

Supporting information

Surface Chemistry Modulated Introduction of Multifunctionality within Co₃O₄ Nanocubes

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Experimental Section

1.1. Materials Used

Methylene blue (MB), sodium hydroxide (NaOH), 2-amino-purine (2AP), 4', 6-diamidino-2-phenylindole (DAPI), Hoechst 33258, and Rhodamine B (RhB) were obtained from Sigma-Aldrich. Co (II) acetate, and bilirubin (BR) were received from Loba Chemie. Tartaric acid, ethanol, ammonia and potassium bromide were purchased from Merck. All the reagents were of analytical grade and used without further purification.

1.2. Synthesis procedure and functionalization of Co₃O₄ NCs

Co₃O₄ nanocubes (NCs) were synthesized by solvothermal route following a previous report¹ with some modification. In a typical procedure, 0.70 g of Co (CH₃COO)₂ · 4H₂O was dissolved in 35 ml of ethanol, and 12 ml of 25% ammonia was added under vigorous stirring. The mixture

was stirred in air for about 10 min to form homogeneous slurry. Then the suspension was transferred into a 50 ml teflon lined autoclave, sealed and maintained at 150 ° C for 3 h. Then, the autoclave was cooled to room temperature naturally. The resulting black solid products were washed with water followed by ethanol via centrifugation redispersion, dried at 60 ° C over a hotplate, and collected for characterization. As-prepared Co₃O₄ NCs were cyclomixed with 0.5 M Na-tartrate solution (prepared in Milli-Q water and pH of the solution were made ~ 7) for 12 h at room temperature. The non-functionalized larger Co₃O₄ NCs were filtered out with a syringe filter of 0.22 μm diameter. The as obtained colorless filtrate was tartrate functionalized Co₃O₄ NCs. To induce the multicolor fluorescence property, functionalized Co₃O₄ NCs were heated at about 70 °C for 15 h under extensive stirring condition maintaining the pH of the solution at ~12 with drop wise addition of NaOH solution. After this high pH and temperature treatment, color of the solution turned to yellow and showed intense fluorescence under UV light (inset of Figure 4a). To prepare the solid powdered samples required for magnetic study (Vibrating sample magnetometry, VSM) and fourier transform infrared (FTIR) spectroscopic measurements, we dialyzed functionalized Co₃O₄ NCs solution (to remove excess ligands) and lyophilized followed by drying over a water bath.

1.3. Characterization techniques:

XRD (x-ray diffraction) patterns were obtained by employing a scanning rate of 0.02° s⁻¹ in the 2θ range from 20° to 80° by Rigaku miniflex II diffractometer equipped with Cu K_α radiation (at 40 mA and 40 kV).

For TEM study samples were prepared by drop casting as-prepared and annealed Co₃O₄ NCs dispersed in EtOH and water soluble functionalized Co₃O₄ NCs on a 300-mesh carbon

coated copper grid and dried overnight in air. Particle size was determined from TEM micrographs and elemental analysis was performed from EDX spectrum recorded by a FEI Tecnai TF-20 field-emission high resolution transmission electron microscope operating at 200 kV.

UV-visible absorbance spectra of the functionalized Co_3O_4 NCs were recorded with a Shimadzu Model UV-2600 spectrophotometer using a quartz cuvette of 1 cm path length. Steady state fluorescence emission and excitation spectra of functionalized Co_3O_4 NCs were recorded on Horiba Jobin Yvon Model Fluorolog fluorimeter. Fluorescence micrographs of as-prepared and functionalized Co_3O_4 NCs were captured using an Olympus BX61 Fluorescence microscope employing 365, 436 and 546 nm excitation wavelengths.

Time-resolved fluorescence transients of functionalized Co_3O_4 NCs were recorded using a picosecond pulsed diode laser [nano LED from HORIBA JOBIN YVON] based TCSPC fluorescence spectrometer, against excitation at 377 and 294 nm, employing MCP-PMT as a detector. The emitted light from functionalized Co_3O_4 NCs solution was collected at a right angle to the direction of the excitation beam maintaining magic angle polarization (54.7°) with a band pass of 2 nm. For 377 nm laser source the full width at half-maximum (FWHM) of the instrument response function was 270 ps, and the resolution was 28 ps per channel. In case of 294 nm excitation, pulse duration was <1 ns. The data were fitted to multi exponential functions after deconvolution of the instrument response function by an iterative reconvolution technique using IBH DAS 6.2 data analysis software in which reduced χ^2 and weighted residuals serve as parameters for goodness of fit. All the optical studies were performed at room temperature (298 K).

