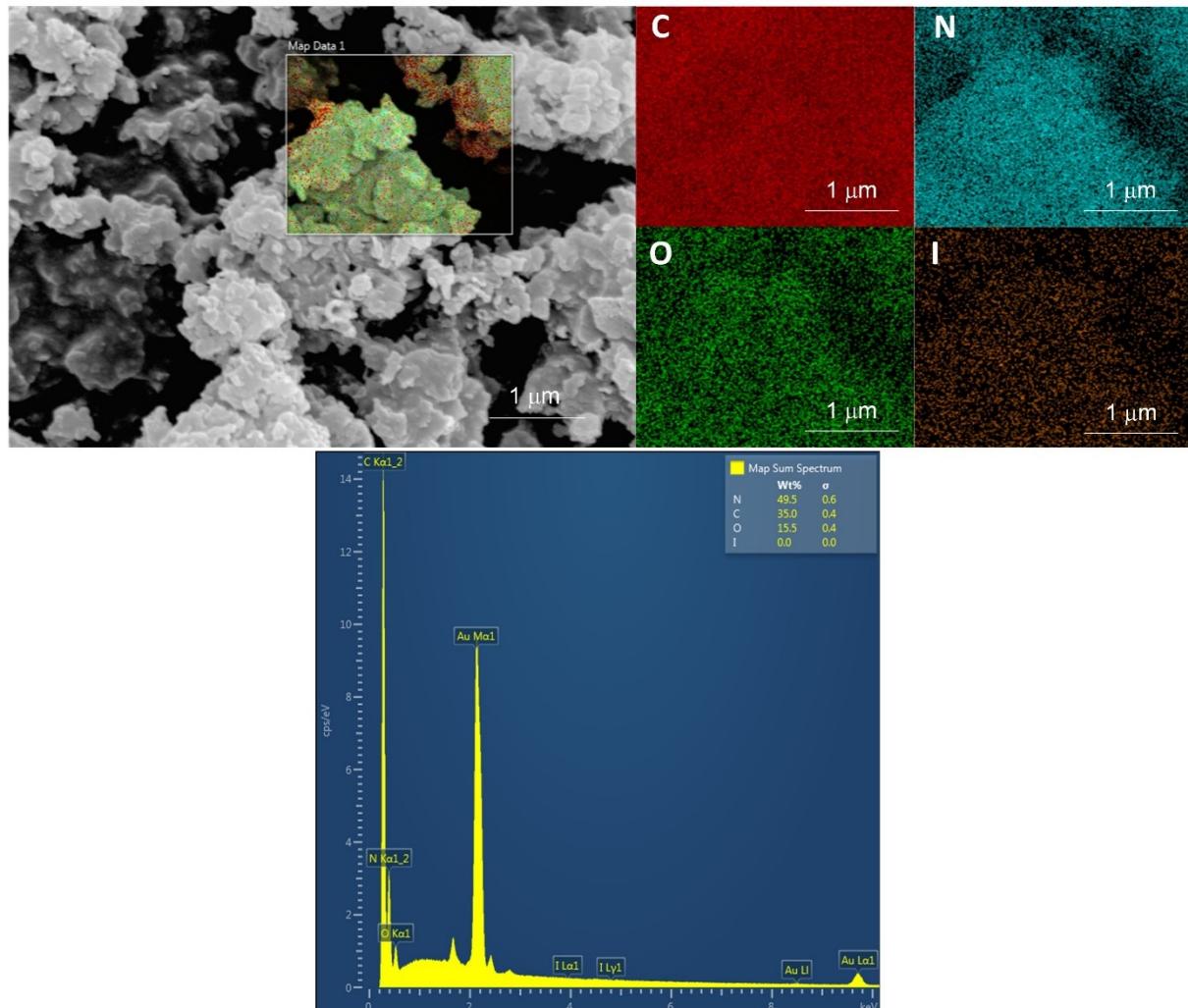
146

147 **Figure S8.** Energy dispersive X-ray (EDX) mapping for C, N, O, and Br and EDX spectrum
148 of BUCN.

149

150

151



152

153 **Figure S9.** Energy dispersive X-ray (EDX) mapping for C, N, O, and I and EDX spectrum of
 154 IUCN.

