Supplementary Information

Shape dependent peroxidase mimetic activity towards oxidation of pyrogallol by H_2O_2

Nagaprasad Puvvada, Pravas Kumar Panigrahi, Dhritabrata Mandal, and Amita Pathak*

Materials and Methods

Iron (III) acetylacetonate (98 %), oleic acid (\geq 99 %), pyrogallol (PG) \succeq 99 %), hydrochloric acid (\geq 35.4 %), and hydrogen peroxide (30%) were purchased from Merck Ltd, India. Benzyl ether (25 %) was purchased from Sigma Aldrich. All other chemicals were of analytical grade and used without further purifications.

Synthesis of Magnetite Nanoparticles

In typical synthesis, iron (III) acetylacetonate and oleic acid were mixed to benzyl ether then the resultant solution was purged with argon gas for 20 min. Initially, purged solution was heated at 170 °C for 20 min and further carried at 290 °C for 20 min. The precipitate was collected by hexane:ethanol mixture (1:1 V/V) and magnetic separation was done after four time wash with water and methanol.

MNPs (5 mg) were dispersed in 10 mL of milli-Q water and subjected to sonication for 20 minutes to obtain MNPs suspension. The H_2O_2 stock solution was prepared by mixing 33µL of commercially available H_2O_2 (30% v/v) with 10 mL of milli-Q water and was kept in dark and cool place. Similarly, pyrogallol stock solution was prepared by weighing 0.062 g of pyrogallol in 10 mL of acetone and kept in dark place.

We attempted to investigate the peroxidase-like activity of MNPs during oxidation of pyrogallol by H_2O_2 where 0.05 M pyrogallol stock solution was prepared in acetone and from this stock 50 μ L was added to 3 mL buffer solution in cuvette. Further, we prepared varing concerations of H_2O_2 from stock solution to examine peroxidase activity.

Characterization of Fe₃O₄ magnetic nanoparticles

Phase analysis of the powders was carried out by X-ray diffraction (XRD) using Cu K α radiation over 2 θ range from 20° to 60° at a scan rate of 1.1° min-1 and with a sampling interval of 0.02 at 30 mA and 40 kV by using Philips PW 1710 diffractometer. Morphology and the particle size of the as-prepared Fe₃O₄ MNPs were measured by using a high-resolution transmission electron microscope (HRTEM) of model JEOL JEM-2100, at an acceleration voltage of 200 kV. Atomic absorption Spectroscopy (AAS) has been performed to determine the concentration of Iron atoms in MNPs by using Perkin Elmer, A Analyst 700. Peroxidase-like activity of Fe₃O₄ MNP's was investigated by spectroscopic method using UV-VIS-NIR spectrophotometer (Varian-5000). Magnetization measurements were analyzed using VSM (Lakeshore VSM, Model no.: 7404).



Fig.S1 Comparative UV/Vis absorption spectra of (a) Pyrogallol, (b) Pyrogallol with H_2O_2 , (c) Pyrogallol with H_2O_2 in presence of spherical shaped MNPs and (d) Pyrogallol with H_2O_2 in presence of TO shaped MNPs (Inset: photographs of corresponding solutions).



Fig. S2 Time dependent response of pyrogallol with H_2O_2 in presence of (a) TO, (b) spherical shaped MNPs; time dependent response of pyrogallol with H_2O_2 in presence of leaching solution of (c, d) TO as well as spherical shaped MNPs (e) without MNPs.



Fig. S3 (a) pH response curves of iron leaching solution of TO MNPs measured at 420 nm (b) atomic absorption spectroscopy (AAS) displayed pH dependence of the Fe leaching from MNPs



Fig. S4 Varying (a) pH and (b) Temperature exhibited differing peroxidase activity measured absorption at 420 nm.



Fig. S5 Simulation structure of Magnetite nanoparticles (from the Diamond Software Demo version 3.2) different orientations (1) {100}, (2) {110}, and (3) {111}