Supplementary Information

Defect enriched CuO/CeO₂ nanostructure: In-depth structural characterization and photocatalytic performance

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Fig. S1 Variation in intensity, broadening and shifting of UV-vis absorption band of CeO_2 and CuO/CeO_2 .

The UV-vis DRS spectrum of CeO_2 and CuO/CeO_2 nanoparticles has been shown in Fig. S2. The mentioned spectra of calculated band gap by Kubelka-Munk (K-M) function for the CeO_2 and is reported to absorb in the UV-region with a bandgap of 3.3 eV. But CuO/CeO_2 has shown the shift towards lower wavelength with a band gap of 3.2eV as shown in the Fig. S2.



Fig. S2 UV-vis diffuse reflectance (UV-vis DRS) spectra of CeO₂ and CuO/CeO₂.



Fig.S3 FTIR spectrum of CuO/CeO₂nanocomposite.



Fig.S4 (a)Variation in intensity, broadening and shifting of peak in XRD pattern for CeO_2 and CuO/CeO_2 , and (b) XRD pattern for CuO nanoparticles.

The Raman peak in CuO/CeO_2 suffers a shift indicating interaction between CuO and CeO_2 . This result agrees with previous reports¹.



Fig. S5 (a) Variation in intensity, broadening and shifting of Raman peaks of CeO_2 and CuO/CeO_2 , and (b) calculated I_D/I_{F2g} values for CeO_2 and CuO/CeO_2 .

The integral area of peak corresponding to Ce^{3+} divided by the summation of areas of all peaks corresponding to Ce 3d i.e. Ce^{3+} and $Ce^{4+2,3}$. It is calculated that 31.2% of Ce^{3+} for CuO/CeO₂ and that of CeO₂ is 24.2% suggesting an increase in oxygen vacancies in CeO₂ due to the addition of CuO.

$$[Ce^{+3}] = \frac{Ce^{+3} Area}{Total Area} \times 100$$

Binding energy (eV)	CeO ₂ (Area)	Binding energy (eV)	CuO/CeO ₂ (Area)
880.9	14774.5	882.3	15132.1
883.8	6523.7	885.2	5863.4
886.8	10243.3	888.1	11216.8
896.9	10801.4	898.3	10849.4
899.8	8132.8	900.8	7614.1
901.9	2496.7	903.3	2087.4
904.6	11507.0	905.7	13214.4
915.2	6683.6	916.6	6855.6
Ce ³⁺	(14774.5+2496.7)	Ce ³⁺	(15132.1+7614.1)
	= 17271.2		= 22746.3
Total Area of Ce 3d	71163.3		72833.5
% of Ce^{3+} =Area of Ce^{3+} Total	17271.2/71163.3		22746.3/72833.5
Area	=24.2 %		=31.2 %

Table S1 The relative integral area (%) of Ce^{3+} were calculated for CeO_2 and CuO/CeO_2



Fig. S6 High-resolution XPS spectra of Ce 3d for CeO₂

Table S2 The relative integral are	of O 1s peak calculated	from the XPS spectra.
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CuO/CeO ₂			CeO ₂		
Peaks assignment	Binding Energy (eV)	Area (A)	Binding Energy (eV)	Area (A)	
O _L	528.4	2219.2	532.4	7907.02	
O _V	530.1	3507.0	534.6	4783.60	
O _C	532.7	1107.8			
O _V /O _L		1.58029921		0.6049814	



Fig. S7 O 1s XPS spectra of (a) CuO/CeO₂ and (b) CeO₂

Thermal stability evaluation

Thermogravimetric analysis (TGA)was performed for both the CuO/CeO₂ nanocomposite and pristine CeO₂at a temperature rangebetween 50 and 600 °C at a heating rate of 10 °C/min. The obtained results are shown in the thermogram (Fig.S8 ESI). The weight loss at temperature 50 to 270 °C corresponds to loss of water molecules physiosorbed on the surface of CuO/CeO₂. The CuO/CeO₂ showing stability up to 600 °C without any decomposition indicates the formation of composites. Compared to the pristine CeO₂ sample the CuO/CeO₂ exhibiting less weight loss and no additional decomposition for Cu, confirming the formation of the composite.



Fig. S8 TGA analysis of CeO₂ and CuO/CeO₂ nanocomposite.



Fig. S9 UV-vis spectra showing degradation of IPU under UV light irradiation and under dark condition (in absence of UV light irradiation).

Scavengers test



Fig. S10 UV-vis spectra showing the photodegradation of IPU by CuO/CeO_2 nanocomposite under UV light irradiation with scavengers; (a) p-benzoquinone (b) AgNO₃, (c) EDTA and (d) Tertiary butyl alcohol.

Adsorption Kinetics Study

Pseudo first-Order Kinetics

 $\ln(q_e - q_t) = \ln q_e k_1 \cdot t \dots \cdot Eq.1$

Where q_t is amount of adsorbate adsorbed at time t, q_e equilibrium adsorption capacity k_1 is first-order rate constant (min⁻¹) and t is time

Pseudo second-Order Kinetics

 $t/q_t = 1/k_2 q_e^2 + 1/(q_e).t$ Eq.2

Where qt is adsorption capacity at time t, q_e equilibrium adsorption capacity k_2 is pseudo-second-order rate constant (min⁻¹) and t is time⁴.



Fig. S11 (a) pseudo-first-order (PFO) and (b) pseudo-second-order kinetics models for CeO_2 and CuO/CeO_2 .



Fig. S12 Possible degradation pathways with intermediates detected by HRMS.







Fig. S13 HRMS fragmentation pattern (a) aqueous solution of pure IPU and (b-g) degradation products of IPU by CuO/CeO₂ nanocomposite.

^{1.} Jiang D, Wang W, Gao E, Sun S, Zhang L. Highly selective defect-mediated photochemical CO₂ conversion over fluorite ceria under ambient conditions. Chemical Communications. 2014;50(16):2005-7. <u>https://doi.org/10.1039/C3CC47806H</u>

^{2.} Akdogan C, GÖKÇAL B, Polat M, HAMALOĞLU K, Kip C, Tuncel A. Porous, oxygen vacancy enhanced CeO_{2-x} microspheres with efficient enzyme-mimetic and photothermal properties. ACS Sustainable Chemistry & Engineering. 2022;10. https://doi.org/10.1021/acssuschemeng.2c01981

^{3.} Liyanage AD, Perera SD, Tan K, Chabal Y, Balkus Jr KJ. Synthesis, characterization, and photocatalytic activity of Y-doped CeO₂ nanorods. Acs Catalysis. 2014 Feb 7;4(2):577-84. https://doi.org/10.1021/cs400889y

4. Wu FC, Tseng RL, Juang RS. Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics. Chemical engineering journal. 2009 Nov 1;153(1-3):1-8. https://doi.org/10.1016/j.cej.2009.04.042