

Supporting Information

Bifunctional hexagonal Ni/NiO nanostructures: Influence of core-shell phase on magnetism, electrochemical sensing of serotonin and catalytic reduction of 4-nitrophenol

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Experimental section

Materials

Nickel acetate tetrahydrate, ammonium carbonate, ethylene glycol (EG), hydrazine hydrate, 4-nitrophenol (4-NP), sodium borohydride were purchased from SRL India Ltd., and serotonin (5-hydroxytryptamine or 5-HT) were purchased from Sigma-Aldrich, used as received. For the preparation of buffer solution, disodium hydrogen phosphate, sodium dihydrogen phosphate, acetic acid, sodium acetate, hydrochloric acid, potassium chloride, sodium hydroxide, and ethanol were purchased from Merck and DD water as solvent.

Synthesis of the Ni/NiO nanostructures:

Ni/NiO nanostructures are prepared by reacting stoichiometric amount of aqueous 0.01 M nickel acetate and 5 % ethylene glycol homogenized for 10 min. After few seconds the pale-green Ni-glycol micelles were formed. The reaction mixture turned to purple after slow addition of 1 mM hydrazine hydrate, which turns to bluish while adding aqueous 0.01 M ammonium carbonate mixture with 0.1:1 ratios. This suspension was stirred for 20 min at 60 °C in magnetic stirrer. Further, the reaction mixture was directly transferred to silica boat and then evaporated in hot plate for combustible redox reaction. Temperature increased till the sample mixtures get ignited and once the complete combustion is over, immediately samples should be removed from the hot plate to arrest the complete oxidation. This reaction mixture is too vigorous and explosive, when we use nickel nitrate instead of nickel acetate. The resulting black spongy powder (as-combusted or Ni-C) was heated in a muffle furnace at 300 °C, 400 °C, and 500 °C for 10 min to improve the crystalline nature.

Characterization techniques

The crystal structure, grain size and lattice parameter of the sample was determined by Rich Siefert 3000 diffractometer with Cu K_{α1} radiation ($\lambda = 1.5406 \text{ \AA}$). XPS measurements were performed by Omicron nanotechnology, GMBH, Germany, with a XM-1000 monochromatic Al K_α source (1483 eV) operated at 300 W (20 mA emission current, 15 kV) and a base pressure of 5×10^{-5} mbar. The survey scan was performed with a step size of 0.5 eV along with 50 eV as the pass energy. The high-resolution scan was done with 0.03 eV as the step size and 20 eV as the pass energy with three sweep segments. Raman spectrum was recorded using laser confocal microscope, Raman-11 Nanophoton Corporation, Japan. The DRS-UV absorbance spectrum was recorded using Perkin Elmer lambda650 spectrophotometer. The morphology of nanopowder was

analyzed by HITACHI SU6600 (FE-SEM) field-emission scanning electron microscopy coupled with EDAX and TEM using a FEI TECNAI G2 model T-30 at accelerating voltage of 200 kV. The magnetic properties were measured at room temperature using vibrating sample magnetometer (Lakeshore 7404, USA).

Electrochemical sensing of 5-HT:

Electrochemical measurements were performed at 298 K using a CHI 1103A. A three electrode cell was used with a saturated calomel electrode (SCE) as reference electrode, platinum wire as counter electrode and the modified glassy carbon electrode (GCE) as the working electrode. The CV and DPV studies were performed at various potential windows at the scan rate of 50 to 500 mVs^{-1} in 0.1 M N_2 saturated phosphate buffer solution. The modifying process of the electrode was followed by literature method. The catalyst suspension was prepared by dispersing 2 mg of sample in 5 mL of ethanol using ultrasonication for 10 min. The 5 μL of the above suspension was spread on the highly polished GCE surface from the aliquots and dried at room temperature. Various (2-9) pH solutions were prepared by mixing the stock solutions: 0.1 M HCl and 0.1 M KCl were used to prepare pH (1-2) buffered saline, acetic acid-buffered saline (ABS, pH 3-5) adjusted with 0.1 M CH_3COOH , 0.1 M CH_3COONa , and phosphate-buffered saline (PBS, pH >6) was prepared by mixing of Na_2HPO_4 , 1.36 g of NaH_2PO_4 , and NaOH into 1 L of deionized water.

Catalytic reduction of 4-nitrophenol:

Aqueous suspension of Ni/NiO nanoparticles (5mL, 0.4 g/L) was added to NaBH_4 aqueous solution (5 mL, 0.3 M), and the mixture was stirred for 10 min at room temperature. 4-nitrophenol (5 mL, 0.003 M) was then added to the mixture, which was stirred until the bright yellow gradually changed to colorless (**Fig. S2, S3**). The reaction progress was monitored by measuring UV-Vis absorption spectra. To study the catalyst durability, the catalyst was centrifuged after reaction for 60 minutes, and the clear supernatant liquid was decanted carefully. The catalyst was washed thoroughly with water and ethanol, followed by drying at 60 °C for 6 h in vacuum oven. Then, the catalyst was reused for subsequent recycle under the same reaction conditions.

