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Supporting Information

$CoFe_2O_4$ Decorated Carbon Nanotubes for Dehydration of Glucose and Fructose

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1. Experimental Section

X - ray diffraction measurements were done using Rigaku Smart Lab XRD spectrometer with Cu K alpha radiation (1.5406 A°) in the range of 20 - 80 degrees. Raman spectroscopic studies were done using micro Raman spectrometer of Technos (Japan) using diode laser for excitation with 532 nm. Fine powders of samples were used for X-ray diffraction studies for phase identification using Brukers D8 DISCOVER instrument with slow scan of resolution 1 sec/step for increment of 0.02° using Cu-target (λ=1.5406). Diffraction data has been analyzed with Diffraction. EVA supplied with Bruker's D8 DISCOVER for reference search patterns (ICDD) database PDF-2 release. The SEM measurements were carried out using a field emission instrument (LEO 1530VP). Samples for SEM analysis were prepared on carbon coated copper grids; the instrument used was ZEISS Libra 200FE scanning electron microscope operated at 200 kV and equipped with a field emission gun, an in-column filter (Omega-filter), and a high-angle annular dark-field (HAADF) detector. All micrographs were taken with a 4K x 4K CCD camera and analysed with the software package Digital Micrographs (Version 1.71.38, Gatan Company).

1.2 *Synthesis of Magnetite Functionalized CNTs:*

Pure CNTs (5.0 g) were dispersed in a solution of conc. HNO_3 (4.0 mL) and conc. H_2SO_4 (16.0 mL). The suspension was ultra sonicated for 3 h at room temperature. Later pure water (100 mL) was added and further sonicated for 10 min. Then the suspension was washed several times thoroughly with water till the neutral pH is attained and dried at 50 °C overnight to get the –COOH functionalized CNTs. The synthesis of Magnetite-CNT was performed by first adding ferrous ammonium sulphate hexahydrate (392.1 mg) and ferric chloride (324.4 mg) in 1: 2 ratio to distilled water (50.0 mL) containing 2.0 g of –COOH functionalized CNTs. The resultant mixture was sonicated for 30 min at room temperature. Then, NH_4OH aq (15 mL) solution was added slowly while sonicating until the complete precipitation formed. The resulting powder was washed several times with water to get the neutral pH. The free flowing

powder was dried for 24 h to get the magnetite functionalized CNTs. Similarly $CoFe_2O_4$ and $ZnFe_2O_4$-CNTs were prepared.

1.3. Synthesis of HMF from fructose:

An oven dried flask was charged with functionalized CNT (0.020 g), fructose (0.180 g). To the flask DMF (3.0 mL) was added and heated to 80 °C with magnetic stirring. After completion of the reaction, the reaction mixture was cooled to room temperature, and catalyst was removed and washed several times with methyl butyl ether and kept at -10°C for 4h to get the crystals of HMF. The reaction mixture was analyzed by using UV-Visible spectroscopy (Figure 2, Supporting Information) Final reaction mixture was analyzed by using HPLC using water and methanol (9:1) using C-18 column.

$$\text{Conversion (\%)} = \frac{Initial\ concentration\ of\ fructose - final\ concentration\ of\ fructose}{Initial\ concentration\ of\ fructose} \text{x100\%}$$

$$= \frac{Concentration\ of\ fructose\ at\ t = 0 - Concentration\ of\ fructose}{Concentration\ of\ fructose\ at\ a\ given\ time} \text{x100\%}$$

$$\text{Selectivity (\%)} = \frac{HMF\ concentration}{Fructose\ concentration} \text{x100\%}$$

2.1. The Spectrophotometric method

After completion of the reaction, 0.5µl reaction mixture was diluted up to 50 mL with HPLC water followed by the addition of 0.5 mL of Carrez solution I and 0.5 mL of Carrez solution II. Aliquots of 5 mL were put into 2 tubes; 5 mL of deionized water was added to one tube (sample solution); 5 mL of sodium bisulfite solution 0.2% was added to the second (reference solution). The absorbance (determined using a Lambda 25 double beam spectrophotometer UV/Vis, Shimadzu) of the aqueous reaction sample at 284 nm (A284) was determined versus reference solution, in order to avoid the interference of other components at that wavelength. The absorbance at 336 nm (A336) was read to subtract the background absorbance. The HMF was quantified by using the proposed formula of the original White method.

