Redox mediated synthesis of hierarchical Bi$_2$O$_3$/MnO$_2$ nanoflowers: A non-enzymatic hydrogen peroxide electrochemical sensor

Chaiti Ray, Soumen Dutta, Anindita Roy, Ramkrishna Sahoo, and Tarasankar Pal*

Department of Chemistry, Indian Institute of Technology, Kharagpur – 721302, India

E-mail: tpal@chem.iitkgp.ernet.in
S1. EXPERIMENTAL SECTION

Electron Microscopy (FESEM) is used with a (Supra 40, Carl Zeiss Pvt. Ltd.) microscope at an accelerating voltage of 20 kV. Transmission electron microscopic (TEM) analyses of the samples are performed on a FEI - TECNAI G2 20S – TWIN transmission electron microscope, operating at 200 kV and energy dispersive X-ray microanalyzer (OXFORD EDAX) has been attached to it for compositional analysis. The nitrogen gas adsorption and desorption study is performed using a Quantacrome autosorb iQ automated gas sorption analyzer. For adsorption study the sample was dried in vacuum for overnight and 20-25 mg amount was loaded in a 6 mm sample holder. In desorption study the sample was used for degassing at 70°C for 2 h and Brunauer–Emmett–Teller (BET) calculations are performed for the analysis of surface area of the sample. Phase purity of the synthesized samples are characterized by recording XRD on a BRUKER-AXS-D8-ADVANCE diffractometer with Cu Kα radiation (λ = 1.5418 Å) in the 2θ range of 10°-80° at a scanning rate of 0.5° min⁻¹. X-ray photoelectron spectroscopy (XPS) analysis is done with a SPECS GmbH, Phoibos 100 MCD Energy Analyzer equipped with an Mg Kα excitation source (1283.6 eV).
Fig. S1: FESEM images of (a) Bi$_2$O$_3$ and (b) MnO$_2$.

Fig. S2: Time dependent synthesis of Bi$_2$O$_3$/MnO$_2$ NFs at (a) 1 h, (b) 5 h, (c) 9 h and (d) 12 h.
Fig. S3: (a, c) Nitrogen adsorption and desorption isotherm and (b, d) pore size distribution plot of Bi$_2$O$_3$ and MnO$_2$ materials respectively.

Fig. S4: XRD pattern of as-synthesized Bi(0) nanoparticles.
Fig. S5: KMnO$_4$ concentration dependent synthesis of Bi$_2$O$_3$/MnO$_2$ NFs at (a) 0.05, (b) 0.1, (c) 0.3 and (d) 0.5 mmol.

Fig. S6: Comparative XRD pattern of as-synthesized various BM NFs composites and MnO$_2$.

**Optical property:** The optical adsorption of as-synthesized BM NFs is measured using UV-Vis Diffuse Reflectance Spectroscopy (DRS), as shown in Figure S7. All the as-prepared BM NFs samples show a spectral response in visible region, whereas Bi$_2$O$_3$ does not have any absorbance in
visible range. In case of BM nanocomposites the humps in visible range rise due to the synergistic
effect of Bi$_2$O$_3$ photosensitizing and the creation of p-n heterojunction. With increase in Mn content
(0.05 mmol to 0.3 mmol), the absorbance in visible region increases due to the enhancement in
number of surface Bi$_2$O$_3$ nanoparticles. Further rise in Mn amount (0.5 mmol) results gradual
decrease in absorbance. From this observation it can be concluded that with a certain amount of Mn
(0.3 mmol) the composite shows maximum absorbance in visible region but further increment in
Mn content cover up the optical activity of Bi$_2$O$_3$ and consequently absorbance in visible region
decreases gradually.

Fig. S7: (a) UV-Vis diffuse reflection spectra of the as-prepared various Bi$_2$O$_3$/MnO$_2$, bare Bi$_2$O$_3$
and MnO$_2$ samples and inset shows enlarged view of various Bi$_2$O$_3$/MnO$_2$ composites.

Fig. S8: Effect of (a) concentration of BM NFs in solution and (b) pH of electrolyte on the
amperometric response of BM NFs/Nf/GCE to 5 μM H$_2$O$_2$. 