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Supplementary Information

New Zn (II) Complex-Composite Material: Piezo-Enhanced Photomineralization of Organic

Pollutants and Wastewater from Lubricant Industry

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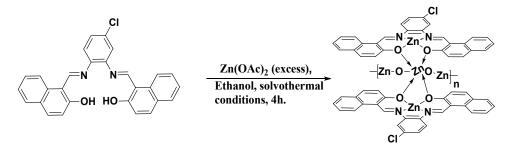
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1. Synthesis of ZnO-[Zn(CPAMN)] complex composite

The [Zn(CPAMN)] complex (1.00 mmol), Zn(OAC)₂.2H₂O (1.00 mmol), stearic acid (3.00 mmol) and Polyvinyl alcohol (2.00 mmol) dissolved in ethanol (50 ml) then heated at 100°C under solvothermal conditions for 4h (Scheme 3). After cooling the formed precipitate was filtered and washed with deionized water. The obtained solid material sintered at 300 °C for 3 hours and the elemental composition of the material was confirmed through XPS data.



Scheme S1. Synthesis of ZnO-[ZN(CPAMN)] complex composite materials

2. Piezo-photocatalytic activity studies

The mineralization of MR/RhB dye solutions were used to evaluate the ability of the piezophotocatalytic system. The photodegradation reactions were achieved in the presence of visible light ($\lambda > 400$ nm) treatment and ultrasonic-vibration, produced by 500 W Tungsten lamp (LPML, Techinstro, India) and Ultrasonic system (35 kHz, 160 W), respectively. In a characteristic piezo-photocatalytic performance, 50 mg of catalyst was suspended into the dye aq. solutions (5 x 10⁻⁵ M). The solution was initially stirred for 60 min in the dark to create an adsorptiondesorption steadiness between the catalyst and the dye solution. In the mineralization procedure, the temperature was kept at ambient condition through ice-cold water flow to eliminate the effect of temperature on the degradation process. 3 mL of the dye solution was taken with a period of 10 min, at the same time remove the catalyst through a centrifugation process. The absorption intensity of the respective dye in supernatant was recorded through JASCO V-760 UV-Vis spectrophotometer.