FTIR studies were performed by a JASCO FTIR-6300 spectrometer, to ensure the attachment and interaction of the tartrate molecules with Co_3O_4 NCs. For FTIR measurements, pellets were prepared after homogeneous mixing of lyophilized powder samples with KBr. The background was corrected by a reference of KBr pellets.

Magnetic study was carried out in a Lake Shore VSM equipped with an electromagnet, capable of generating field of up to 1.5 T at 300 K.

For the study of catalysis, functionalized Co_3O_4 NCs were added in the 7.8 μM aqueous solution of bilirubin (BR) kept in a quartz cuvette in the dark maintaining the pH of the solution ~ 7 , with stirring condition and the absorbance of BR in the reaction mixture was measured time to time by the UV-visible spectrophotometer.

For the study of photo-catalysis we used 8 W UV lamp as UV light source from Philips. 5 μM aqueous solution of methylene blue (MB) and functionalized Co_3O_4 NCs were homogeneously mixed for 1h in a quartz cuvette in the dark maintaining the pH of the solution ~ 3 . Then the cuvette was placed ~ 2 cm apart from the light source and the absorbance of MB in the reaction mixture was measured time to time by the UV-visible spectrophotometer.

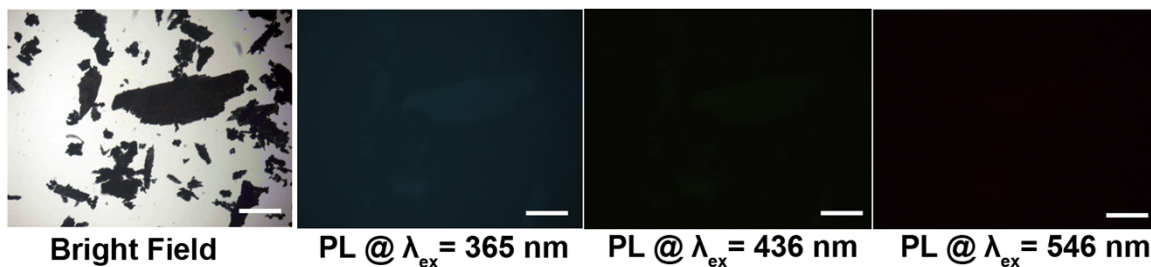


Figure S1. Fluorescence micrographs of bare Co_3O_4 NCs, under bright field, UV, blue, and green light. The scale bars in all the images are 500 μm .

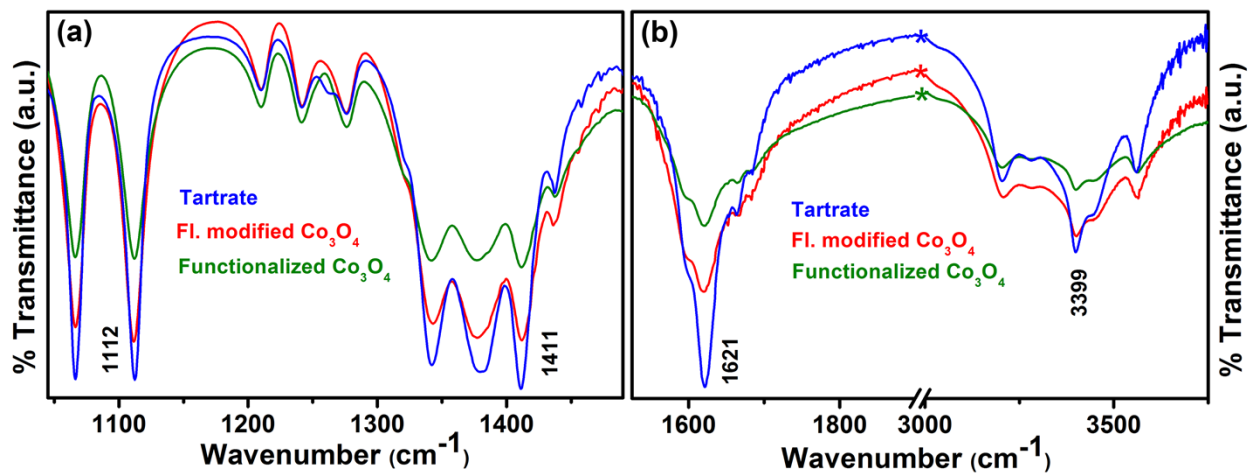


Figure S2 (a,b) FTIR spectra of functionalized Co₃O₄ NCs and fluorescence modified (heated after increasing pH) Co₃O₄ NCs along with Na-tartrate alone.

