Supplementary Material (ESI) for Chemical Communications

Supplementary Information

ZnO: A versatile template to obtain unusual morphologies of silica, gold and carbon nanostructures

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Experimental procedure:

Preparation of ZnO microdrums:

For the preparation of ZnO nanodrums, a NaAOT microemulsion was first prepared by adding 0.3718 g of $Zn(NO_3)_2 \cdot 6H_2O$ (MERCK) to 50 ml of water and stirred for 5 min to dissolve completely. To this a solution containing 0.22 g of NaAOT (MERCK) in 5 ml of 1-butanol was added with vigorous stirring. The stirring was continued for 2 h and then 0.280 ml of liquor ammonia ($NH_3 \cdot H_2O$) was added dropwise to the well-stirred microemulsion. After addition, stirring was further continued for 3 h at room temperature. The resulting milky white mixture was subsequently kept at 70 ºC for 12 h. A white suspension obtained was suction-filtered to separate the precipitate, which was later washed several times with distilled water and absolute ethanol. Finally, a white powder was obtained by drying the solid product in an oven at 60 ºC.

Preparation of ZnO pencils:

Hexagonally faceted pencil shaped ZnO nanorods were synthesized using a reported procedure (26). In a typical synthesis, 5.0 g of NaOH and 2.75 g of zinc acetate (MERCK), each in 25 ml of water was prepared separately, mixed in a Teflon lined stainless steel autoclave of 65 ml capacity. The autoclave was sealed and heated to 393 K in an oven for 6 h. It was then allowed to cool naturally to room temperature. The solid

product was separated from the solution by filtration, washed with distilled water several times and dried in an air-oven maintained at 323 K.

Silica-coating of ZnO structures:

The zinc oxide-silica core shell structure was obtained by sol-gel method using tetraethylorthosilicate (TEOS) as a precursor (28). In a typical procedure, 30 mg of zinc oxide microdrums/faceted nanorods were dispersed in 3.0 ml 2-propanol. Under continuous mechanical stirring, 0.4 ml of deionized water, 0.1 ml of ammonia solution (28 % w/w) and 20 µl of TEOS (amount can be varied to vary the coating thickness) was consecutively added to the dispersed solution. The reaction mixture was kept for 3 h without stirring. A white solid product settled at the bottom was obtained after the reaction. The solution was then filtered and washed several times with deionized water and anhydrous ethanol respectively.

Silica nanostructures were obtained by the removal of ZnO core in dilute HCl solution. In the process, the core-shell structures were added to the 1 N HCl solution. After 3 h, the solution was filtered and the product was washed several times with deionized water and anhydrous ethanol respectively.

Gold-coating of ZnO structures:

To obtain gold nanostructures, 30 mg of ZnO template was placed over a thin glass wafer and were sputter coated with gold for 5 min using sputter coater machine. The process is