155

156

157

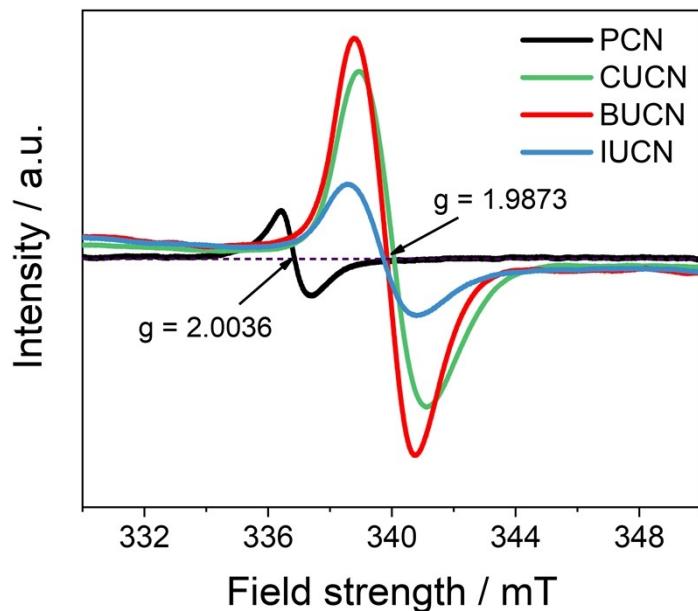
158

159

160

161

162



163

164 **Figure S10.** Electron spin resonance (ESR) spectra of PCN and XUCN catalysts.

165

166

167

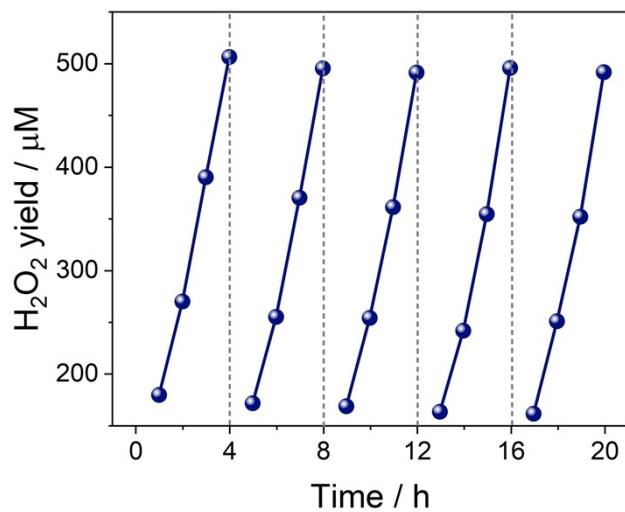
168

169

170

171

172



173

174 **Figure S11.** Cyclic photocatalytic H₂O₂ generation over BUCN catalyst to check durability for
175 five cycles.