$HMF(mg) = (A284 - A336) \times 149.7 \times 5/W,$ where W is the weight of the fructose, the factor 149.7 is a theoretical value linked to the molar extinction coefficient of HMF at 284 nm, which is 16830. In this work we studied the experimental extinction coefficient of HMF to check the correspondence with the theoretical behaviour of HMF.

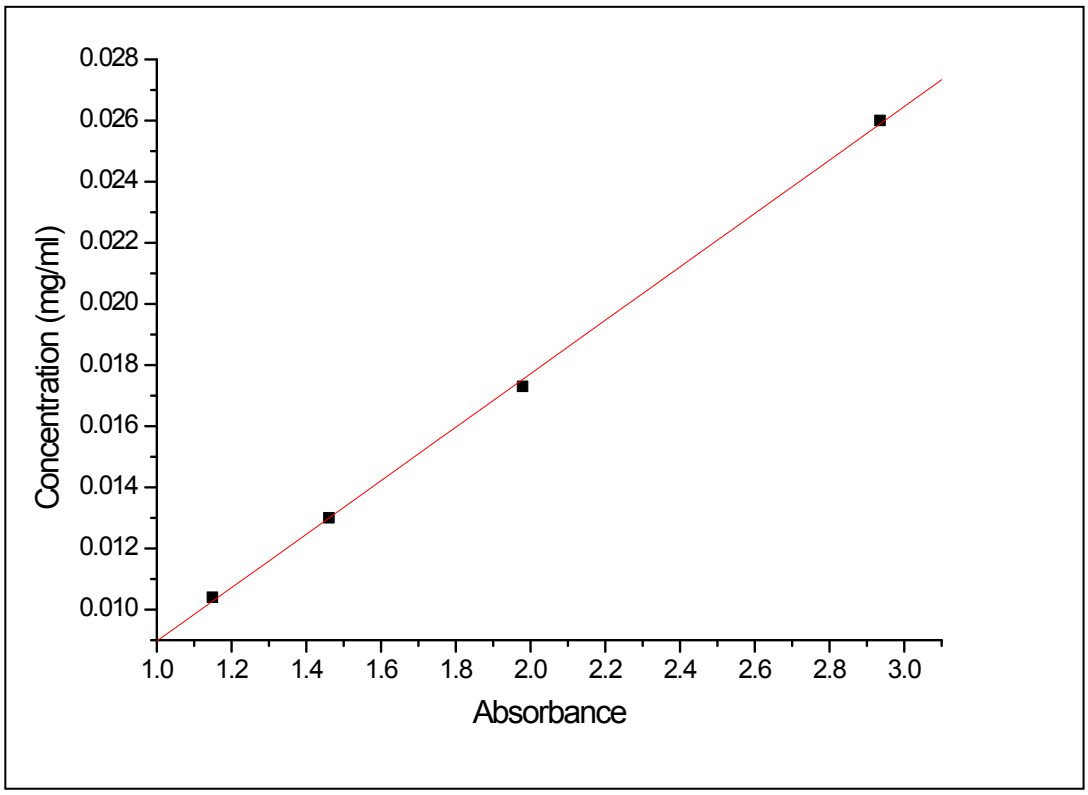


Fig. 1 Calibration Curve for the HMF using UV-spectrometer.

