

Supplementary Information

Fabrication and characterization of poly (ethylene oxide) templated nickel oxide nanofibers for dye degradation

Deepika Malwal^a and P.Gopinath^{a,b}*

^aNanobiotechnology Laboratory, Centre for Nanotechnology, ^bDepartment of Biotechnology, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand-247667, India.

EXPERIMENTAL SECTION:

Materials: Poly (ethylene oxide) (PEO, $M_w = 900,000$ g/mol) and Nickel (II) acetate tetrahydrate, $C_2H_4NiO_4 \cdot 4H_2O$ (NiAc, > 99.0 %) were purchased from Sigma-Aldrich, Co. (USA), Congo red ($M_w = 696.68$) was obtained from Himedia (India). Sodium hydroxide pellets (NaOH, $M_w = 40.00$), Polyvinylpyrrolidone (PVP), K-30 with molecular weight 40000 were purchased from SRL (India). Hydrochloric acid (HCl) was obtained from RFCL (India). All the reagents were of analytical grade and used as received without further treatment. Ultrapure water was used in all the experiments.

Fabrication of PEO templated NiO nanofibers: For the fabrication of NiO nanofibers, 4.5 wt % aqueous PEO solution and 20 wt% aqueous nickel acetate solution was mixed in a ratio 3:1 and magnetically stirred at 50°C to obtain a light green colored homogenous solution. This viscous solution was electrospun using a 2 mL syringe with a metal needle, kept at a distance of 15 cm from the collector. The flow rate was optimized to 0.25 mL/h with the applied voltage of 15 kV between the needle and the grounded collector which was covered with aluminium foil or aluminium plate to collect uniform randomly aligned nanofibers. The obtained nanofibers were dried at 60°C for 12 hours in hot air oven which were then calcined at 500°C for 4 hours in the presence of air with a heating rate of 2.3°C/min to obtain NiO nanofibers.¹

Synthesis of NiO nanoparticles: NiO nanoparticles were prepared using nickel acetate tetrahydrate in 60 mL double distilled water. The as-prepared solution was added dropwise in 150 mL solution of NaOH (3g) and polyvinylpyrrolidone (2 g) with continuous stirring (1000 rpm) at room temperature. The resultant light green solution was filtered and then washed with deionized water and ethanol for 5-10 times. It was further dried at 50°C for 24 hours to obtain fine powder which was finally calcined at 450°C for 6 hours in the presence of air resulting in the formation of NiO nanoparticles.²

Characterization of NiO nanofibers and nanoparticles: The surface morphologies of the electrospun PEO/NiAc nanofibers and NiO nanofibers obtained after subsequent calcination were examined using FE-SEM operating at a voltage of 20 kV. Prior capturing the micrographs, all the samples were sputter-coated with gold thin film. The samples were investigated for their elemental composition using energy dispersive x-ray spectroscopy (EDX) equipped with FE-SEM. The cross sectional micrographs of NiO nanofibers and NiO nanoparticles were obtained using TEM (FEI TECHNAI G2 and JEOL 2100 UHR-TEM) with operating voltage of 200 keV with machine resolution 0.4 nm. The TEM sample preparation involves the dispersion of nanofibers and nanoparticles in 1 mL ethanol using bath sonication for 10 min separately. 10-20 μ L of the as-prepared sample was dropped onto the non-shining side of the carbon coated copper grids. The crystalline nature of the sample was also evaluated using selected area electron diffraction (SAED) patterns obtained from TEM. The diameter distribution histograms to estimate the mean diameter along with standard deviation (σ) for nanofibers and nanoparticles were constructed using image analysis software Image J. Followed by this, the structural information of the nanofibers and nanoparticles were extracted from XRD pattern recorded by Bruker AXS D8 Advance powder X-ray diffractometer using Cu-K α radiation ($\lambda = 0.15406$ nm). The samples were scanned in the range 0-90° with a scan rate of 0.5°/min. Thermal decomposition studies were performed using thermal gravimetric analyzer. About 10 mg sample was placed on an aluminium pan and heated up to 600°C with a constant heating rate maintained at 10°C/min. Air was constantly supplied with the inflow rate of 100 mL/min during the test.

