

Boosted oxygen vacancy in ZnO-Co₃O₄ composite by copper doping for Bisphenol A abatement by persulfate

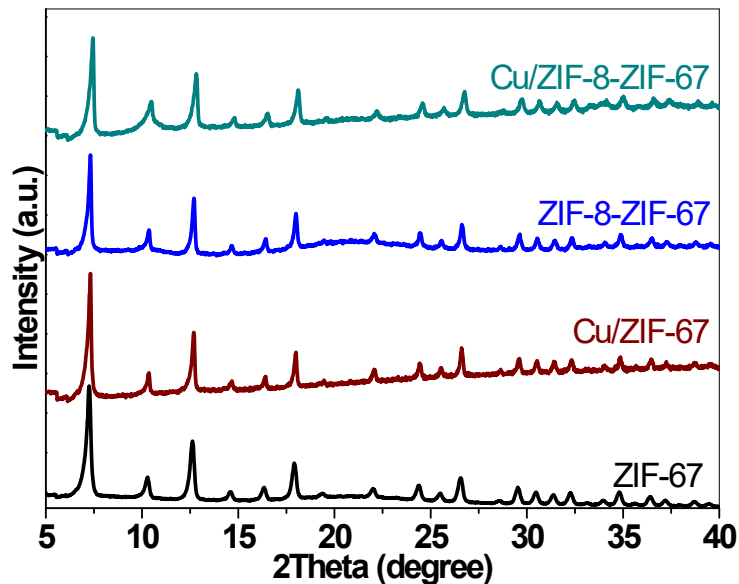
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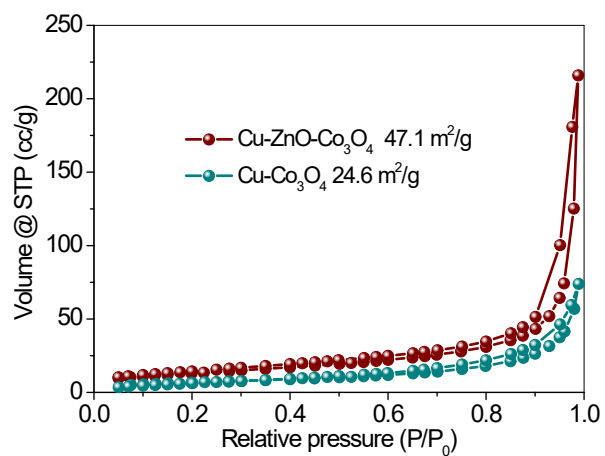


SFig.1 XRD patterns of the different precursors.

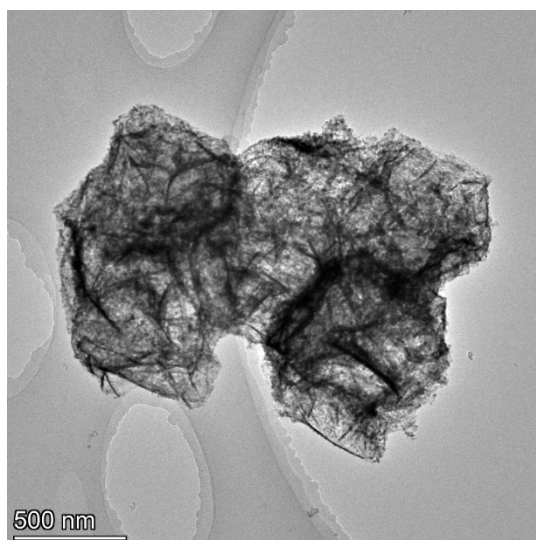
STable 1 ICP-AES data of element content in the copper doped samples.

Co (wt.%)	Cu (wt.%)	Zn (wt.%)
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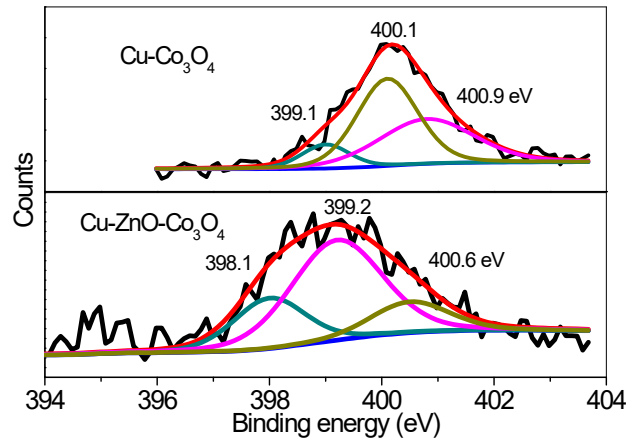
Cu-Co ₃ O ₄ /NC	57.3	12.2	/
Cu-ZnO-Co ₃ O ₄ /NC	24.5	4.7	32.1



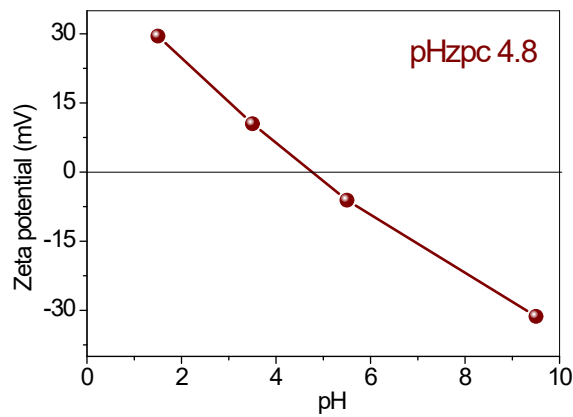
SFig. 2 N₂ adsorption-desorption isotherms of the samples.