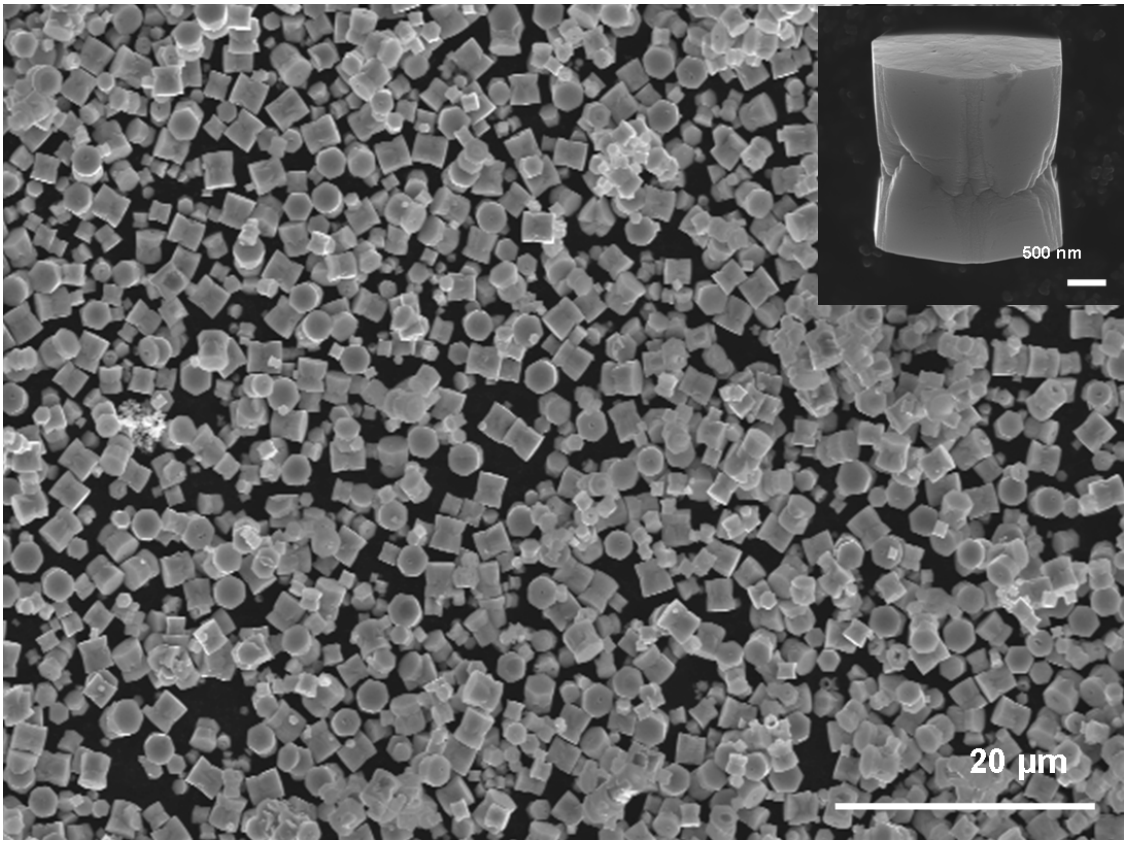
carried out in high vacuum and at an optimal applied voltage. The gold coated ZnO on glass wafer was then soaked in a beaker containing 3 ml of 1 N HCl for 3 h to dissolve the ZnO. The resultant product (gold nanostructures) was then washed with deionized water and ethanol respectively and dried.

Carbon-coating of ZnO structures:

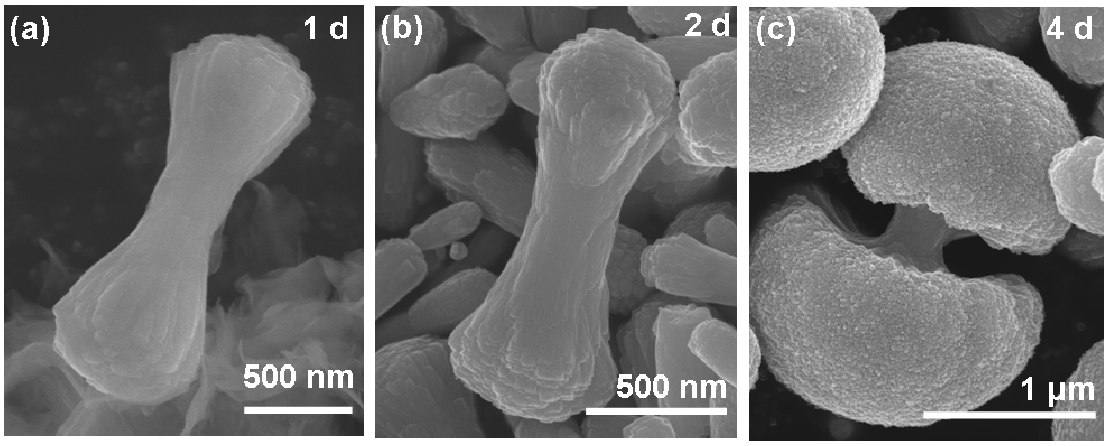
Carbon coating on ZnO template was done with arc discharge process. By generating an arc between two graphite rod tips at high voltages, carbon vapour was generated inside a vacuum chamber. The vapour was allowed to settle on the ZnO powder placed on a glass substrate in the vacuum chamber. The process of arc-discharge completes in a few seconds and the resultant carbon-coated ZnO was acid treated for the removal of ZnO core to obtain carbon nanostructures.