176

177

178

179

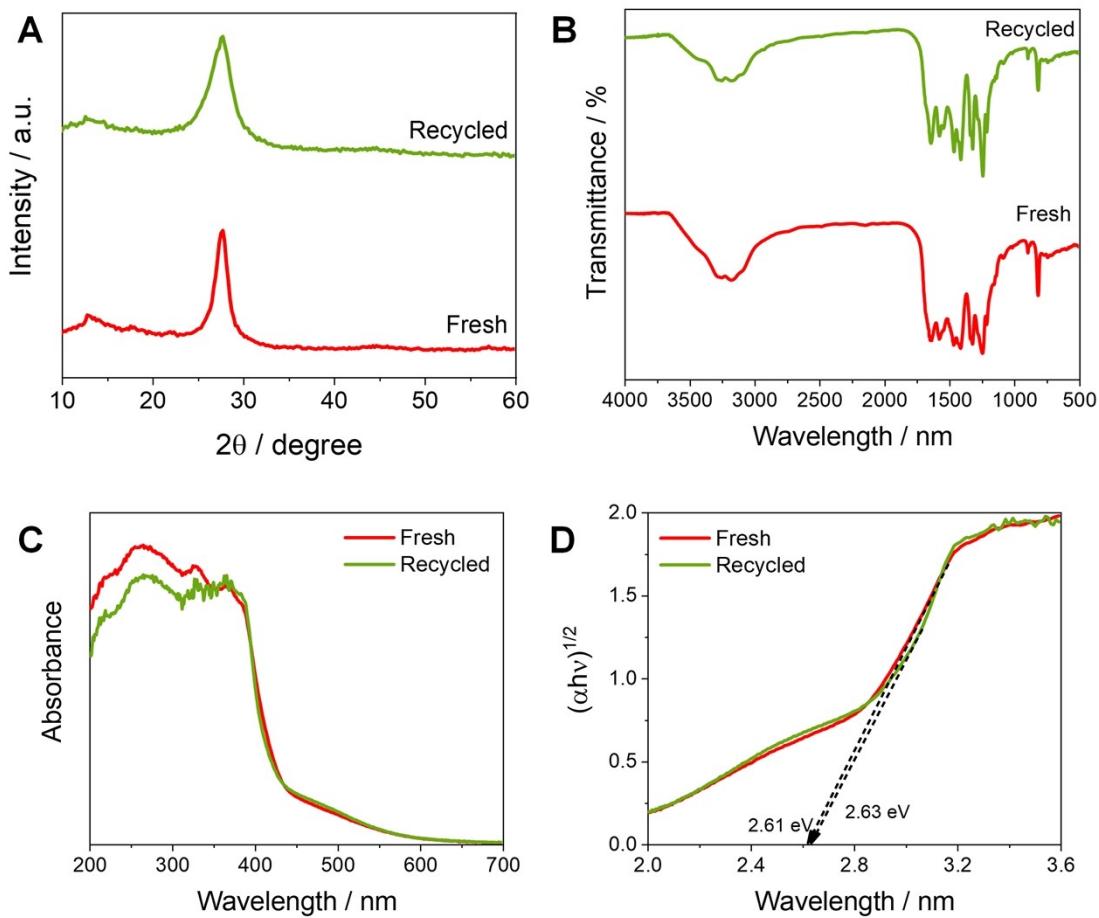
180

181

182

183

184



185

186 **Figure S12.** (A) XRD, (B) FTIR, (C) UV-DRS spectra, and (D) KM plot of freshly prepared
187 BUCN (Fresh) and recycled BUCN (Recycled) catalyst after fifth cycle of H₂O₂ generation.

188

189

190

191

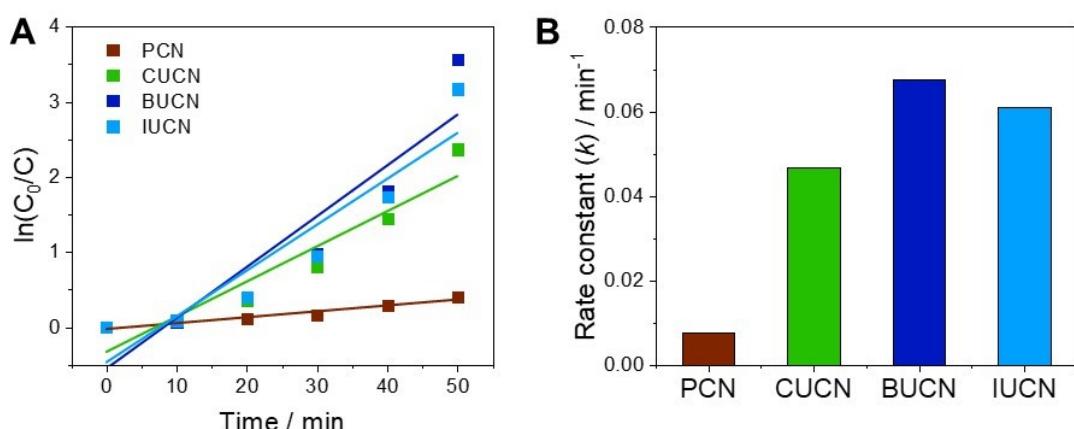
192

193

194

195

196



197
198 **Figure S13.** Cr (VI) reduction rate constant calculated by pseudo first order kinetic fitting.

199

200

201

202

203

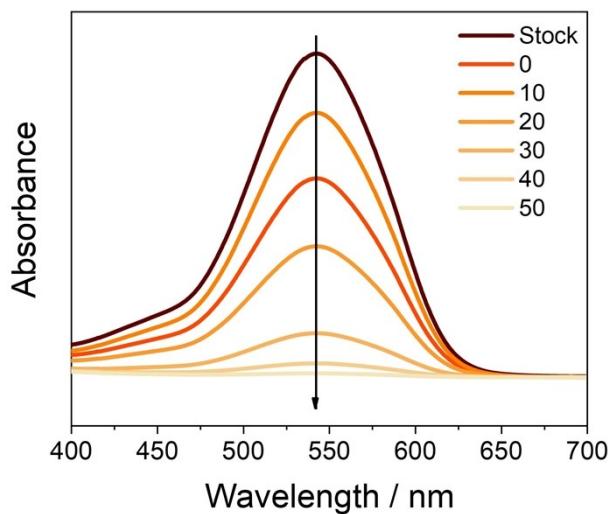
204

205

206

207

208



209

210 **Figure S14.** UV-Visible absorption spectra for Cr (VI) reaction mixture on light irradiation
211 with time.