$$\mathbf{Y = (87.4x10^{-4})\ (X) + 2.264x10^{-4}}$$

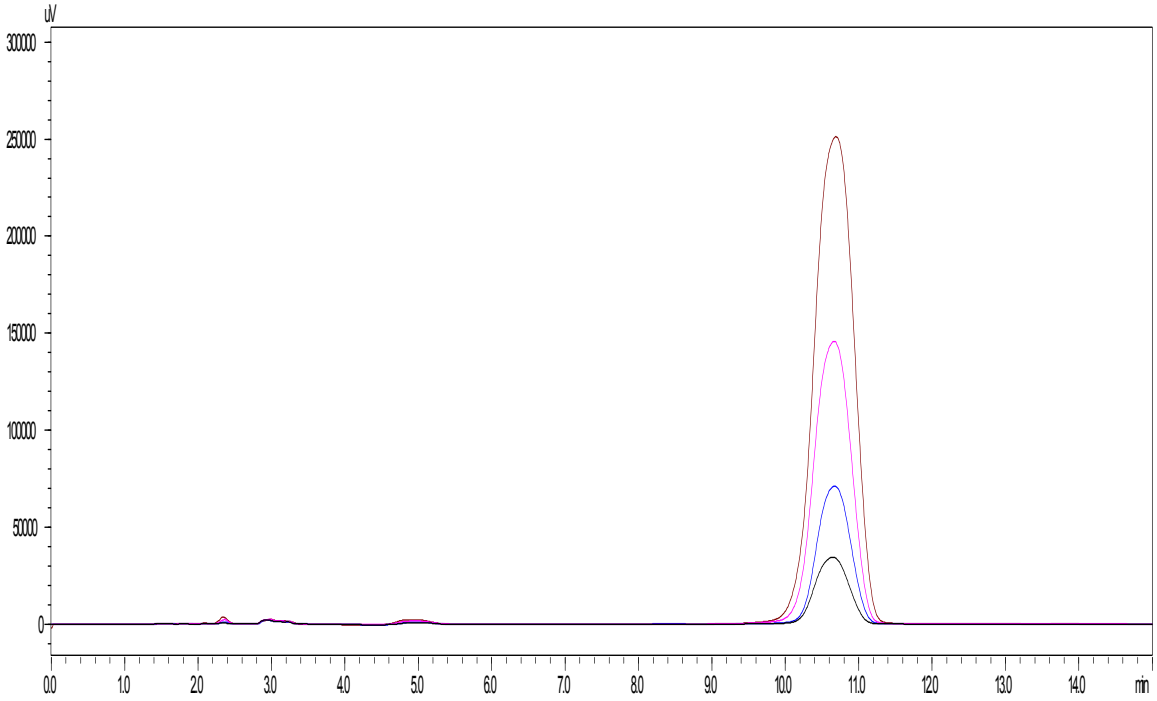


Fig 2. Calibration Curve for the HMF using HPLC (C-18 column, H_2O:DMF/MeOH: 9.5:0.5:1, flow rate: 1.0 mL/min).

