Facile synthesis of nano Zn/Bi - reduced graphene oxide for enhanced photocatalytic elimination of chlorinated organic pollutants under visible light

Karan Goswami and Rajakumar Ananthakrishnan

aDepartment of Chemistry, Green Environmental Materials & Analytical Chemistry Laboratory, Indian Institute of Technology Kharagpur 721302, India.

E-mail: raja.iitchem@yahoo.com

Figure-S1: Powder XRD pattern of ZB-LDH.
Figure S2: XPS spectra of Zn 2p, Bi 4f and O 1s.
Figure S3: EDX spectra of (a) ZB-MMO and (b) ZB-RGO. The percentages of all the elements are inserted into the corresponding plot in tabular form.

Figure S4: DRS plot of (a) ZnO and (b) Bi$_2$O$_3$.

Figure S5: N$_2$ adsorption-desorption isotherm of (a) ZnO and (b) Bi$_2$O$_3$. 
Figure S6: FESEM images of (a) ZnO and (b) Bi$_2$O$_3$.

Figure S7: (a) Comparison study of degradation of 2-CP with respect to time. (b) Reusability of ZB-RGO for degradation of 2-CP.
Figure S8: GC-MS peaks of 2-CP analyzed by taking samples after 60 min of light reaction over ZB-RGO.
Figure S9: (a) Comparison study of degradation of 2,4-DCP with respect to time over the catalysts. (b) Reusability of ZB-RGO for degradation of 2,4-DCP.
Figure S10: GC-MS peaks of 2,4-DCP analyzed by taking samples after 60 min of light reaction over ZB-RGO.
Scheme-S1. Proposed mechanism for degradation of 2,4-DCP.
Experimental evidences for LMCT mechanism:

In the scheme (scheme-3), it has been shown that $O_2^-$ radical was generated through LMCT mechanism during the reaction. The occurrence of LMCT has been proved in this work by proving the presence of $O_2^-$ radical in the reaction medium. For this purpose we took a model dye, methyl orange (MO) dye and carried out three set of experiments.

(i) In the first set of experiment, 10 mL, 10 ppm 2,4-DCP was stirred with ZB-RGO (1g/L) for 40 min under dark condition. The solution then filtered and separated from the catalyst. A 6 ppm, 10 mL MO dye solution was added to the 10 mL centrifugates (2,4-DCP solution, which now contains the $O_2^-$ radical due to LMCT) and the mixture solution was kept for 60 min. The total volume of the mixture solution (MO and 2,4-DCP) was 20 mL and the concentration of MO dye in the mixture solution became 3 ppm due to half dilution. After 60 min it was found that the 3ppm MO dye was degraded almost completely.

(ii) In the second set of experiment, we mix a MO dye solution with a fresh solution of 2,4-DCP (i.e, the 2,4-DCP was not treated with the catalyst) and kept for 60 min and no change in the concentration of MO dye was observed.

(iii) The third set of experiment was similar with the first set of experiment, but we added a quencher of $O_2^-$ radical (1,4-benzoquinone) along with MO dye and after 60 min we found no significant change in the concentration of MO dye.

The three set of experiments proved the presence of $O_2^-$ radical in the solution which again indirectly proved that the LMCT mechanism was happening between 2,4-DCP and the catalyst during the reaction.
Scheme S2: The proposed electron-hole mechanism for degradation of 2-P and 2,4-DCP.

\[
\text{Catalyst} + \text{hv} \rightarrow \text{Catalyst} (e^{CB} + h^{VB+})
\]
\[
\text{Catalyst} (h^{VB+}) + \text{H}_2\text{O} \rightarrow \text{Catalyst} + \text{H}^+ + \cdot\text{OH}
\]
\[
\text{Catalyst} (e^{CB}) + \text{O}_2 \rightarrow \text{Catalyst} + \text{O}_2 \cdot
\]
\[
\text{O}_2 \cdot + 2 \text{H}^+ \rightarrow 2 \cdot\text{OH}
\]
\[
\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2
\]
\[
\text{H}^+ + \text{O}_2 \cdot + 2 \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\]
\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot\text{OH}
\]
\[
\text{Contaminants} + \cdot\text{OH} \rightarrow \text{photo degradation products}
\]