212

213

214

215

216

217

218

219

220

221

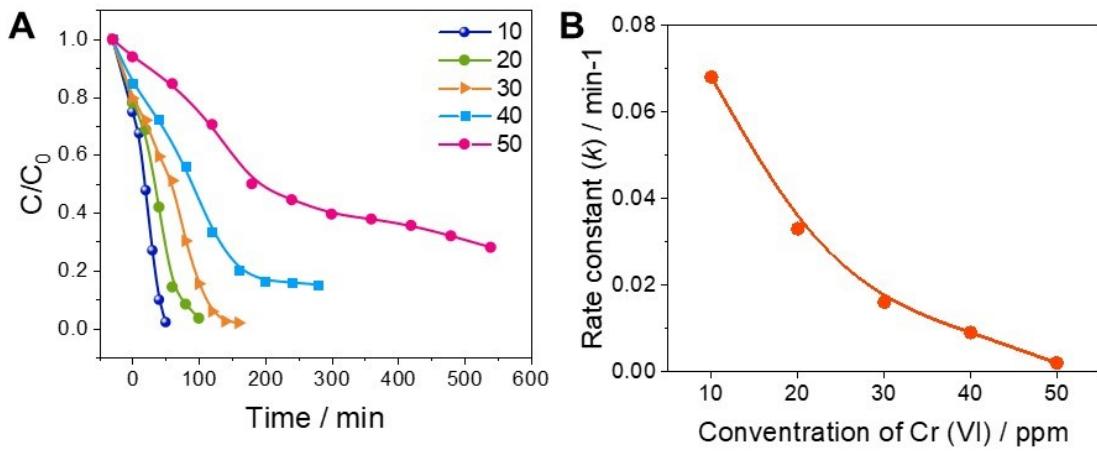
222

223

224

225

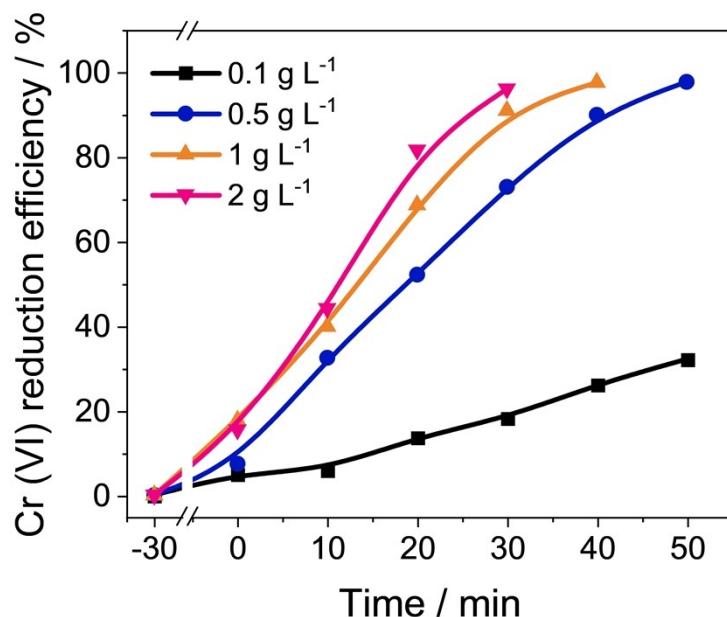
226



227
228

229 **Figure S15.** Photocatalytic activity evaluation of BUCN catalyst for increased Cr (VI)
230 concentration up-to 50 mg L⁻¹.

231
232
233
234
235
236
237



238

239 **Figure S16.** Photocatalytic Cr (VI) reduction performance evaluated by varying BUCN
240 catalyst's dosage.