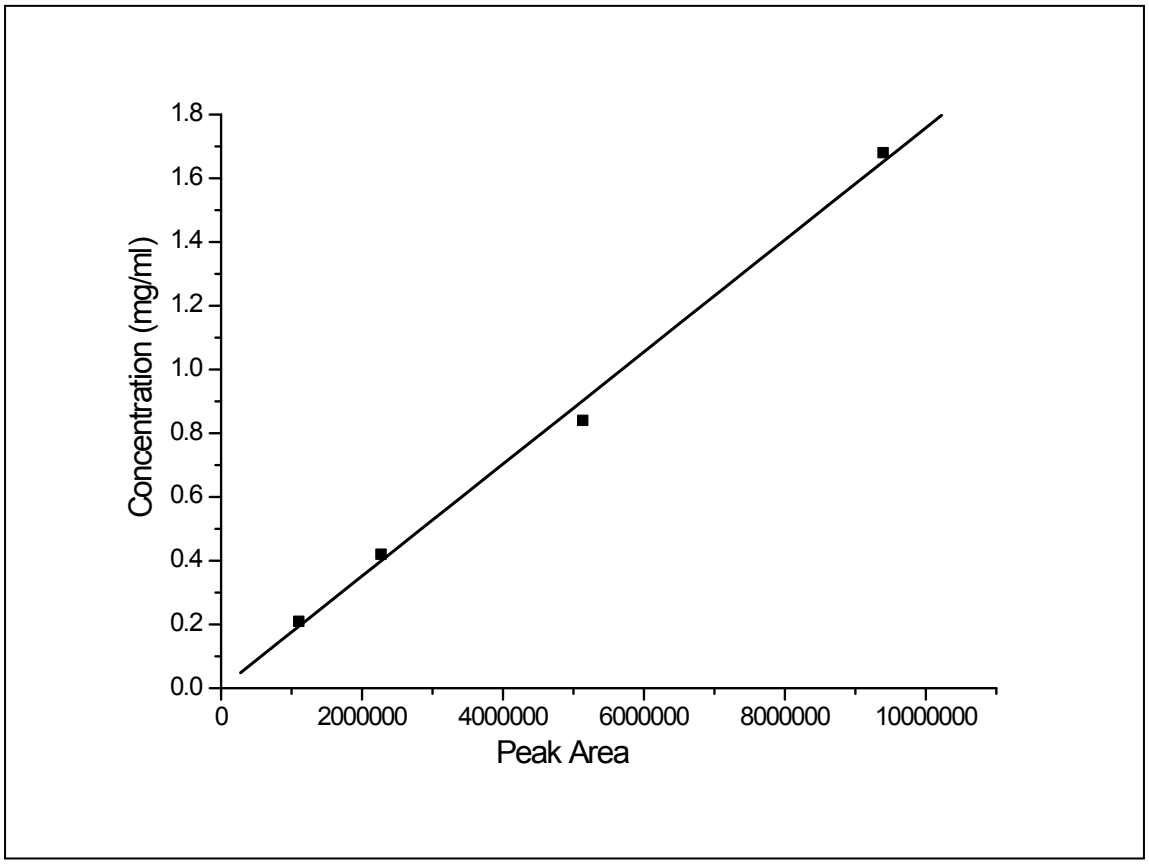


Fig. 3. HPLC-calibration curve for HMF ($Y = (1.76 \times 10^{-3}\ x + 5.2)10^{-4}$

