In-situ construction of $ZnFe_2O_4$ nanosphere on CoO nanosheet for durable photodegradation of organics: Kinetics and mechanistic insights

Mohammad K. Okla[a], V. Subhiksha[b], C. Akshhayya[b], Saud S. Al- amri[a], Ibrahim A. Alaraidh[a], Abdullah A. Al-ghamdi[a], Walid Soufan[c], Mostafa A. Abdel-Maksoud[a,**], Mohammed Aufy[d], Christian R. Studenik[d], S. Sudheer Khan[e,*]

[a]Botany and Microbiology Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

[b]Nanobiotechnology Laboratory, Department of Biotechnology, Bannari Amman Institute of Technology, Sathyamangalam, Tamil Nadu, India

[c]Plant Production Department, College of Food and Agriculture Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia.

[d]Department of Pharmaceutical Sciences, Division of Pharmacology and Toxicology, University of Vienna, Austria.

[e]Department of Oral Medicine and Radiology, Saveetha Dental College and Hospitals, Saveetha Institite of Medical and Technical Sciences (SIMATS), Chennai- 600077, Tamil Nadu, India

*Corresponding author

Dr. S. Sudheer Khan

Email: sudheerkhans.sdc@saveetha.com

**Corresponding author

Dr. Mostafa A. Abdel-Maksoud

Text S1. Characterization

SEM (Jeol JSM 6390, USA) and HR-TEM (JEOL JEM 2100) was performed to evaluate the morphological changes of as-prepared photocatalysts. XRD analysis was performed to determine the crystalline nature of photocatalysts with help of X-ray diffractometer. The surface and chemical composition of the elements are evaluated using X-ray photoelectron spectroscopy (Thermo Scientific). The absorption spectrum was observed and calculated using UV-visible spectrophotometer (Systronics, India). The UV-vis diffuse reflectance spectroscopy was employed to determine the optical absorption characteristics of the as-prepared samples. Electrochemical workstation was used to examine the electrical impedance spectra (EIS). The signal of ESR could be observed under visible light illumination. Fourier transform infrared spectroscopy was employed to analyse the functional groups present in the prepared photocatalysts. BET analysis was performed to identify the porosity, pore distribution, and surface areas of the as-prepared samples.

Text S2. Evaluation of Photocatalytic activity

In order to determine $CoO/ZnFe_2O_4$ NCs photocatalytic activity, MB dye degradation was performed. A 500 W halogen lamp was used as the light source for the photocatalytic degradation of MB dye. A distance of 18.3 cm is maintained between samples and the source of light during the experiment. Here, 25 mg of powder catalyst was added to 50 mL of aqueous solution (500 mg/L) in order to prepare stock solutions of photocatalytic suspension. The same stock solution was used during all phases of the experiment so that handling errors could be minimized. From the stock solution, 120 μL was taken in account of maintaining 3 mg/L concentration of NCs and it was added into 30 mg/L MB dye solution. After preparing the working solution, it was kept in dark conditions for 30 min to bring adsorption-desorption equilibrium. In order to examine the degradation kinetics, the solution was directly placed under visible light irradiation. Every 20 min, absorbance intensity was recorded for the purpose of determining degradation kinetics. The amount of MB dye residue in the working solution was calculated using a UV-visible spectrophotometer (Systronics, India) every 20 min. The photocatalytic performance of $CoO/ZnFe_2O_4$ NCs (20, 40 and 60%) was done based on the efficiency in MB dye degradation under visible light illumination.

The MB dye degradation percentage was calculated using the formula mentioned below

$$Degradation\ (\%) = \frac{A_0 - A_t}{A_0} \times 100 \qquad (1)$$

where A_0 and A_t are the initial absorption and absorption of MB solution at irradiation time (t) respectively.

Experimental and theoretical optimizations were done in order to determine their effects on MB dye degradation by carrying out different dye concentration and different NCs concentration studies. The pristine material CoO and $ZnFe_2O_4$ was also kept under light for

3

same duration in order to evaluate the degradation efficiency of as-prepared NCs. The aim of this study was to correlate and identify their different reaction rates and the resultant efficiency of different dosages of the solutions.

The efficiency to reuse the NCs was validated from the performance of photocatalytic experiments for about six cycles. Henceforth, the NCs were centrifuged, collected and then re-dispersed in MB solution during each cycle. The recovered NCs from the sixth cycle were analysed via XRD analysis to determine their structural stability and photo corrosive nature during photocatalysis.

Several experiments were carried out for the purpose of trapping reactive species formed by $CoO/ZnFe_2O_4$ NCs under visible light exposure. For the evaluation of the photocatalytic mechanism, scavenging experiments was carried out with different scavenging agents. The scavenger includes 1,4-benzoquinone (p-BZQ), tert-Butyl alcohol (t-BuOH), silver nitrate ($AgNO_3$), ethylenediamine tetra acetic acid (EDTA) and are used for capturing $O^{2-}\bullet$, $OH\bullet$, e^- and h^+ respectively.

Figure S1. EDS spectra of the as-prepared CoO/ZnFe$_2$O$_4$ NCs.
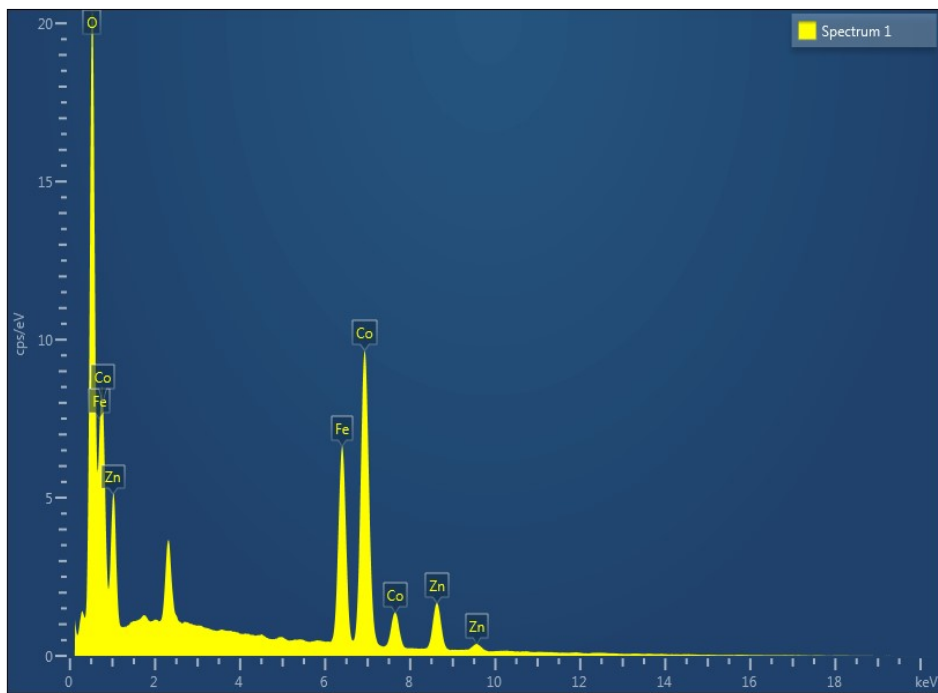
Figure S2. (a) The plot of C_t/C_0 versus time and (b) the plot of -Ln C_t/C_0 versus time at different concentration of NCs. (c) The plot of C_t/C_0 versus time and (d) the plot of -Ln C_t/C_0 versus time at different concentration of dye.