241

242

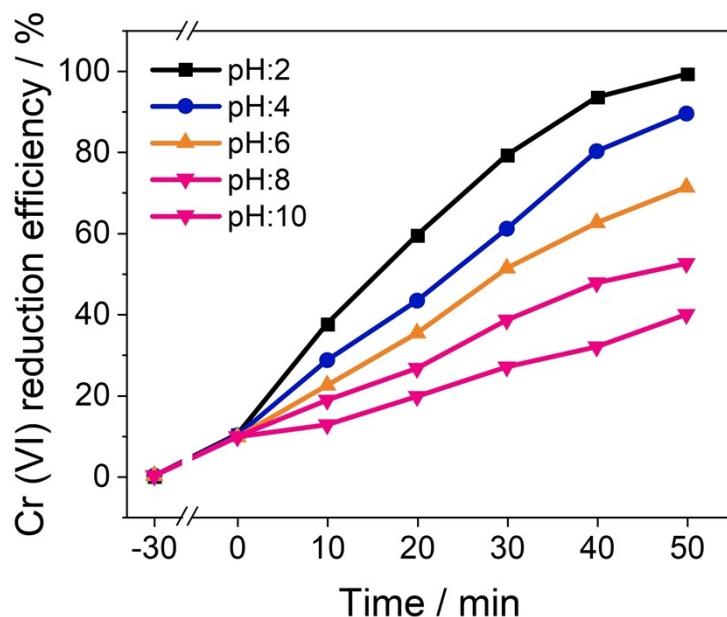
243

244

245

246

247



248

249 **Figure S17.** Effect of pH on Cr (VI) reduction activity by BUCN catalyst.

250

251

252

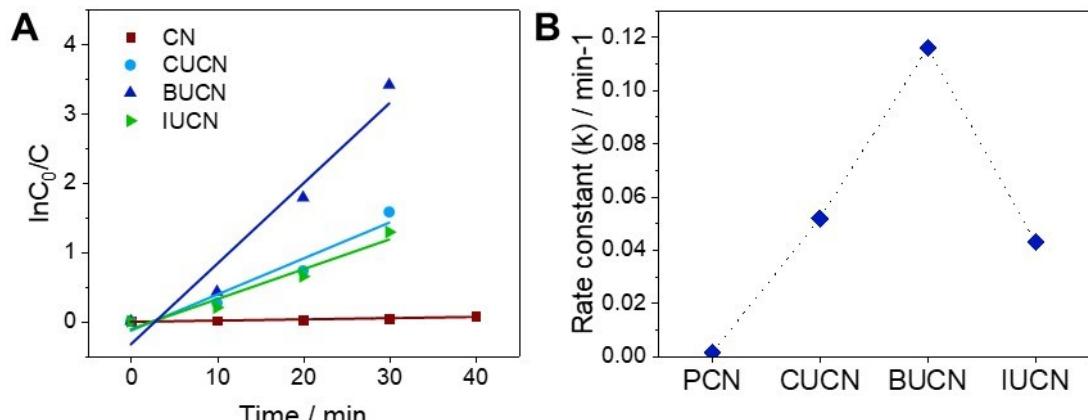
253

254

255

256

257



258

259 **Figure S18.** Rhodamine B rate constant values for PCN and XUCN catalysts calculated by
260 pseudo first order kinetic fit model.

261

262

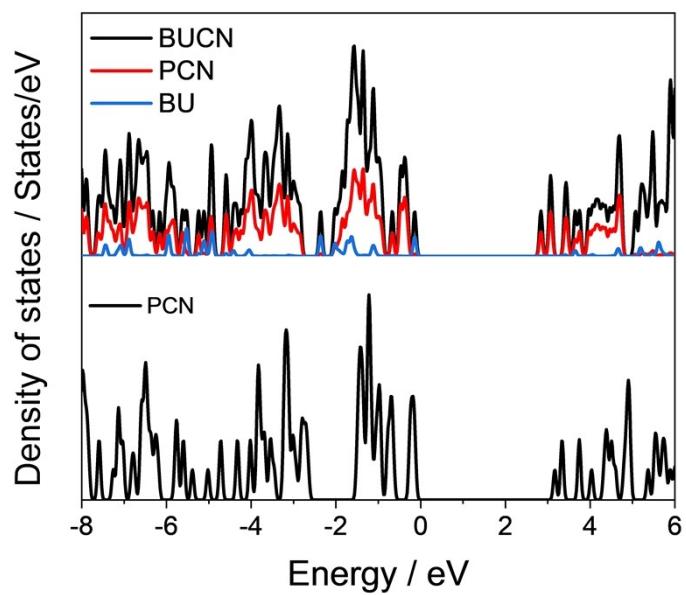
263

264

265

266

267



268

269 **Figure S19.** Density of states of calculated for PCN, BU, and BUCN.

