

Multi-function NiFe₂O₄ Nanoparticles for Sodium-ion Battery, Sensing and photocatalysis

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Chemicals required

All the precursors used in this synthesis were of analytical grade. Nickel nitrate hexahydrate [Ni(NO₃)₂·6H₂O, >98%], Ferric nitrate nonahydrate [Fe(NO₃)₃·9H₂O, >99%], methyl orange and Evan's blue from SD fine chem. limited, sodium hydroxide pellets from Merck private limited. Oleic acid used as a surfactant. Dilute Hydrochloric acid used to maintain the pH in degradation process. Uric acid (UA) and silicone oil (as binder) were purchased from Himedia. A stock solution of UA (25×10⁻⁴M) was prepared in double deionized water. Graphite powder (50µm particle size) was purchased from Loba. All chemicals were of analytical grade. The chemicals for the preparation of buffer solution were purchased from Merck. The 0.2M phosphate buffer solution was prepared by mixing standard stock solutions of 0.2M NaH₂PO₄·H₂O and 0.2M Na₂HPO₄. All the solutions were freshly prepared prior to analysis. All the other solutions were prepared using double distilled water.

Synthesis of NiFe₂O₄ nanoparticles

A typical preparation method used to obtain the precursors for the synthesis of nickel ferrite nanoparticles by chemical co-precipitation method is the following: Fe(NO₃)₃·9H₂O and Ni(NO₃)₂·6H₂O. Each starting molar ratio of metal salts was weighed and dissolved in distilled water. The sodium hydroxide (0.2 M) used as a precipitating agent; it was added drop wise to the above salts solution until the solution of pH reaches 10. The 2-3 drops of oleic acid were added as a surfactant to

the above solution. The precipitation occurs in a reacting solution and then taken to a reaction temperature of (about) 90 °C with constant stirring about one hour. At that time, the solution was allowed to room temperature and kept for constant stirring about 3-4 hours. The obtained sample was washed 3-4 times with distilled water and ethanol by centrifugation method (3000 RPM) in order to remove the surfactant and excess or unreacted sodium hydroxide solution. The centrifuged sample was dried overnight in a furnace at 60 °C to remove the moisture and impurities. Then the dried sample was grinded well in the mortar and calcinated at 600 °C about 4h.

Characterization

The morphology and structure of the nanoparticles were inspected by field emission scanning electron (FESEM) (CARL Zeiss) and high-resolution transmission electron microscopy (HRTEM) (Jeol/JEM 2100, Source LaB6). The chemical composition and elemental distribution were calculated by emission dispersive spectra (Oxford Xmax80 LN2 free). The crystallite size, structure, and phase were studied by powder X-ray diffraction (XRD) analysis (Shimadzu-7000 X-ray diffractometer, Cu K α radiation and Ni filter with $\lambda = 1.5418 \text{ \AA}$). Formation of Metal-Oxygen (M-O) bond analyzed by Fourier transform infrared spectroscopy (FTIR) (Bruker alpha-P spectrophotometer) in the wavenumber region of 350-4000 cm^{-1} . The optical properties of the sample were examined via UV-Vis diffuse reflectance spectrophotometer (UV-Vis DRS) (Reflectance mode by Agilent technology Cary-60). The surface area of the samples was measured by physical adsorption of N₂ at 77.35 K using Brunauer–Emmett–Teller (BET) surface analyzer (Nova-1000). UV-Vis absorption spectrophotometer at room temperature (Agilent technology Cary-60) was used to measure absorbance of organic dyes in degradation process. Electrochemical experiment (cyclic voltammetry) was conducted on model CHI-660C model (CH instrument-660 electrochemical workstation). A conventional three electrode system was used in a single compartment electrochemical cell with platinum as counter electrode, saturated calomel electrode (SCE) as a reference electrode, and bare carbon paste electrode or nanoparticles modified carbon paste electrode as working electrode.

Electrochemical Measurements:

NiFe₂O₄ Nps was probed as SIB anode and its electrochemical properties were characterized in coin cell configuration (CR2032, Hohsen Corporation, Japan) having both reference and counter electrode as sodium (Aldrich) metal. A slurry of active material, Super P black (Aldrich) and sodium carboxymethyl cellulose (CMC, Aldrich) in the weight ratio 75:15:10 was prepared. Then, it was evenly coated on a pre-treated copper foil and dried at 110 °C for overnight in a vacuum oven. The pre-treatment of Cu foil was carried out by etching the foil in 5 N HNO₃ and then washing it with a plenty of DD water, followed by acetone and finally drying in air. 1 M NaPF₆ (Aldrich) dissolved in ethylene carbonate and propylene carbonate (1:1 v/v) (Aldrich) was used as electrolyte and Whatman filter paper (Aldrich) as a separator.