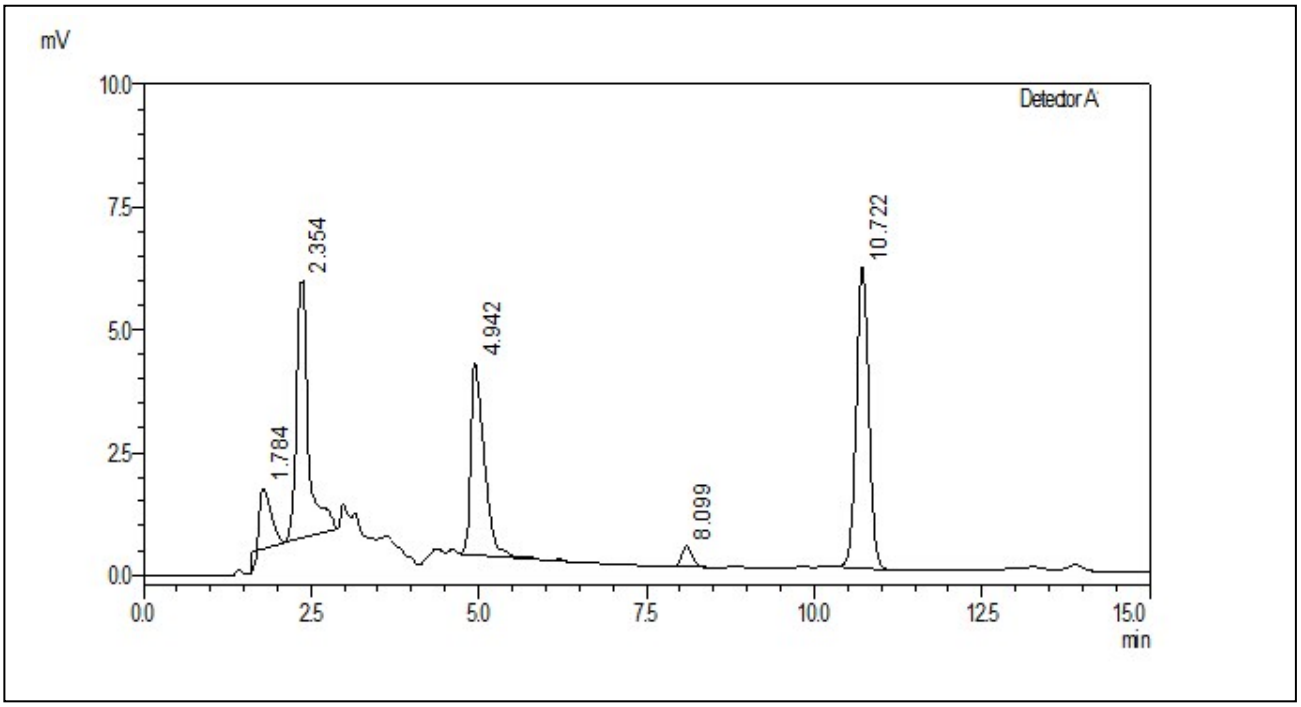


Fig. 4. HPLC spectrum of HMF synthesis using CoFe2O4 nanoparticles

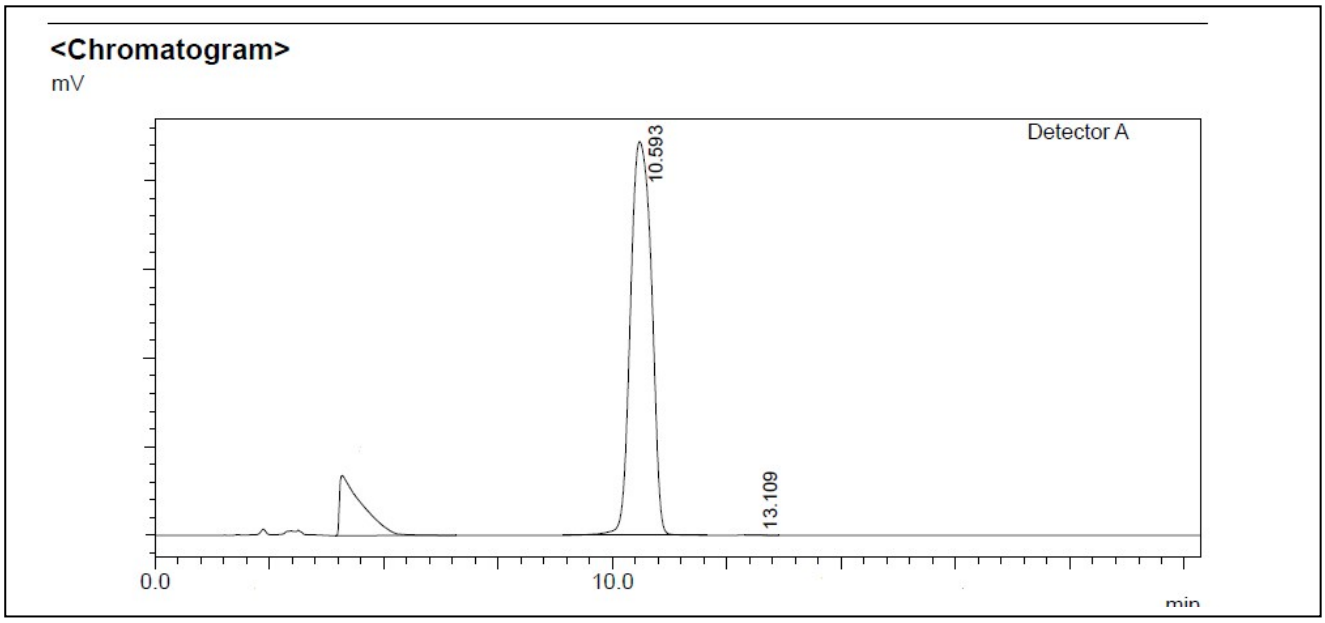


Fig. 5. HPLC spectrum of HMF synthesis using cobalt ferrite decorated CNT nanoparticles