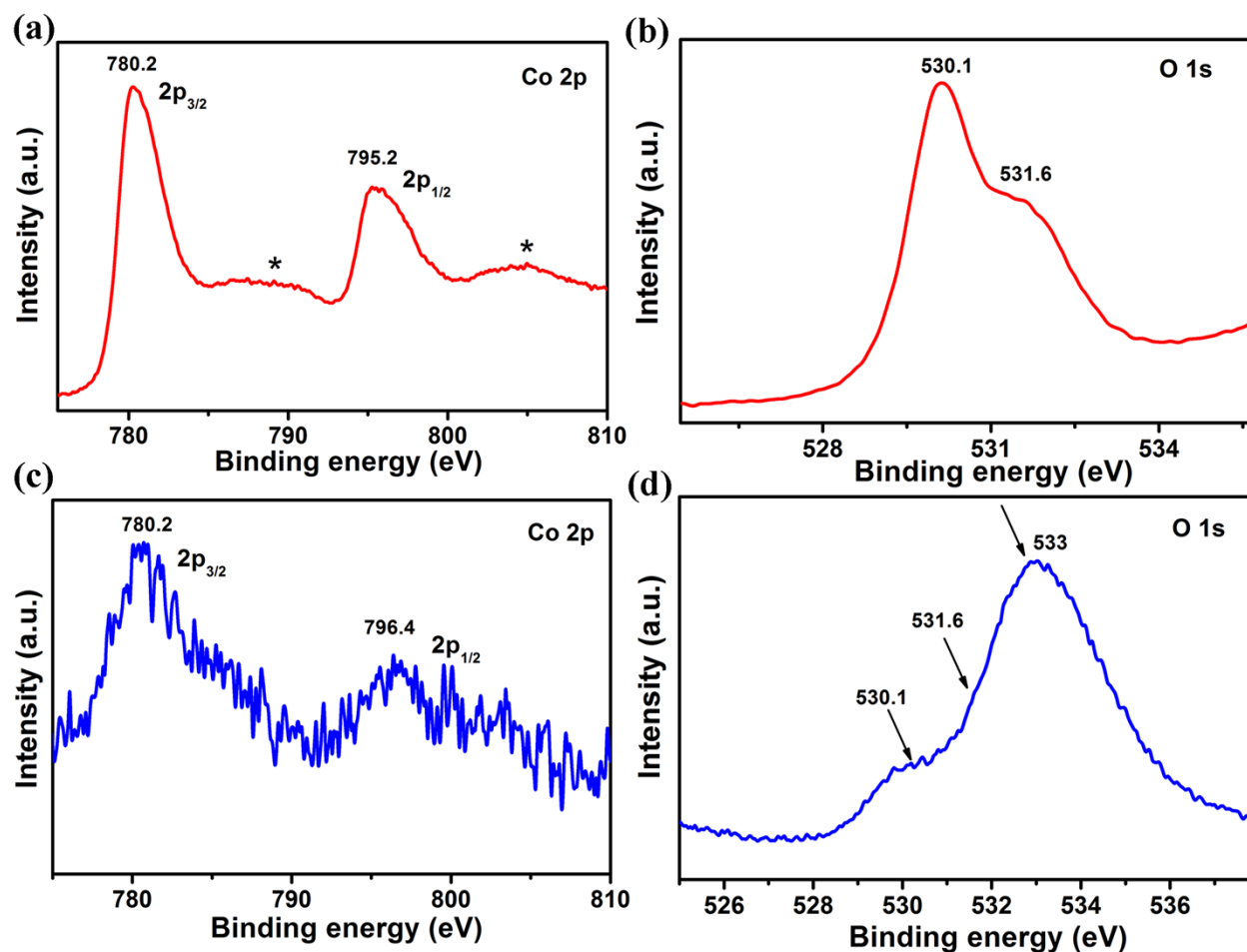


Figure S3: High resolution XPS spectrum of bare Co_3O_4 NCs showing (a) Co $2p_{3/2}$ and $2p_{1/2}$ core-level signals with binding energy at 780.2, and 795.2 eV, respectively, along with low intensity shakeup satellites at ~ 8.8 eV from the main spin-orbit components, and (b) oxygen species (O1s) with binding energy at 530.1, and 531.6 eV. High resolution XPS spectrum of functionalized Co_3O_4 NCs showing (c) Co 2p core-level signals with binding energy at 780.2 and 796.4 eV for $2p_{3/2}$ – $2p_{1/2}$ doublet, and (d) oxygen species (O1s) with binding energy at 530.1, 531.6 and 533 eV.

Reference:

1. Dong, Y.; He, K.; Yin, L.; Zhang, A., A facile route to controlled synthesis of Co_3O_4 nanoparticles and their environmental catalytic properties. *Nanotechnology* **2007**, *18* (43), 435602.