The coin cells were fabricated in argon filled glove box. Cyclic voltammetry and galvanostatic charge-discharge cycling testing were performed in the voltage window 0.01–3.00 V using Biologic Science BCS-8xx series. All the electrochemical experiments were carried out in an air-conditioned room at 22 ± 1 °C.

Preparation of bare carbon paste electrode

The bare carbon paste electrode (BCPE) was prepared by manual grinding, graphite Powder and silicone oil at a ratio of 70:30 (w/w) in an agate mortar for about 30 minutes to get a homogenous carbon paste. A small amount of obtained paste was packed into the cavity of a homemade electrode and then polished the surface by rubbing on a weighing paper.

Preparation of nickel ferrite modified carbon paste electrode (NiFe₂O₄ MCPE).

The modified carbon paste electrode was prepared by manual grinding of nickel ferrite, 70:30 (w/w) graphite powder and silicone oil in an agate mortar to get homogenous paste. The obtained paste was packed tightly into the cavity of a homemade electrode and then polished the surface by rubbing on a weighing paper.

Photodegradation setup

Photocatalytic procedures for dye degradation were examined during the summer season under natural solar light radiations in the month of February at Tumakuru. In a typical liquid-phase decomposition of organic dye experiment, 25 mg of the NiFe₂O₄ catalyst in 100 mL aqueous solution containing mixed dyes EB and MO for degradation. Before irradiation, the mixed dye solution was kept in dark place about 1 h with constant stirring to reach a well adsorption-desorption equilibrium between the catalyst and organic dyes. A natural solar light was chosen as a light source to afford the illumination of radiation and trigger the photocatalytic reactions. The NiFe₂O₄ sample was uniformly distributed in the aqueous solution by constant stirring during the light irradiation. At a given time of irradiation during photodegradation reaction, an approximately 3 mL aqueous solution was collected and centrifuged to separate the photocatalyst. The concentration changes in mixed dye solution (collected samples) were monitored by the UV-visible absorption spectrophotometer.

Mechanism of photodegradation

Figure S2: shows the mechanism of photodegradation under solar light irradiation. The electrons can be excited from the valence band (VB) to the conduction band of NiFe₂O₄, at the same time the same number of holes are created in the VB. The photoinduced holes directly react with organic dyes or can interact with the surface bound H₂O or OH⁻ to generate the OH· radicals species that are very strong oxidant for the degradation of organic dyes. In the interim, the electrons that are formed can react with

the adsorbed molecular oxygen to yield O_2^- . The generated O_2^- then further combine with H^+ to produce $HOO\cdot$ which can react with the trapped electrons to generate $OH\cdot$ radicals. All the reactive species such as holes, O_2^- , $HOO\cdot$ and $OH\cdot$ could oxidize organic pollutants to some degree.

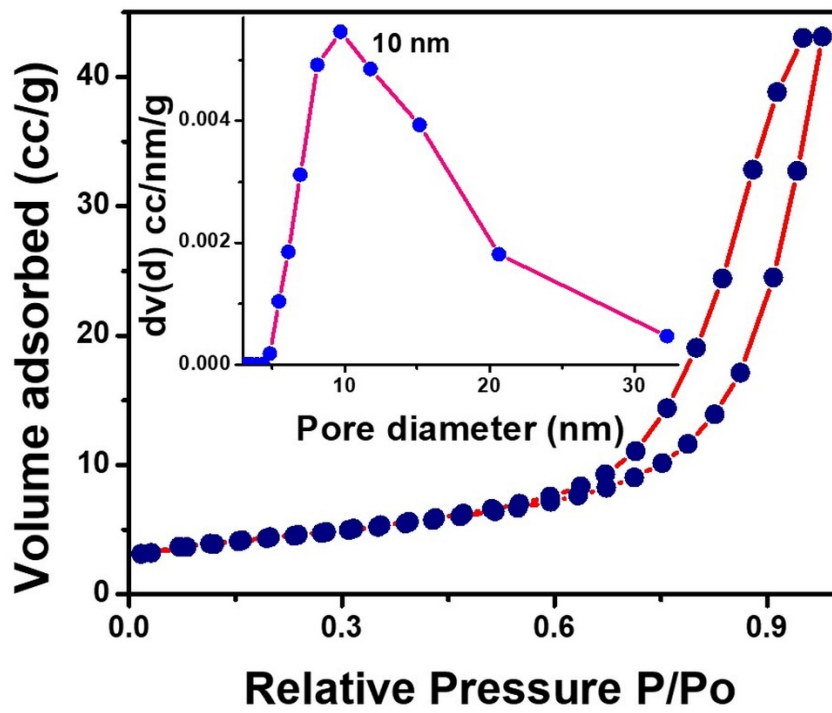


Figure S1: N₂ adsorption-desorption isotherm and pore size distribution (insert) of NiFe₂O₄ NPs.

Figure S2: Mechanism of photodegradation of organic dye under solar light irradiation.