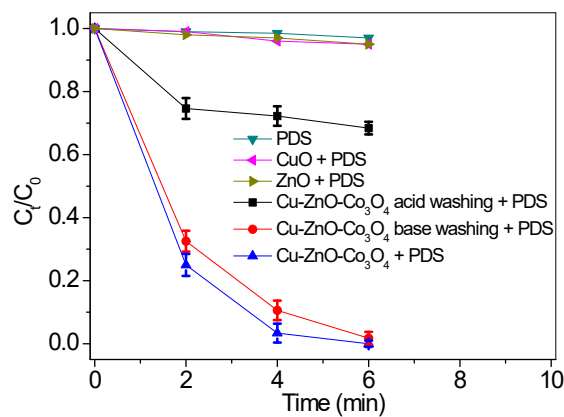
SFig. 3 TEM image of ZnO-Co₃O₄ derived from ZIF-8-ZIF67.



SFig. 4 XPS spectra of Ni1s of the Cu-ZnO-Co₃O₄ and Cu-Co₃O₄.



SFig. 5 Zeta potential of Cu-ZnO-Co₃O₄ as a function of pH in water.



SFig. 6 BPA degradation under different conditions. [0.1 g·L⁻¹ catalyst, 20 mg·L⁻¹ BPA, 0.1 g·L⁻¹ PDS]

As shown in SFig.6, the PDS could not result in the degradation of BPA under the present reaction. Besides, the very slight degradation of BPA was achieved in the ZnO, CuO and Co₃O₄ in presence of PDS. Furthermore, it was suggested that after KOH treatment, a slight loss of the BPA degradation efficiency of Cu-ZnO-Co₃O₄ as indicated by the apparent degradation rate of 0.66

min⁻¹ (R²= 0.97) was observed possibly because the ZnO nanoparticles could be leached due to the reaction of $ZnO + 2KOH + H_2O = K_2[Zn(OH)_4]$ and Cu doped Co₃O₄ could be almost remained. However, after treating with H₂SO₄, both ZnO and Co₃O₄ nanoparticles in the composite could be almost removed and it was reasonable that a significant loss of the activity as suggested by the apparent degradation rate of 0.06 min⁻¹ (R²= 0.67) was observed. Thus, in the composite, the Cu doped Co₃O₄ nanoparticles and slight carbon species in the composite could be responsible for the activation of PDS.

Treatment condition: 5 mg of ZnO, CuO and Co₃O₄ were employed as catalyst, respectively. 5 mg of Cu-ZnO-Co₃O₄ were washed by 2 mL 0.5 M H₂SO₄ and 0.5 M KOH under sonication for 5 min to remove metal oxides and ZnO in the composite, respectively. After washed by distilled water for twice, the remained solids were used for BPA degradation with PDS.

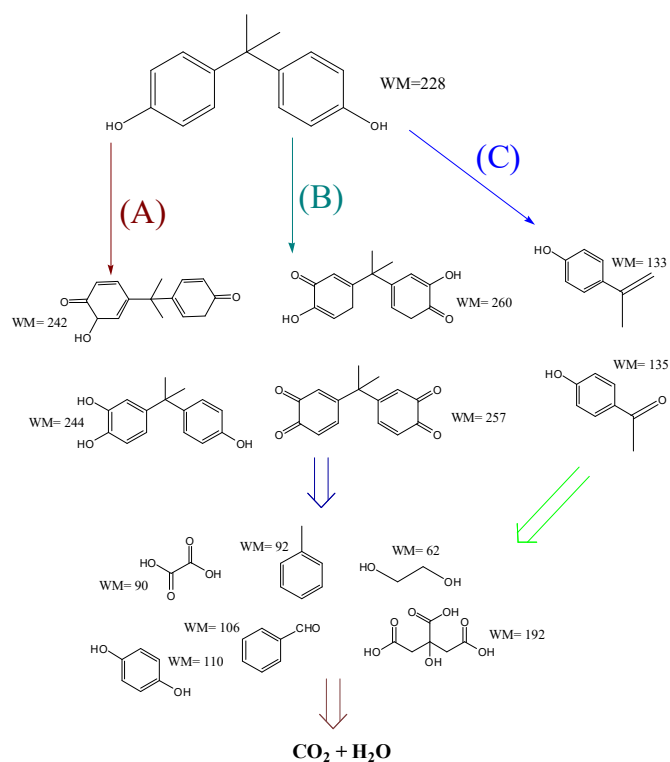
STable 2 Comparison of BPA degradation activities over different catalysts