270

271

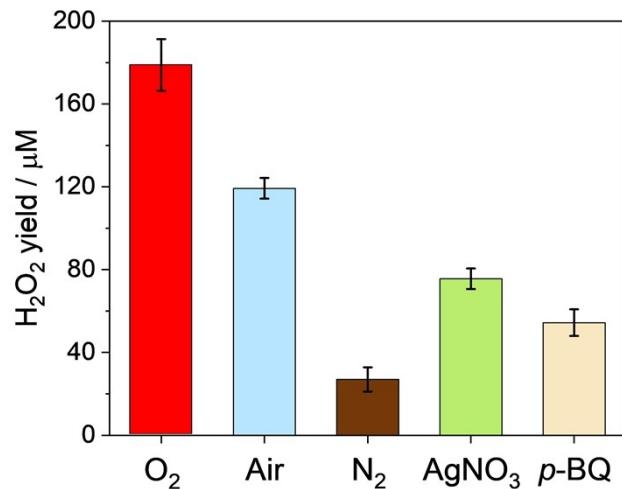
272

273

274

275

276



277

278 **Figure S20.** The photocatalytic H_2O_2 generation rates of BUCN under different reaction gases
279 or different sacrificial agents.

280

281

282

283

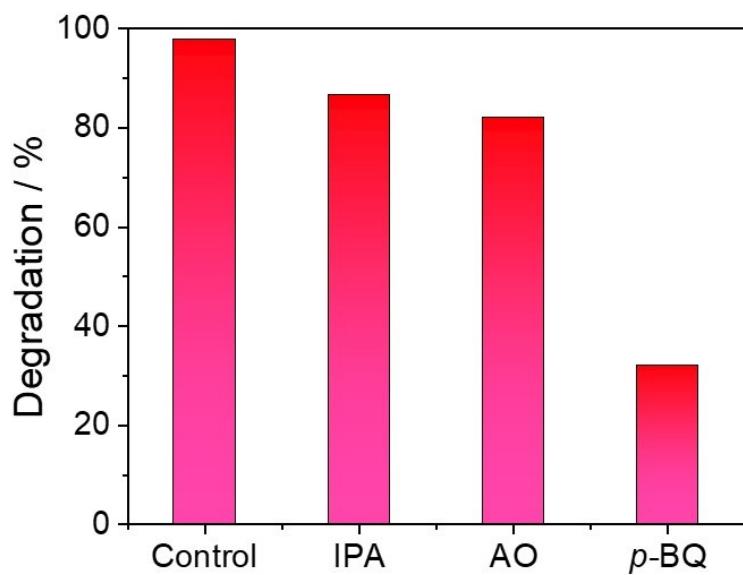
284

285

286

287

288



289

290 **Figure S21.** Percentage Photocatalytic RhB degradation by BUCN catalyst in presence of
291 scavenging agents.

292

293

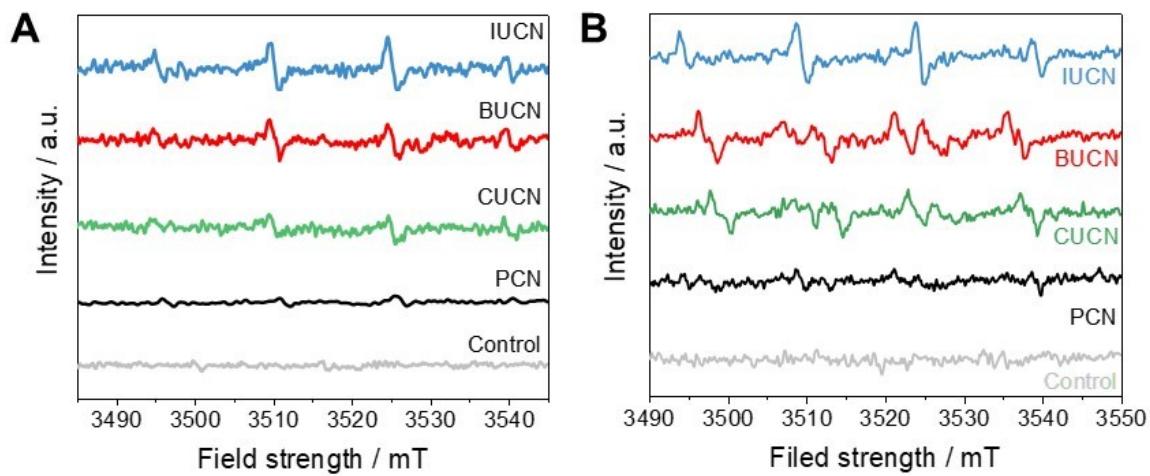
294

295

296

297

298



299

300 **Figure S22.** Electron spin resonance spectra of (a) DMPO-·OH adduct and (b) DMPO-·O₂
301 adduct in DMSO of PCN and XUCN catalysts.