Sample Characterization:

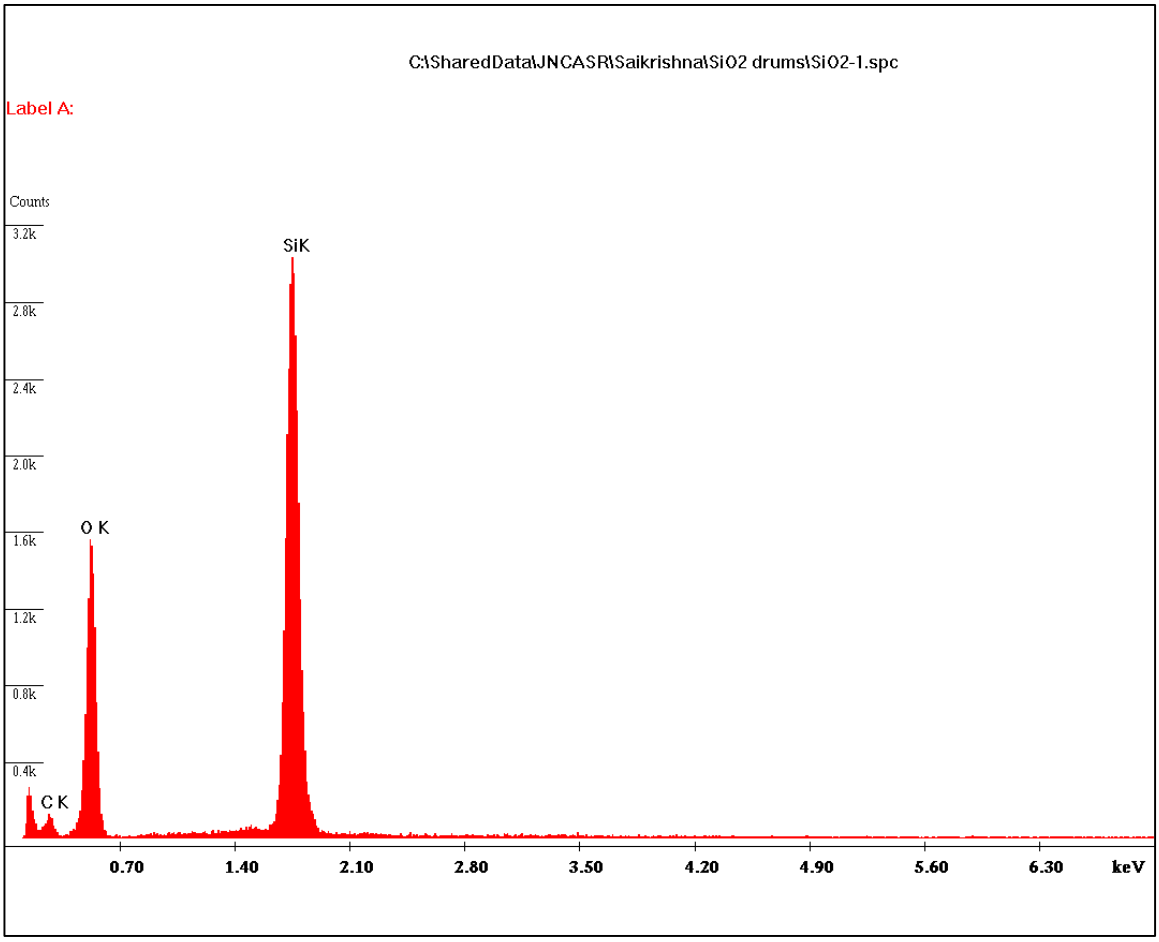
The as-synthesized samples were analyzed with a field-emission scanning electron microscope (FE-SEM, FEI Nova-Nano SEM-600, The Netherlands). Transmission electron microscopy (TEM) was carried out at 300 kV with a JEOL JEM-3010. Powder X-ray diffraction (XRD) patterns were obtained by using a RICH-SIEFERT 3000-TT diffractometer employing CuKα radiation.