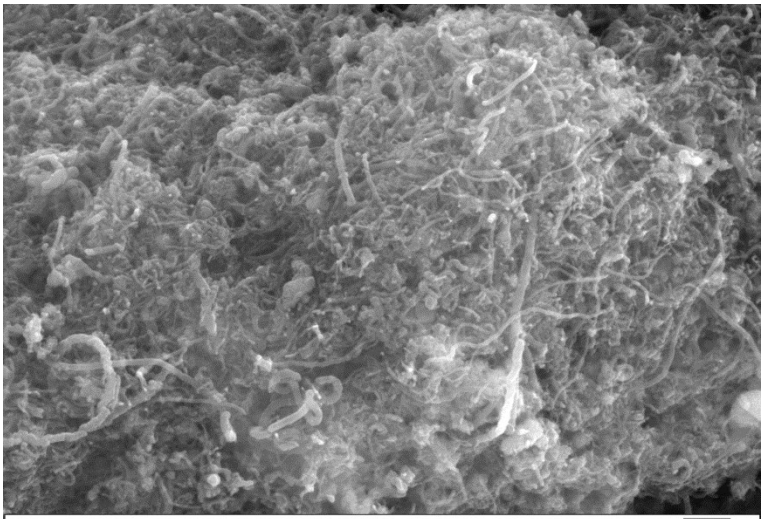


Fig. 6. SEM image of Fe_3O_4-CNT

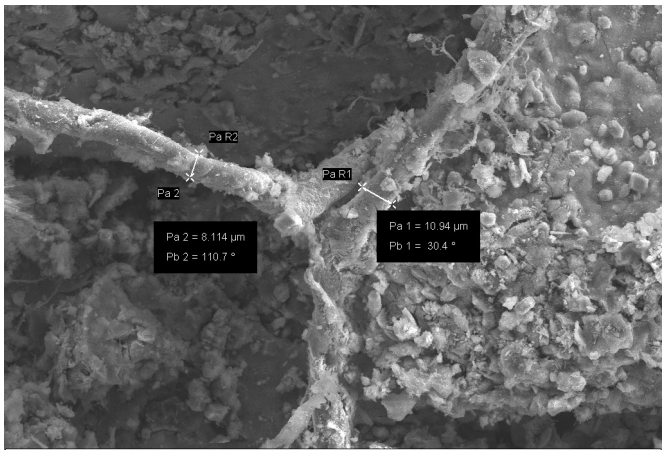
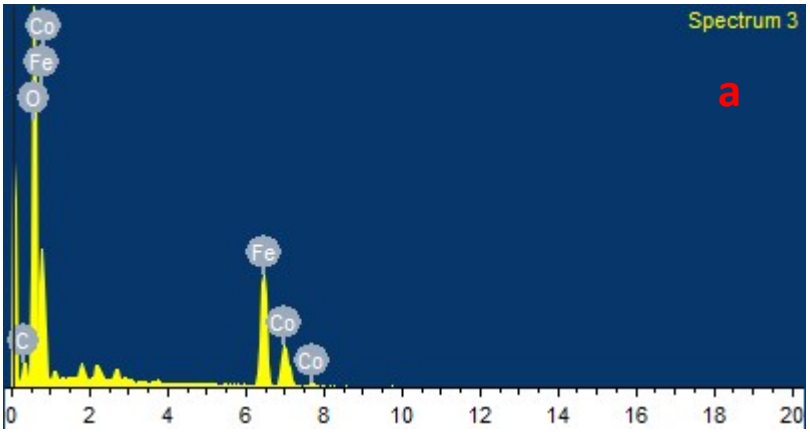


Fig. 7. SEM image of $CoFe_2O_4$-CNT



C 92.12%
O 5.07%
Fe 1.41%
Co 1.4%

Fig. 8. SEM-EDS of $CoFe_2O_4$-CNT

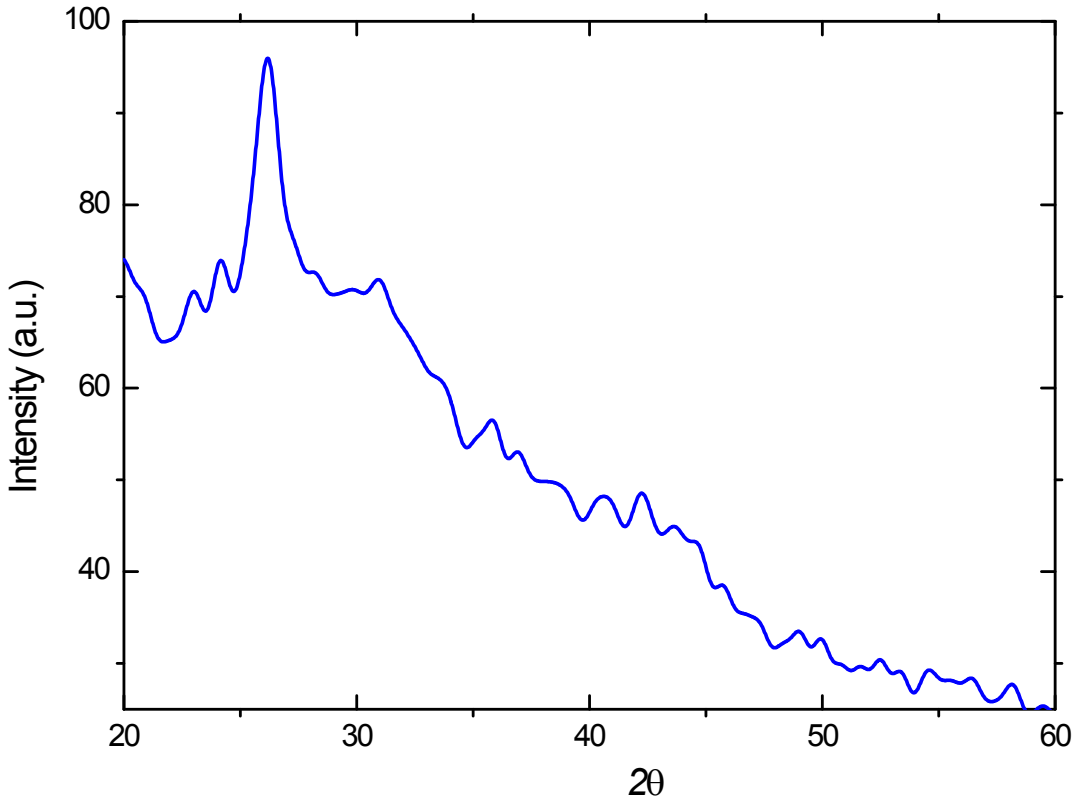


Fig 9. XRD of –COOH functionalized MWNT.