302

303

304

305

306

307

308

309

310

311

312

313

314

315

316

317

318 **Table S1.** Elemental analysis of PCN and XUCN catalysts.

| Sample | Elements (mol%) | | | C/N ratio |
|--------|-----------------|--------------|--------------|-----------|
| | Carbon (%) | Nitrogen (%) | Hydrogen (%) | |
| PCN | 33.35 | 54.82 | 1.91 | 0.61 |
| CUCN | 33.82 | 54.95 | 1.86 | 0.62 |
| BUCN | 32.98 | 54.07 | 2.02 | 0.61 |
| IUCN | 32.57 | 53.41 | 2.18 | 0.61 |

319

320

321

322

323

324

325

326

327

328

329

330

331

332

333

334

335

336 **Table S2.** Summary of BET surface area and BJH pore radius and pore volume of the PCN
337 and XUCN catalysts.

| Sample | S _{BET} (m ² g ⁻¹) | D _r (nm) | D _v (cm ³ g ⁻¹) |
|--------|---|------------------------|--|
| PCN | 10.6 | 1.23 | 0.0133 |
| CUCN | 83.3 | 1.63 | 0.1547 |
| BUCN | 37.8 | 1.64 | 0.0839 |
| IUCN | 28.6 | 1.62 | 0.0609 |

338 S_{BET}: Specific surface area

339 D_r: Pore radius

340 D_v: Pore volume

341

342

343

344

345

346

347

348

349

350

351

352

353 **Table S3.** Summary of the photoluminescence decay time of the PCN and XUCN catalyst.

| Sample | Lifetime / ns | | | Intensity | | | Average Lifetime / ns |
|--------|---------------|----------|----------|-----------|----------|--------|-----------------------|
| | τ_1 | τ_2 | τ_3 | A_1 | A_2 | A_3 | |
| PCN | 3.46 | 0.83 | 15.32 | 2816.37 | 13060.70 | 243.63 | 1.5 |
| CUCN | 0.63 | 2.94 | 11.02 | 8954.94 | 3329.61 | 486.21 | 1.6 |
| BUCN | 1.01 | 3.89 | 16.75 | 10109.50 | 2792.01 | 268.58 | 1.9 |
| IUCN | 1.20 | 4.21 | 16.41 | 7336.87 | 4163.04 | 681.16 | 3.1 |

354

355

356

357

358

359

360

361

362

363

364

365

366

367

368

369

370

371

373 **Table S4.** Comparison of H₂O₂ yield by reported catalysts and present work.

| Sr. No. | Catalyst | Yield ($\mu\text{mol h}^{-1}$) | Light source | Sacrificial agent | Catalyst dose | Ref. |
|---------|---|----------------------------------|--|-------------------|--|--------------|
| 1 | PI assembled nanosheeted g-C ₃ N ₄ (PI _x -NCN) | 60 | 300 W Xe lamp | - | 50 mg in 50 mL | ¹ |
| 2 | CoP-decorated g-C ₃ N ₄ | 70 | 300 W Xe lamp | Ethanol | 20 mg in 20 mL | ² |
| 3 | Biphenyl diimide (BDI) doped g-C ₃ N ₄ | 9.6 | $\lambda > 420$ nm | - | 50 mg in 30 mL | ³ |
| 4 | CN _{QDs} @MA-Ag nanocomposites | 39.82 | 300 W Xenon lamp with a 420 nm cutoff filter | IPA | 1mg/ml | ⁴ |
| 5 | P doped g-C ₃ N ₄ | 90 | | IPA | 0.5 mg/mL | ⁵ |
| 6 | Red phosphorous decorated g-C ₃ N ₄ RP/GCN | 125 | 500 W Xe lamp | None | 100 mg in 100 mL water | ⁶ |
| 7 | Au NPs supported graphitic carbon nitride (Au/g-C ₃ N ₄) | 100 | 300 W Xe lamp | Ethanol | 400 mg in 100 mL alcohol/water mixture | ⁷ |
| 8 | polyoxometalates- | 9.7 | 300 W | - | 100 mg | ⁸ |