1. XPS Studies

The binding energies (E_B) of obtained spectra were charge corrected by referencing the C 1s peak to 284.6 eV. The deconvoluted C 1s spectrum in the range of 281-290 eV is showed in **Fig. S1(a,c)**.

The O (1s) core level spectra of binding energy vs. intensity were shown in **Fig. S1(b, d)**. It can be noticed that the two peaks with binding energies of 528-535.7 eV are due to hybrid metal oxide (Ni-O) and surface hydroxyl group respectively. The presence of surface hydroxyl group was due to the hygroscopic character of the metal oxide.^{29, 30}

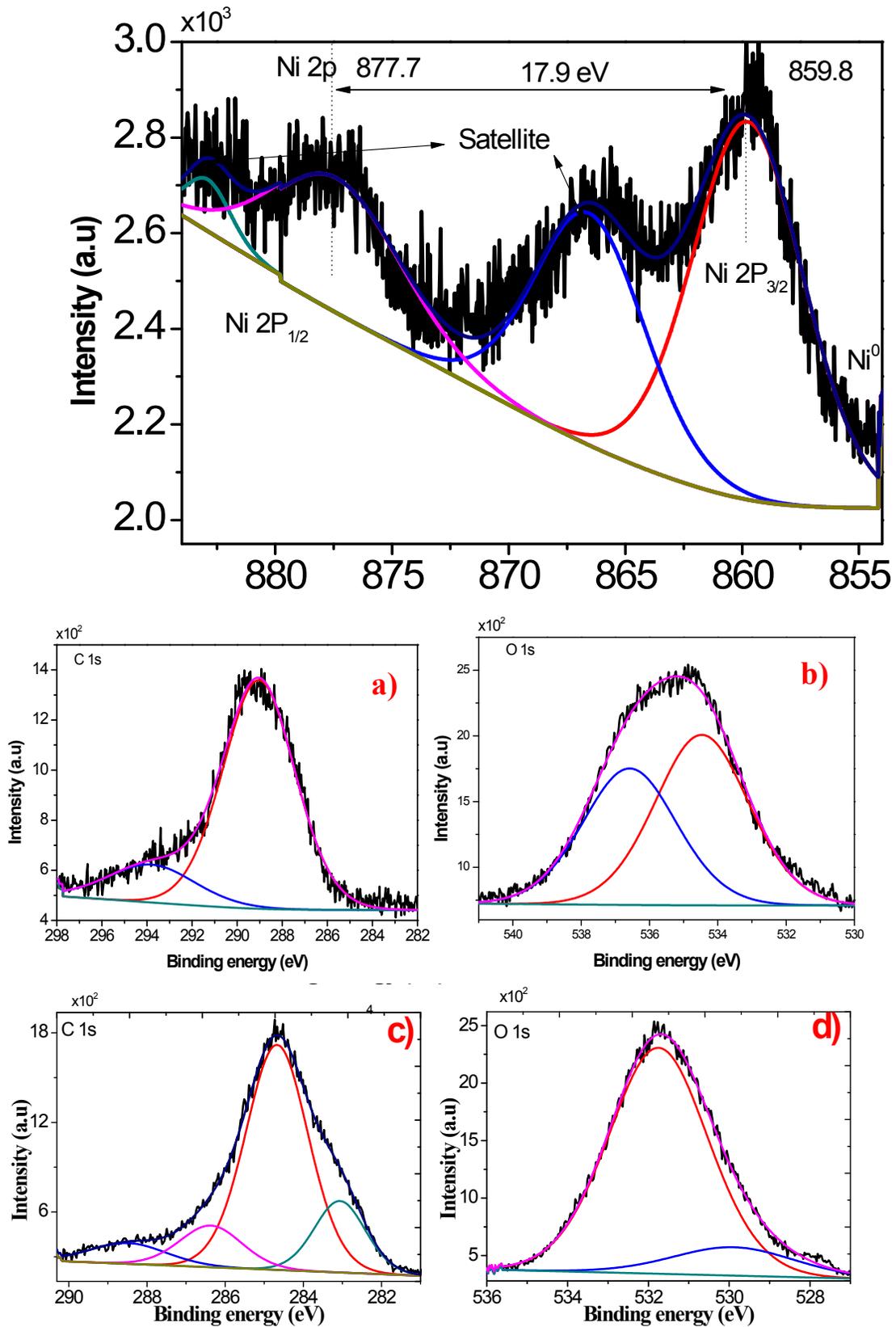


Fig. S1) XPS core level emission of a) carbon b) oxygen for NiO-500 c) carbon

d) Oxygen for Ni-C (Ni/NiO).