Evaluation of photocatalytic property and stability of NiO nanofibers: The dye degradation batch experiment was performed with initial concentration of 60 ppm congo red dye (CR) aqueous solution. To evaluate the photocatalytic activity of the NiO nanofibers, 6 mg

photocatalyst was added to the CR solution (60 ppm) and observed the decoloration under visible light ($\lambda > 420$ nm) irradiation for 9 hours at room temperature. Sample aliquots of 1-mL were collected intermittently during the irradiation and analyzed using UV-Visible double beam spectrophotometer (Lasany, LI-2800). The sample was scanned in the range of 220-700 nm and the data was analyzed using software “UV-VIS Analyst” equipped with the instrument. The concentration of the dye can be correlated with the absorbance by plotting a calibration curve between different concentrations of dye (ppm) vs absorbance as represented in the fig. S1.

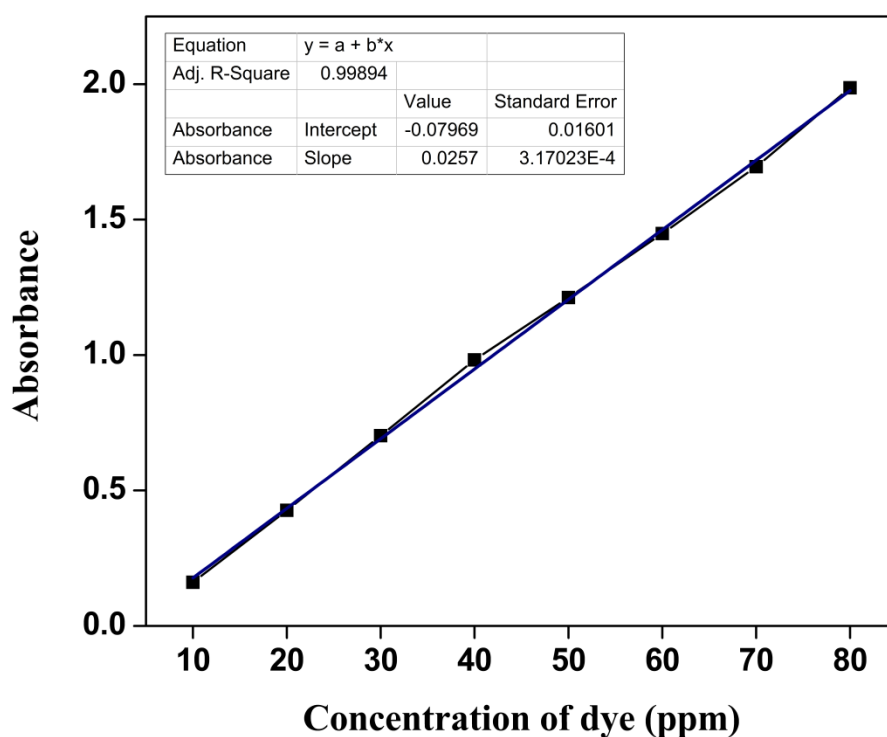
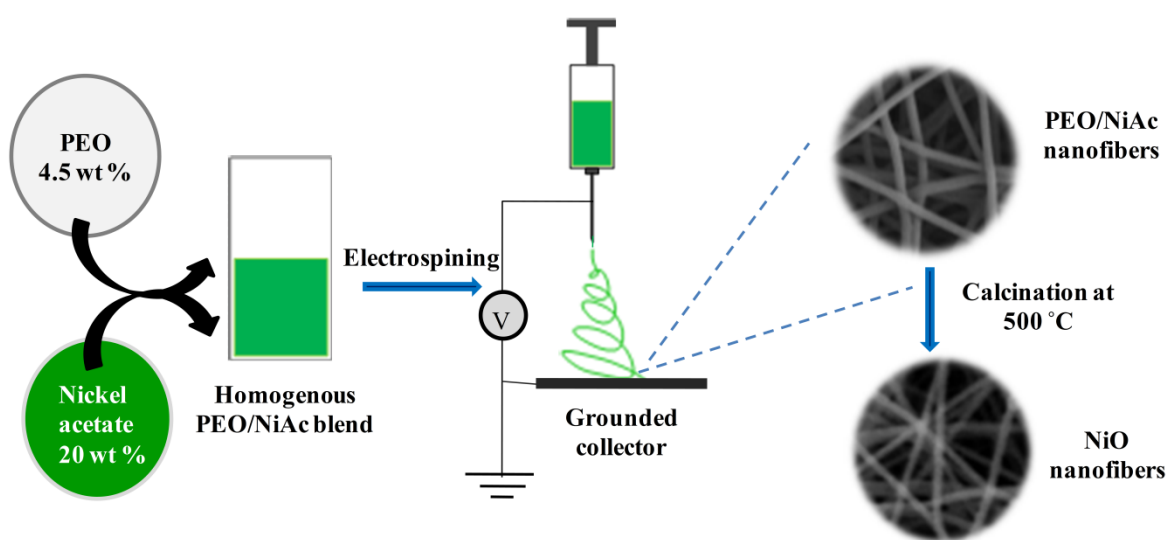


