Supplementary Information

Effective Photocatalytic Dechlorination of 2,4-Dichlorophenol by A Novel Graphene Encapsulated ZnO/Co₃O₄ Core-shell Hybrid under Visible Light

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Instrumentation

Powdered X-ray Diffraction (PXRD) was measured by Bruker APEX-2 diffractometer. Fourier Transform Infra Red spectra (FT-IR) were carried out with a Perkin-Elmer FT-IR spectrophotometer RXI. The X-ray Photoelectron Spectroscopy (XPS) was performed by Specs (German). Thermogravimetric Analysis (TGA) was analysed on Perkin-Elmer instrument, Pyris Diamond TG/DTA with Al₂O₃ crucible. Transmission Electron Microscopy (TEM) and High Resolution TEM (HRTEM) were performed with JEOL JEM2010 electron microscope operating at 200 kV. Energy Dispersive X-ray (EDX) measurement was carried out with FEI TECNAI-G2-20S-TWIN (USA). BET surface area and N₂ sorption isotherms (77K) were carried out by Quantachrome Autosorb-1 instrument. Photoluminescence spectra were recorded by F-7000 FL Spectrophotometer. The photodegradation of 2,4-DCP were measured by UV- 1601, Shimadzu spectrophotometer and high performance liquid chromatography (HPLC, Thermo Fisher Scientific Dionex UltiMate 3000). The HPLC were consisted of a UV/Vis Diode Array Detector and a reversed-phase Acclaim Polar Advantage-II column (3 µm, 120 Å, 3 ×150 mm). The chromatographic conditions were: 80: 20 for
mobile phase (V) acetonitrile: water, 0.3 mL min\(^{-1}\) for the flow rate of mobile phase, 20 µL for the injection volume, 30 °C for column temperature and the detection wavelengths for 2,4-DCP and its degradation products \(o\)-chlorophenol (\(o\)-CP), \(p\)-chlorophenol (\(p\)-CP) and phenol were 285 nm, 274 nm, 280 nm and 270 nm, respectively. The GCMS study of the photo-degraded products was carried out using a Thermo Scientific Trace 1300 gas chromatograph and ISQ Single Quadrupole MS system.

**Figure S1** a) FT-IR spectra and b) PXRD pattern of the synthesized Zn-Co NCP precursor and synthesized ZnO-Co\(_2\)O\(_4\) heteronanostructure after calcination of Zn-Co NCP at 550 °C.
Figure S2. TEM image of the prepared a) Zn-Co NCPs, b) ZnO-Co$_3$O$_4$ nanostructures prepared from Zn-Co NCPs after calcinations and c) SAED pattern of prepared ZnO-Co$_3$O$_4$ heteronanostructures.

The average size of the Zn-Co NCP and corresponding derived ZnO-Co$_3$O$_4$ heteronanostructures are ~60 nm and ~25-40 nm. The SAED pattern indicates high crystalline nature of the ZnO-Co$_3$O$_4$. 
Figure S3. Zeta potentials of APS-modified ZnO-Co$_3$O$_4$ and GO in aqueous solution at different pH values.
**Figure S4.** TEM image of the GE/ZnO/Co$_3$O$_4$ core-shell hybrid.

The TEM shows the ZnO-Co$_3$O$_4$ is wrapped by thin graphene shells.
Figure S5. The retention time of the standard substance of $o$-CP, $p$-CP and Phenol.
Figure S6 TOC removal at different time during photocatalytic mineralization of 2,4-DCP under visible light irradiation in presence of GE/ZnO/Co$_3$O$_4$. 
Figure S7 Plot of \( \ln \frac{C_0}{C_t} \) vs. Time for determination of the rate constant of the GE/ZnO/Co\(_3\)O\(_4\), GO and bare ZnO/Co\(_3\)O\(_4\) ([2,4-DCP]=20 mg/L, [catalyst]= 1.0 g/L, pH=5.0).
Figure S8. a) PXRD pattern and b) TEM image of the GE/ZnO/Co$_3$O$_4$ hybrid after 6$^{th}$ cycle of photocatalytic reaction.

The PXRD patterns indicate that there is no remarkable alteration or shift of the peak in the crystal structure of the catalyst after 5$^{th}$ cycle of operation, and TEM image of the hybrid shows the ZnO/Co$_3$O$_4$ core still is wrapped by graphene shells and hence no noticeable change in morphology is observed after 5$^{th}$ cycle.
Figure S9. GC-MS spectrum of the photo-degraded products of 2,4-DCP after 5 h of photocatalytic reaction.

The GC-MS spectrum of the degraded products of 2,4-DCP after 2 h of photocatalytic reaction (Fig. 15, in the manuscript) exhibits the mass peaks of (a) unreacted 2,4-DCP (m/z, 162.15) and also its fragmented products, like (b) chlorophenols (m/z, 128.21), (c) phenol (m/z, 94.04), (d) p-benzoquinone (m/z, 108.2), (e) acetic acid (m/z, 60.02) and (f) 1,3-butadiene (m/z, 53.23).

However, the GC-MS spectrum of samples subjected to photodegradation for 5 h (above Fig. S9) show significant degradation of the 2,4-DCP. The mass peaks of phenol (m/z, 94.04), p-benzoquinone (m/z, 108.2), acetic acid (m/z, 60.02) and 1,3-butadiene (m/z, 53.23) are mainly observed in the photo-degraded products of 2,4-DCP after 5 h of reaction, however, the peaks related to 2,4-DCP (m/z, 162.15) and chlorinated-phenols (m/z, 128.21) have not been observed.