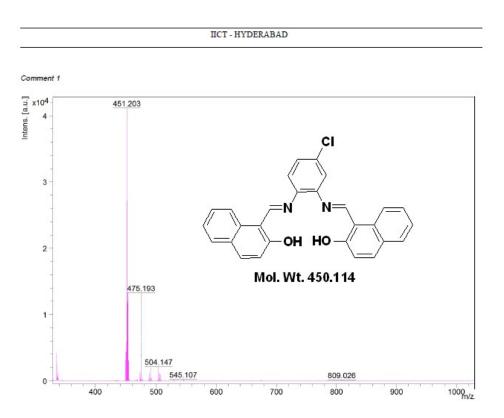


Figure S1. Maldi mass spectrum of CPAMN ligand

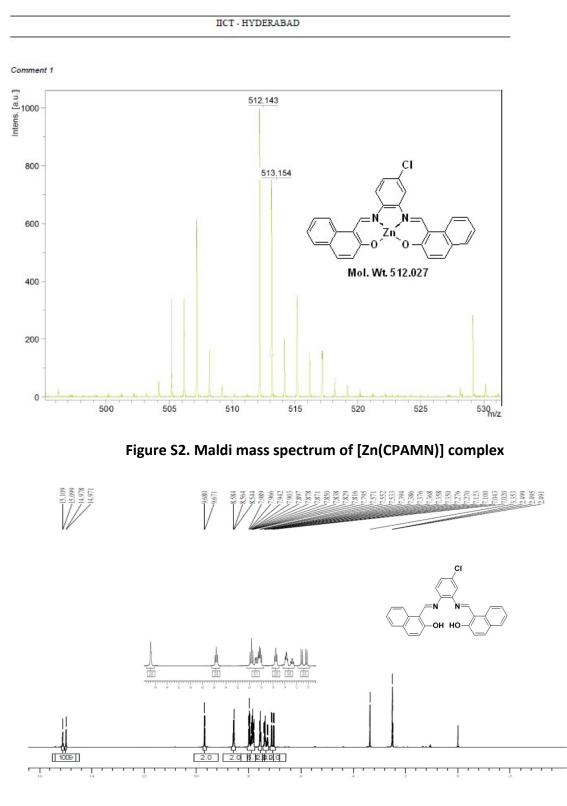


Figure S3. ¹H-NMR spectral pattern of CPAMN ligand

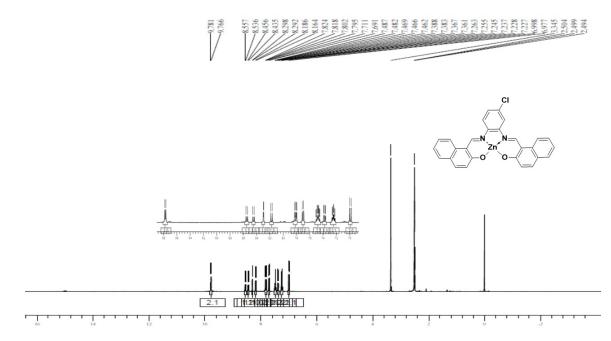


Figure S4. ¹H-NMR spectral pattern of [Zn(CPAMN)] complex

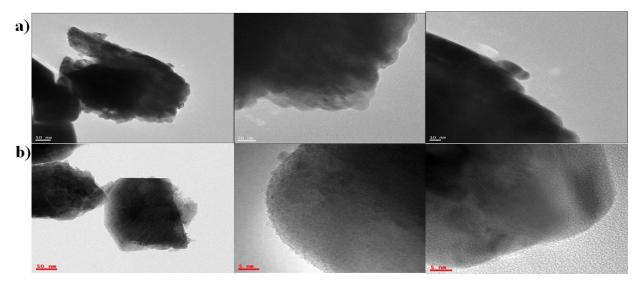


Figure S5 HRTEM images of a) ZnO and b) [Zn(CPAMN)] complex.

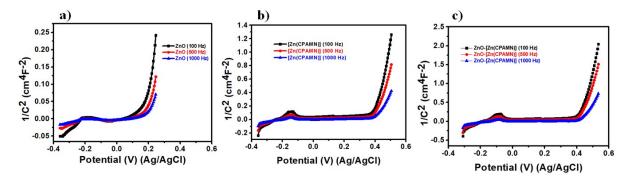
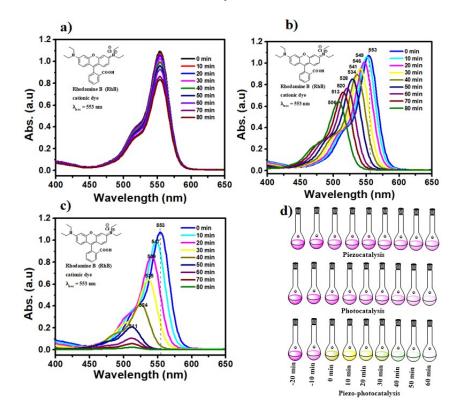


Figure S6 Mott Schottky plots a) ZnO b) [Zn(CPAMN)] complex and ZnO-[Zn(CPAMN)] complex



composite.

Figure S7 UV-visible absorption spectrum of RhB dye solution mineralized in the presence of ZnO, [Zn(CPAMN)] and ZnO-[Zn(CPAMN)] catalyst through (a) piezocatalysis, (b) photocatalysis and (c) piezo-photocatalysis. (d) The conforming color modification of the sample solutions.

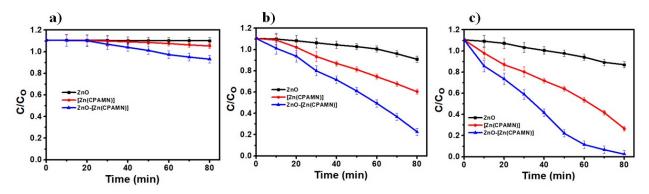


Figure S8. In the presence of a) ZnO, b) [Zn(CPAMN)] and c) ZnO-[Zn(CPAMN)] complex composites mineralization rates of RhB dye solution through piezocatalysis, photocatalysis and piezo-photocatalysis techniques.

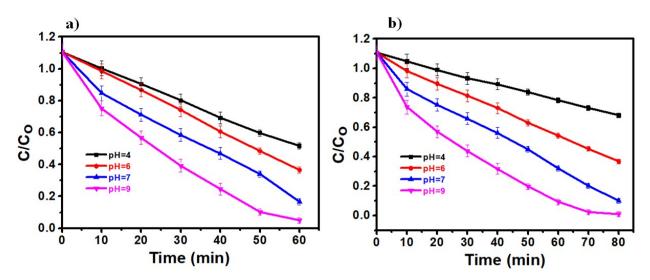


Figure S9 Effect of pH of the solution on piezo-photodegradation of MR and RhB dyes in the presence of ZnO-[Zn(CPAMN)] catalyst