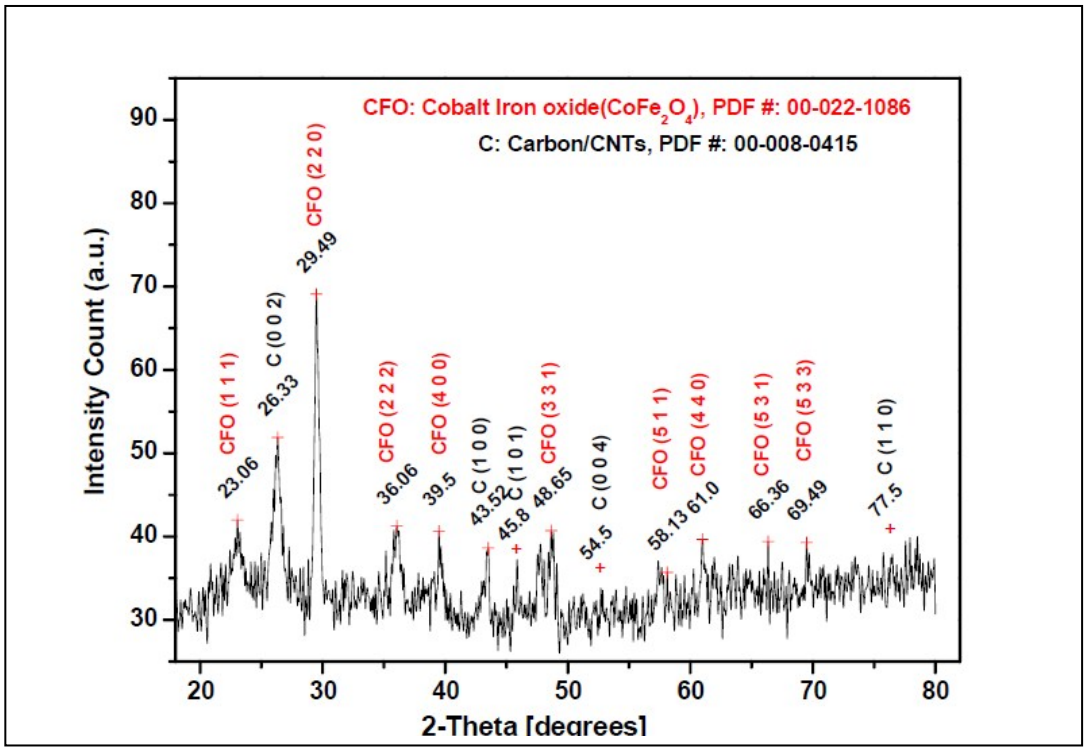


Fig 10. XRD of $CoFe_2O_4$-MWCNT.