FTIR and TG-DTG analyses:

Herein, N-N containing hydrazidocarbonic derivatives could be the reason behind the combustible behaviour, which were identified by the characteristic FTIR results (**Fig. S2**). The convoluted peaks at 836, 1085, 1392 and the band around 1044 in the finger print region are corresponds to the C-O and N-N bonds (hydrazinocarboxylate salts), respectively. Moreover, broad spectrum observed around 1600-1650 cm^{-1} , 3200–3500 cm^{-1} is attributed to N-H vibration and in this same region O-H vibration also having transmittance. Furthermore, thermo gravimetric analysis (**Fig. S3**) shows two significant decomposition peaks in between the temperature range of 50 to 300 $^{\circ}\text{C}$ attributed to endothermic dehydration and decomposition of metal hydrazinocarboxylate, are in good agreement with the reports^{xx}.

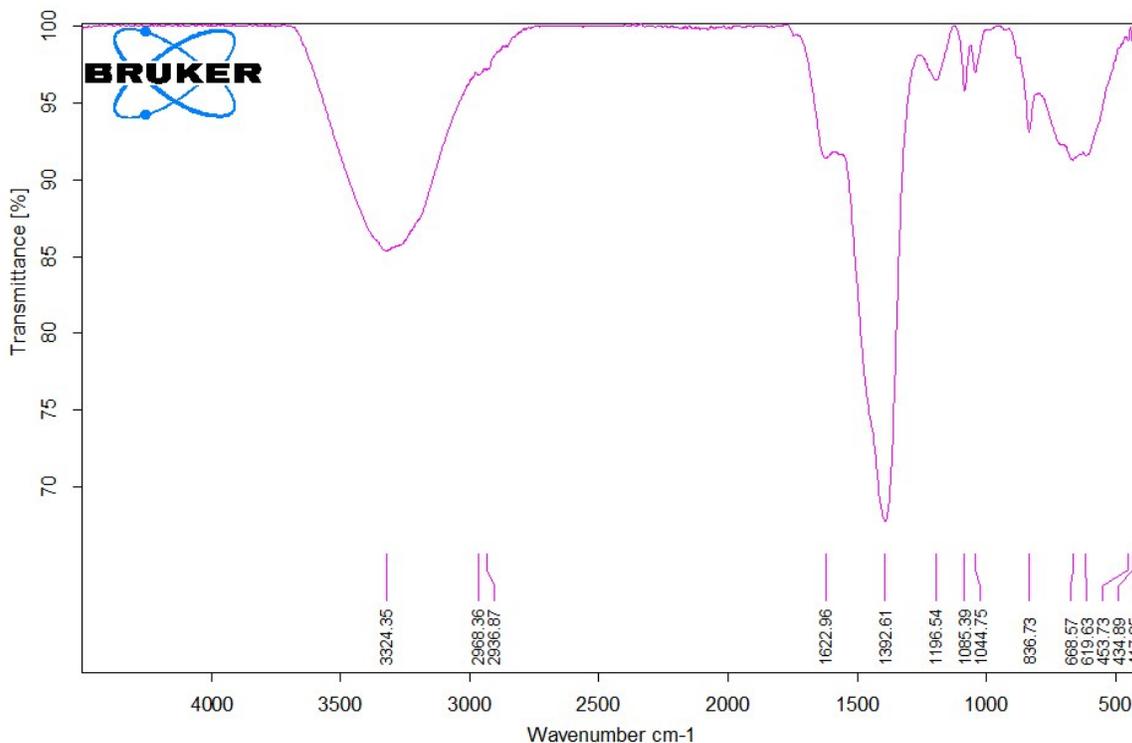


Fig. S2: FTIR spectrum of precursor

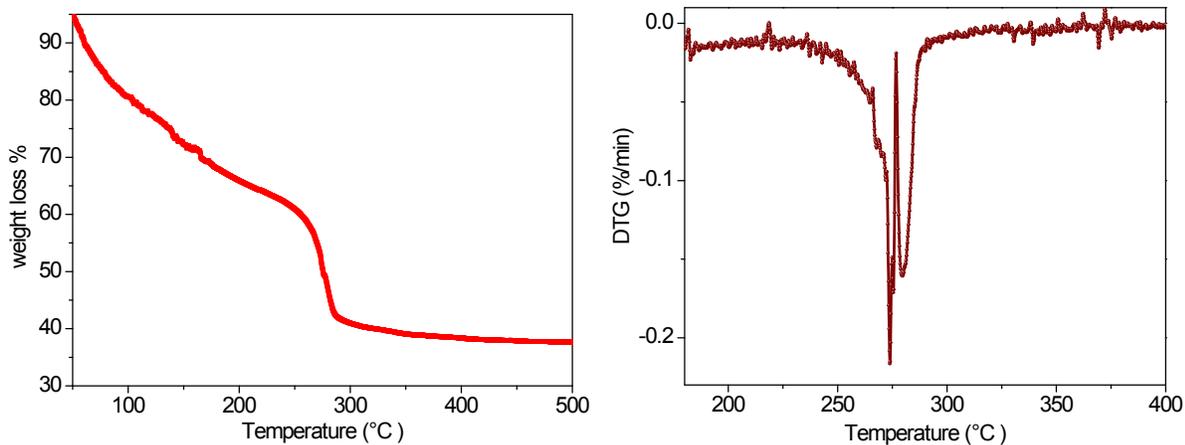


Fig. S3: TGA and DTG of precursor

Catalytic reduction of 4-nitrophenol:

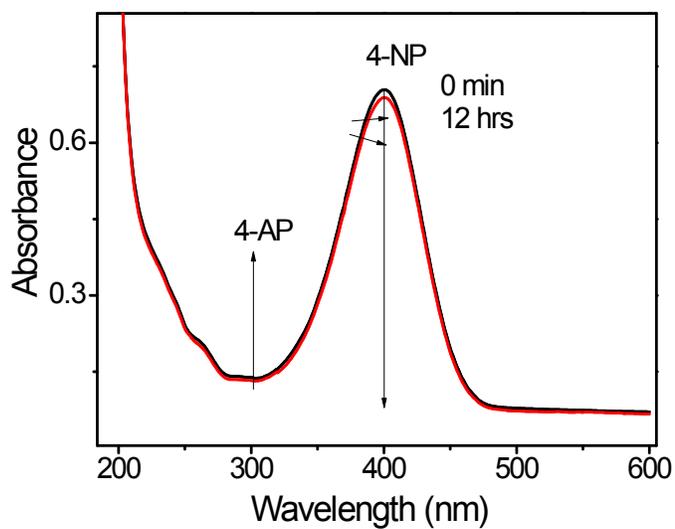
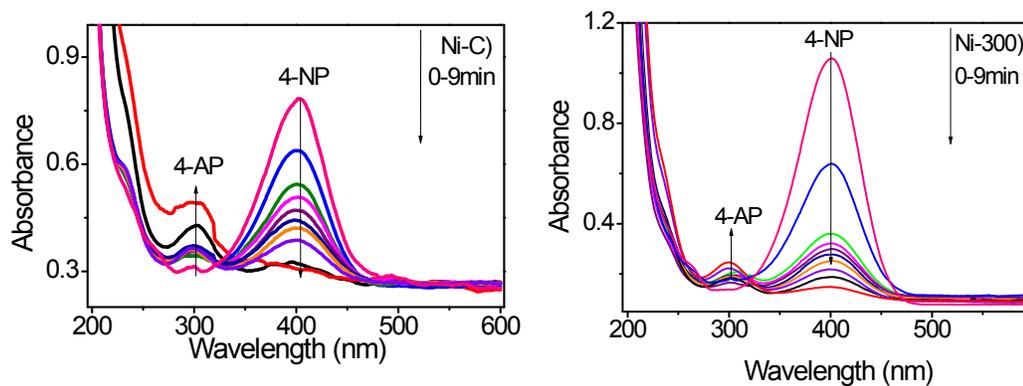


Fig. S4) UV-Vis spectra of aqueous 4-NP reduction in the absence of catalyst



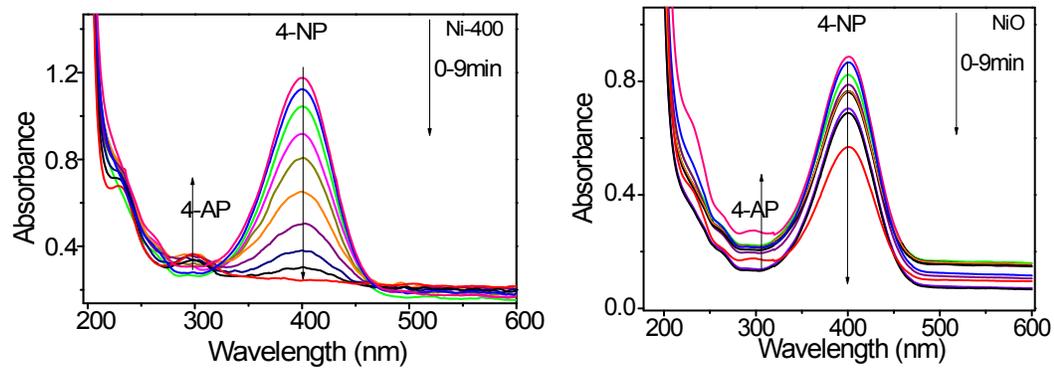


Fig. S5) Time-dependent UV-visible spectra for the catalytic reduction of 4-NP