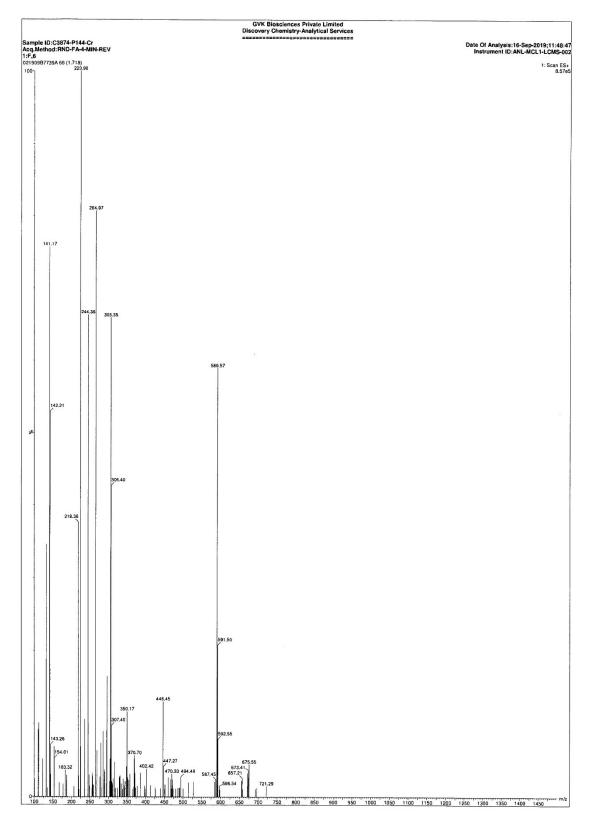


Figure S10 LC-MS data of IWW sample primary without exposed to ultrasonication and visible light irradiation

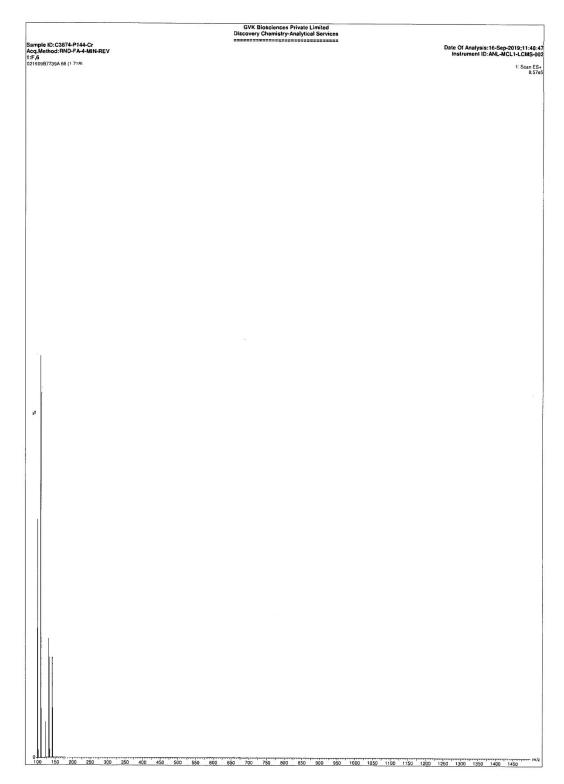


Figure S11 LC-MS data of IWW sample primary after exposed to ultrasonication and visible light irradiation

Catalytic system	Dyes or pollutants	Degradation time	References
ZnO-[Zn(CPAMN)]	MR, RhB and IWW	60 min, 80 min and 180 min	Present work
Bi _{0.5} Na _{0.5} TiO ₃ @TiO ₂	RhB	90 min	1
BaTiO ₃ nanowires	MO	80 min	2
ZnO nanoparticles	MB	120 min	3
ZnO nanowire	MB and crude oil pollutant	180 min and 20% in 6 h.	4
ZnO	Diclofenac	350 min	5
ZnO nanowires	MB	120 min	6
BaTiO ₃ /KNbO ₃	lake blue 5B	180 min	7
ZnO/ZnS/MoS ₂	MB	60 min	8

Table S1 Compare the ZnO-[Zn(CPAMN)] piezo-photocatalyst with reported catalytic systems

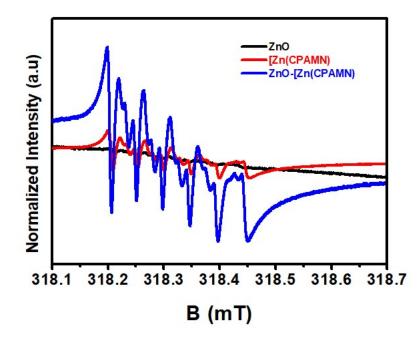


Figure S12 Spin trapping EPR spectra of ZnO, [Zn(CPAMN)] and ZnO-[Zn(CPAMN)] for DMPO- $^{\circ}O_2^{-}$ (in methanol dispersion)

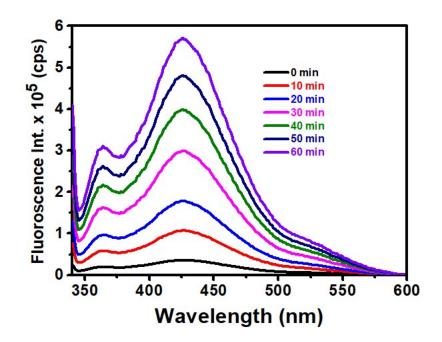


Figure S13 PL spectral increases under piezo-photocatalysis process with regular intervals of time on ZnO-[Zn(CPAMN)] complex composite in terephthalic acid.

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