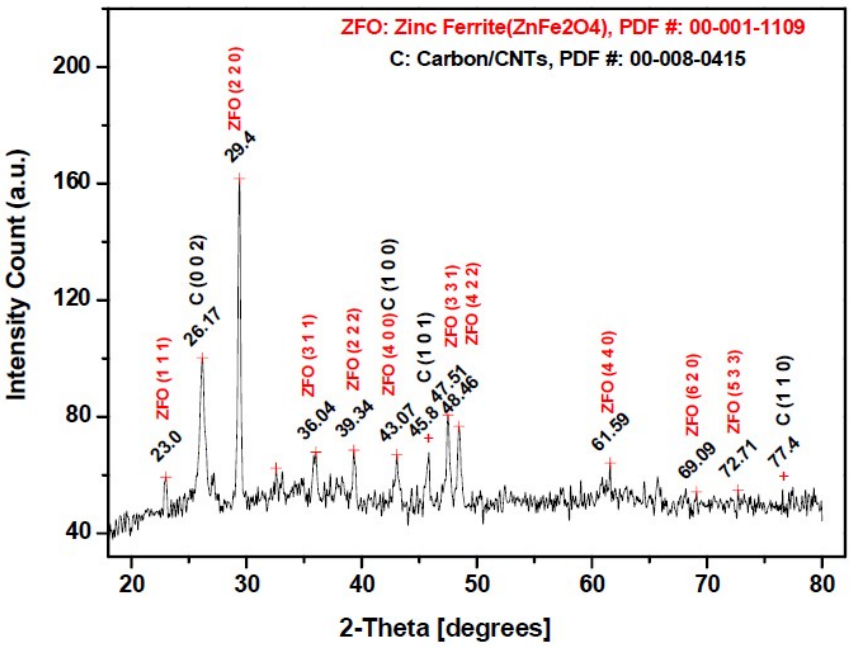


Fig 11. XRD of $ZnFe_2O_4$-CNT.

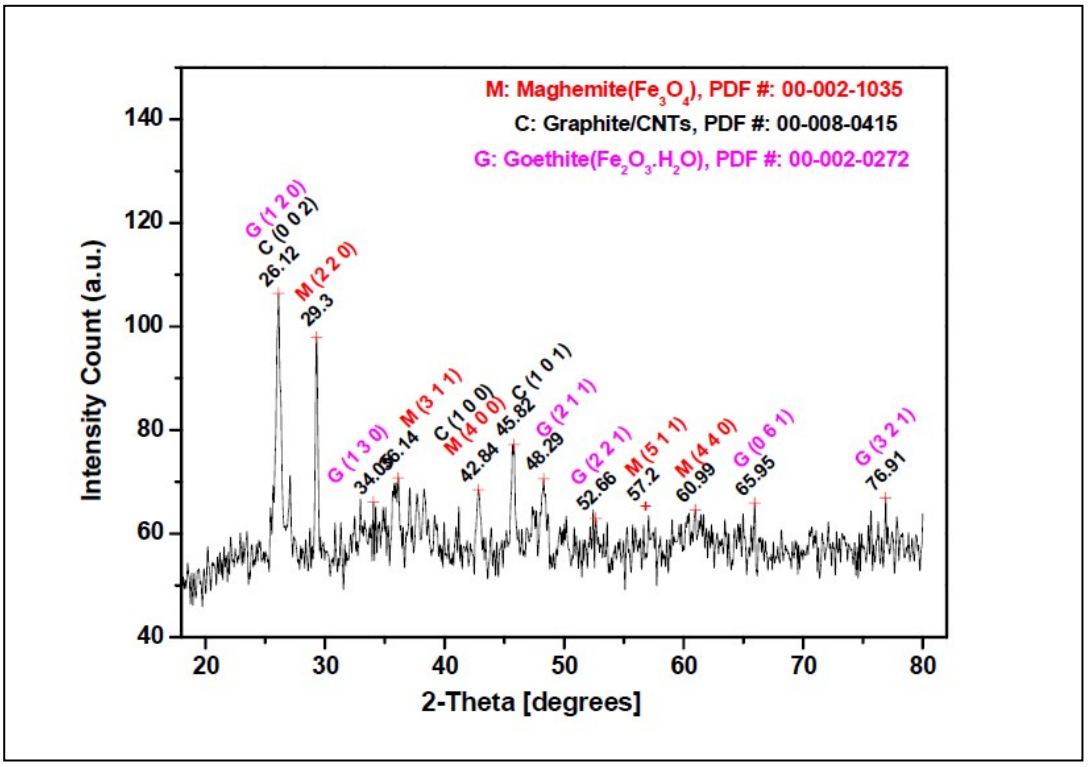


Fig 12. XRD of Fe_3O_4-CNT.

Table 1. XRD of the ferrite decorated CNTs

Sample name	Phase present	Lattice	Space group
Iron oxide on CNTs	Magnetite (Fe_3O_4) + Goethite (Fe_2O_3. H_2O) + Carbon/CNTs	Cubic + hexagonal	Fd-3m+ Pbnm+ P63/mmc
Zinc Iron oxide on CNTs	Zinc Iron oxide ($CoFe_2O_4$) + Carbon/CNTs	Cubic	Fd-3m P63/mmc
Cobalt Iron oxide on CNTs	Cobalt Iron oxide ($CoFe_2O_4$) + Carbon/CNTs	Cubic	Fd-3m P63/mmc