Supporting Information

Hierarchical Growth of ZnFe\textsubscript{2}O\textsubscript{4} for Sensing Applications

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S1: a) Materials: All reagents were AR grade. Anhydrous FeCl$_3$ and ZnSO$_4$ were purchased from E-Merck. Urea was purchased from Spectrochem. 3,3',5,5' tetramethylbenzidine (TMB) was purchased from Sisco Research Laboratory, Mumbai, India. HgCl$_2$, ZnCl$_2$, MnCl$_2$, Cr$_2$(SO$_4$)$_3$, CuCl$_2$, PbCl$_2$, CdCl$_2$ were purchased from SRL Company. Acetone and H$_2$O$_2$ were purchased from Merck. Doubly distilled water was used to wash all the glasswares and to prepare the solutions.

b) Instruments:

Powder X-ray diffraction (XRD) has been done with a PW1710 diffractometer (Philips, The Netherlands) instrument. The XRD data analysis has been done using JCPDS software.

X-ray photoelectron spectroscopy (XPS) analysis was performed with VG Scientific ESCALAB MK II spectrometer equipped with a Mg Kα excitation source (1253.6 eV) and a five-channeltron detection system to analyze the elemental state.

Field emission scanning electron microscopy (FESEM) was carried out with a Supra 40 (Carl Zeiss Pvt. Ltd) instrument and EDAX machine (Oxford link and ISIS 300) attached to the instrument was used to find out the composition of the nanocrystal.

Transmission electron microscopy (TEM) was done on a Hitachi H-9000 NAR instrument using an accelerating voltage of 300 kV.

All UV−vis absorption spectra were recorded on a SPECTRASCAN UV 2600 digital spectrophotometer (Chemito, India).

Nitrogen adsorption and desorption measurements were measured at 77 K using a Quanta-chrome Autosorb Automated Gas Sorption System by Brunauer-Emmett-Teller (BET) calculations for the surface area and Barrett-Joyner-Halenda (BJH) calculations for the pore-size distribution after the samples were degassed in a vacuum overnight.
c) Gas sensor device fabrication and sensor set up

For gas sensor fabrication zinc ferrites were initially sonicated in deionised (DI) water for 10 minutes. Then they were drop casted on Pt- interdigitated electrodes (purchased from Synkera Technologies, Inc.) and heated at 100°C for 5 minutes to remove the water.

For gas sensing, the samples were kept inside an air tight stainless steel chamber. The chamber has an inbuilt heater which was used for high temperature measurements. The measurements were performed under dynamic flow of gases. The flow of the gases was controlled by mass flow controllers (MFCs). The MFCs were controlled by (MKS 247) four channel power supply/readout. The resistances of sensing layers were measured using two probes which are connected inside the chamber. This resistance data was directly captured using Agilent 34972A LXI data acquisition card (DAQ) equipped with 34901A 20 channel multiplexer module. BenchLink Data Logger Pro software was used for data acquisition. The detail of the experimental set up was described in literature. ¹²

References:


Synthesis of FeO(OH) nanomaterials:

To synthesize FeO(OH) nanomaterials the following procedure has been utilized: Typically 0.16g anhydrous FeCl$_3$ (0.05 M) were dissolved in 20 mL distilled water and 0.3g urea (0.25 M) was added to it. Then the whole solution was stirred for 10 min to make the solution homogeneous. Next, the brown solution was transferred to the 20 mL screw capped test tube and was subjected to modified hydrothermal (MHT) reaction condition at 180 °C for 18 h. Subsequently, it was cooled to room temperature and the brick red colored mass was collected through centrifugation and washed with distilled water. Finally it was cooled to room temperature and collected for characterization and use.

Characterization of FeO(OH) nanomaterials:

To characterize the as-synthesized material we have performed FESEM, TEM and powdered XRD analysis. Figure S1 demonstrates the powdered XRD of the product which confirms that the as-synthesized material is crystalline FeO(OH) (JCPDS No: 75-1594). Figure S2 illustrates the FESEM and TEM images of the as-synthesized material from which we can see that the product is composed of nano rice morphology.
S2. kinetic data obtained from the experiment are fitted into the Michaelis-Menten equation:

\[ V_0 = \frac{V_{\text{max}} S_0}{K_m + S_0} \]  \hspace{1cm} 1

And the kinetic parameters are evaluated from the Linewaver-Burk plot (1/V₀ vs. 1/S₀):

\[ \frac{1}{V_0} = \frac{1}{V_{\text{max}}} + \frac{K_m}{V_{\text{max}} S_0} \]  \hspace{1cm} 2

Here, \( V_0 \) stands for the rate of conversion, \( S_0 \) for the initial substrate concentration, \( V_{\text{m}} \) is the maximum rate of conversion and \( K_m \) is the Michaelis constant. Michaelis–Menten equation correlates the rate of conversion of substrate by enzyme and substrate concentration. \( K_m \) actually signifies the attraction of the enzyme for the substrate and the value of \( K_m \) is equivalent to the concentration of the substrate at which rate of conversion is half of the maximum rate of conversion (i.e. \( V_{\text{max}} \)).
**Scheme S1:** Catalytic oxidation of TMB in presence ZnFe$_2$O$_4$ and H$_2$O$_2$.

**Figure S1:** XRD of the as-synthesized nanorice.
**Figure S2:** FESEM (a) and TEM (b) image of FeO(OH) nanomaterials.

**Leaching experiment of ZnFe$_2$O$_4$ in acid and base solution:** 50 mg of ZnFe$_2$O$_4$ NFs was subjected to 0.01 M NaOH and HCl solution, separately and left for 2 hr. After that it was filtered and collected. The filtrate, collected from NaOH solution was dried in water bath and FTIR measurement was done. Both the residue, collected from HCl and NaOH solution was taken for FESEM measurements.

**Figure S3:** FESEM images of ZnFe$_2$O$_4$ NFs at 0.01 M HCl solution (a) and 0.01 M NaOH solution (b)
**Figure S4:** FTIR spectra of leached solution from ZnFe$_2$O$_4$ NFs in 0.01 M NaOH solution.

**Figure S5:** FESEM images of the product coming from the two precursor, Zn(CH$_3$COO)$_2$ (a) and ZnCl$_2$ (b) (which have been used instead of ZnSO$_4$ for preparation of flower-like ZnFe$_2$O$_4$)
**Figure S6:** FESEM images of ZnFe$_2$O$_4$ nanoflowers at different reaction time.

**Figure S7:** EDX spectra of the as-synthesized ZnFe$_2$O$_4$ nanoflowers.
**Figure S8:** UV-vis spectra of TMB oxidation in different concentration of Hg$^{2+}$. 