| | | | | | | |
|----|---|---------------|----------------------|------------|-----------------------|------------------|
| | derived metal oxides incorporated into graphitic carbon nitride (g-C ₃ N ₄ -CoWO) | | Xe lamp | | in 100 mL water | |
| 9 | Ti ₃ C ₂ nanosheets and porous g-C ₃ N ₄ | 2.2 | 300 W Xe lamp | IPA | 50 mg in 50 mL | ⁹ |
| 10 | Boron nitride quantum dots decorated ultrathin porous g-C ₃ N ₄ (BNQDs/UPCN) | 72.3 | 50 mg 50 mL | IPA | 50 mg in 50 mL | ¹⁰ |
| 11 | B-C ₃ N ₄ @Bi ₂ S ₃ | 42.05 | 300 W Xenon lamp | None | 50 mg in 50 mL | ¹¹ |
| 12 | polydopamine (PDA) surface-modified g-C ₃ N ₄ composites (CNPX) | 23 | 300 W Xenon lamp | None | 30 mg in 30 mL | ¹² |
| 13 | 5-Bromo uracil doped carbon nitride (BUCN) | 126.55 | 50 W LED lamp | IPA | 50 mg in 50 mL | This work |

374

375

376

377

378

379

380

381

382

383 **References**

- 384 1. L. Yang, G. Dong, D. L. Jacobs, Y. Wang, L. Zang and C. Wang, *Journal of Catalysis*,
385 2017, **352**, 274-281.
- 386 2. Y. Peng, L. Wang, Y. Liu, H. Chen, J. Lei and J. Zhang, *European Journal of Inorganic
387 Chemistry*, 2017, **2017**, 4797-4802.
- 388 3. Y. Kofuji, S. Ohkita, Y. Shiraishi, H. Sakamoto, S. Tanaka, S. Ichikawa and T. Hirai,
389 *ACS Catalysis*, 2016, **6**, 7021-7029.
- 390 4. M. Yin, X. Chen, Y. Wan, W. Zhang, L. Feng, L. Zhang and H. Wang, *ChemCatChem*,
391 2020, **12**, 1512-1518.
- 392 5. X. Dang, R. Yang, Z. Wang, S. Wu and H. Zhao, *Journal of Materials Chemistry A*,
393 2020, **8**, 22720-22727.
- 394 6. J. Zhang, J. Lang, Y. Wei, Q. Zheng, L. Liu, Y.-H. Hu, B. Zhou, C. Yuan and M. Long,
395 *Applied Catalysis B: Environmental*, 2021, **298**, 120522.
- 396 7. G. Zuo, S. Liu, L. Wang, H. Song, P. Zong, W. Hou, B. Li, Z. Guo, X. Meng, Y. Du, T.
397 Wang and V. A. L. Roy, *Catalysis Communications*, 2019, **123**, 69-72.
- 398 8. S. Zhao and X. Zhao, *Applied Catalysis B: Environmental*, 2019, **250**, 408-418.
- 399 9. Y. Yang, Z. Zeng, G. Zeng, D. Huang, R. Xiao, C. Zhang, C. Zhou, W. Xiong, W.
400 Wang, M. Cheng, W. Xue, H. Guo, X. Tang and D. He, *Applied Catalysis B: Environmental*, 2019,
401 **258**, 117956.
- 402 10. Y. Yang, C. Zhang, D. Huang, G. Zeng, J. Huang, C. Lai, C. Zhou, W. Wang, H. Guo,
403 W. Xue, R. Deng, M. Cheng and W. Xiong, *Applied Catalysis B: Environmental*, 2019,
404 **245**, 87-99.
- 405 11. S. M. Ghoreishian, K. S. Ranjith, M. Ghasemi, B. Park, S.-K. Hwang, N. Irannejad, M.
406 Norouzi, S. Y. Park, R. Behjatmanesh-Ardakani, S. M. Pourmortazavi, S. Mirsadeghi,
407 Y.-K. Han and Y. S. Huh, *Chemical Engineering Journal*, 2023, **452**, 139435.
- 408 12. Z. Gong, L. Chen, K. Chen, S. Gou, X. Zhao, L. Song, J. Ma and L. Han, *Journal of
409 Environmental Chemical Engineering*, 2023, **11**, 109405.

410