Catalysts	Condition	Performances	TOC (%)	Refs.
N-doped carbon	([BPA] = 20 mg/L, [PDS])	0.126 min ⁻¹	65.9 in 20	1

nanoparticles	=3.25 mM, [Catalyst] = 0.12 g/L, and initial solution pH=7.0)		min	
CuO decorated on hexagonal boron nitride mesoporous silica spheres-doping CuO (CuO/MSS)	[BPA] = 5 mg L ⁻¹ , [PDS] = 0.5 g L ⁻¹ , [CuBN-4] = 2.0 g L ⁻¹ , and pH = 4–5. [BPA] = 50 mg/L, [catalyst] = 1.5 g/L, [PDS] = 100 mM, temperature = 25 °C, pH = 7	0.1 min ⁻¹	82 in 150 min	2
Zn-OMS-2	BPA (20 mg L ⁻¹), Zn-OMS-2, (0.5 g L ⁻¹), PDS (0.5 g L ⁻¹)	85% removal in 26 min	53 in 55 min	4
RC/CNTs/Fe ₃ O ₄	[Catalyst] ₀ = 0.2 g/L, [PDS] ₀ = 0.05 mM, pH ₀ = 6.07, [BPA] ₀ = 5 ppm, T = 30°C	0.157 min ⁻¹	27.41 in 60 min	5
ZnCo ₂ O ₄ /NC	[Catalyst] ₀ = 0.2 g/L, [PDS] ₀ = 0.4 g L ⁻¹ , pH = 7.6, [BPA] ₀ = 20 ppm, T = 30°C	0.42 min ⁻¹	68 in 12 min	6
Cu-ZnO-Co ₃ O ₄	[Catalyst] ₀ = 0.1 g/L, [PDS] ₀ = 0.1 g L ⁻¹ , pH = 7.6, [BPA] ₀ = 20 ppm, T = 25°C	0.84 min ⁻¹	52 in 6 min	This work

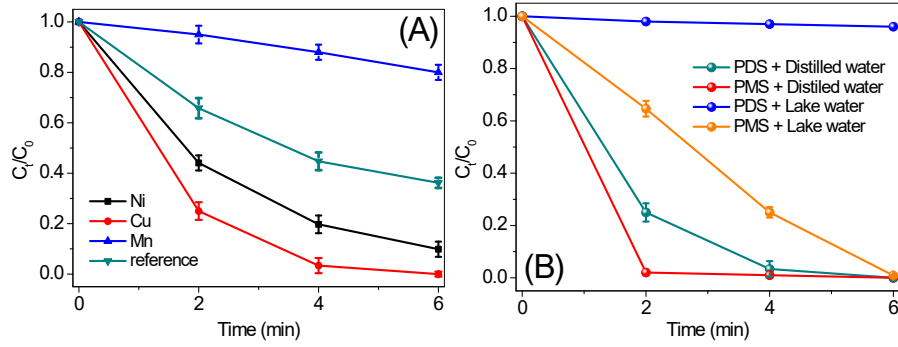
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Scheme 1 Possible degradation paths of BPA with Cu-ZnO-CO₃O₄ and PDS.

The possible degradation pathways of BPA were proposed as present in Scheme 1. It was suggested that a composite degradation mechanism (radical and non-radical pathway) may occur during the BPA oxidation. It was found that the dehydrogenation (path A) and hydroxylation (path B) reactions were occurred for BPA to form monohydroxylated BPA ($m/z = 243$) via hydroxylation, dehydroxylated bisphenol A ($m/z = 259$) and BPA 4,5-quinone ($m/z = 241$), respectively, which similarly could transform into 4-[2-(3,4-dihydroxyphenyl) propan-2-yl]-quinone ($m/z = 257$) through sequential electron transfer reaction. In addition, the fragments such as 4-isopropenylphenol ($m/z = 133$) and 4-hydroxyacetophenone ($m/z = 135$) as well as hydroquinone ($m/z = 133$), 4-isopropylphenol ($m/z = 135$) and 2-phenylpropan-2-ol ($m/z = 135$) demonstrated that BPA could undergo β -scission reaction (path C) and the direct C–C cleavage, which confirmed the existence of $^1\text{O}_2$ generated by the catalyst and PDS. Finally, with the assistance of the active species, such as $\text{SO}_4^{\cdot-}$, HO^{\cdot} , $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$, the generated small organic molecules such as organic acids, acetone and phenol were further mineralized into harmless CO_2 and H_2O .



SFig. 7 (A) BPA degradation in the presence of different catalysts (20 ppm BPA, 0.1 g/L catalyst, 0.1 g/L PDS) and (B) in the presence of Cu-ZnO-Co₃O₄ under different condition (20 ppm BPA, 0.1 g/L catalyst, 0.1 g/L PDS or PMS).