Fig. S1 Calibration curve for CR dye to calculate the concentration of dye using absorbance obtained by UV-Vis spectrophotometer; inset represents the equation along with the R-square value and standard error.

The photocatalytic activity depends on various factors like concentration of dye, amount of the photocatalyst loaded etc. Therefore, the effect of amount of NiO nanofibers to be added was also investigated using 2 mg, 4 mg and 6 mg nanofibers with the same concentration of dye. The rate constants for the degradation reactions were calculated by determining the type of the kinetics

followed by the reaction. In addition to this, the photocatalytic activity of NiO nanofibers was compared with the corresponding nanoparticles. 2.12 mg of nanofibers and nanoparticles were added to different batches of dye having the same concentration of dye (60 ppm) and analyzed for 72 hours under visible light irradiation. Auto-degradation property of CR in the presence of light was also examined. Finally, reusability studies were performed by using the same nanofibers for three batches of 60 ppm dye solution along with the observation in the morphology of the used nanofibers using FE-SEM. Along with this, effect of pH on the stability of the nanofibers and leaching of nickel in the treated water was also investigated using AAS. Five dye solutions with same concentration of dye were prepared with different values of pH i.e. 3, 5, 7, 9 and 11. Various pH was set with the help of 0.1 N HCl and 0.1 N NaOH.



Scheme S1 Schematic representation of the fabrication of NiO nanofibers using electrospinning technique with subsequent calcination.

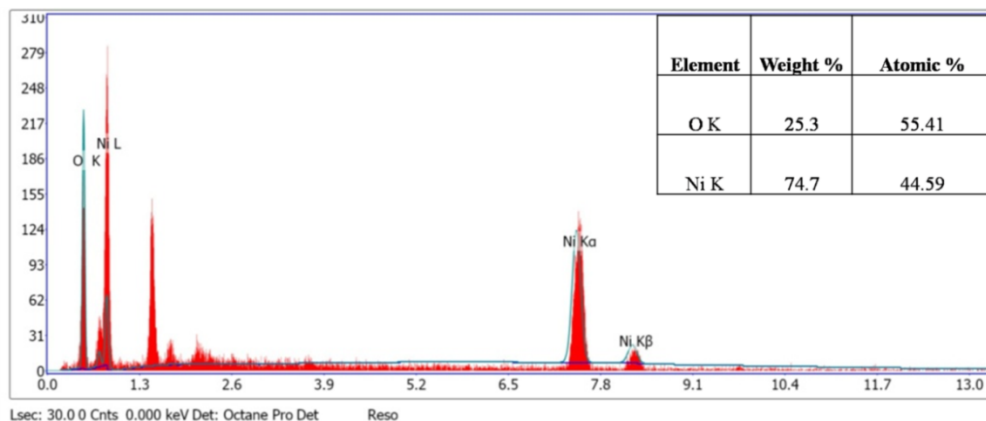


Fig. S2 EDX spectrum and EDX data (inset) representing the elemental composition of calcined NiO nanofibers.

Amount of NiO nanofiber loaded	Rate constant (h ⁻¹)
2 mg	1.67 X 10 ⁻¹
4 mg	3.46 X 10 ⁻¹
6 mg	5.63 X 10 ⁻¹

Table S1 Rate constants evaluated for different concentration of the photocatalyst loaded for photodegradation reaction.

S. No.	pH of the CR solution	Concentration of Ni leached (µg/mL)
1.	3	1.837
2.	5	0.161
3.	7	0.013
4.	9	0.024
5.	11	0.052

Table S2: concentration of nickel released in the treated water at different pH conditions.

References:

1. N. A. M. Barakat, B. Kim, H. Y. Kim, *J. Phys. Chem. C*, 2009, **113**, 531.
2. Y. B. M. Mahaleh, S. K. Sadrnezhaad, D. Hosseini, *Journal of Nanomaterials*, 2008, **470595**, 1.