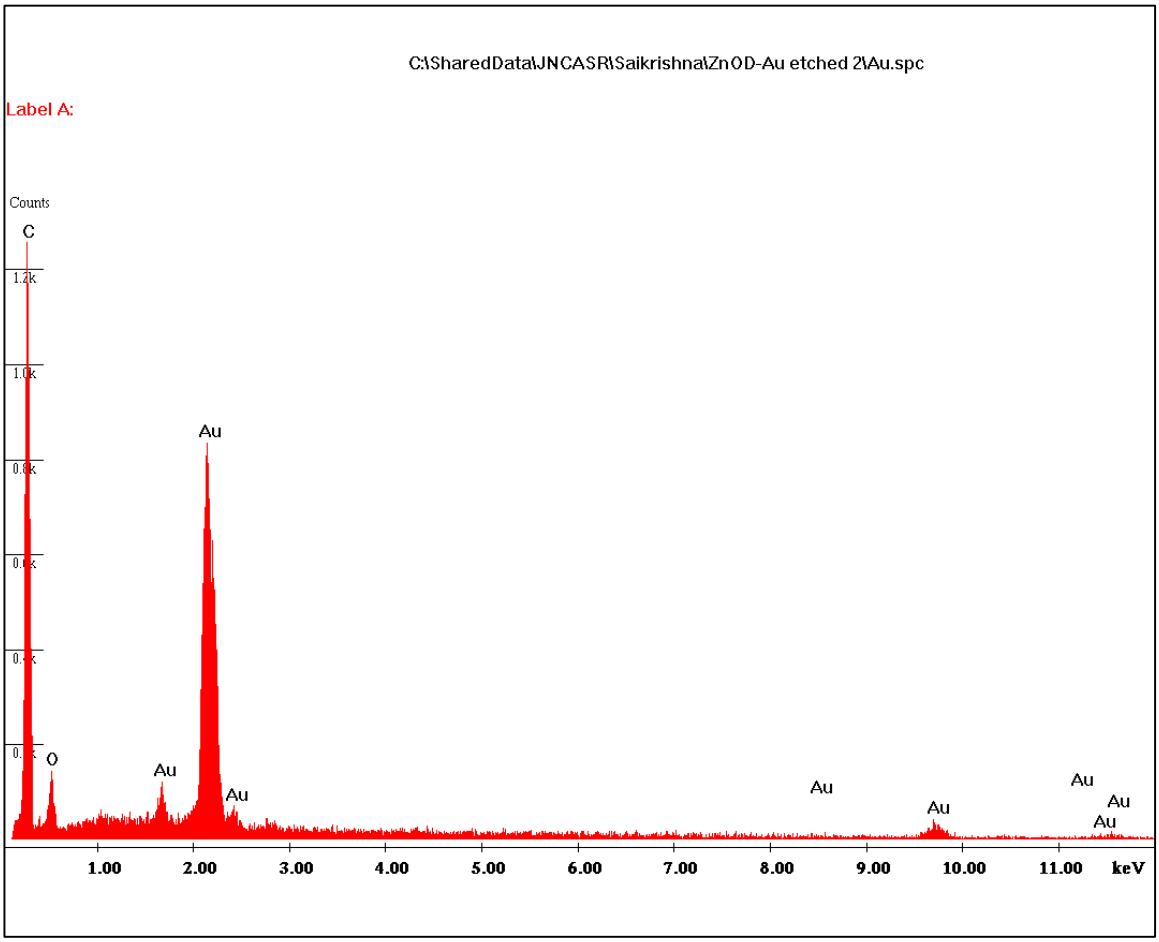
Supplementary Information 1: Low-magnification FESEM image of ZnO microdrums formed at 5 days of reaction time. Inset shows a single magnified drum.



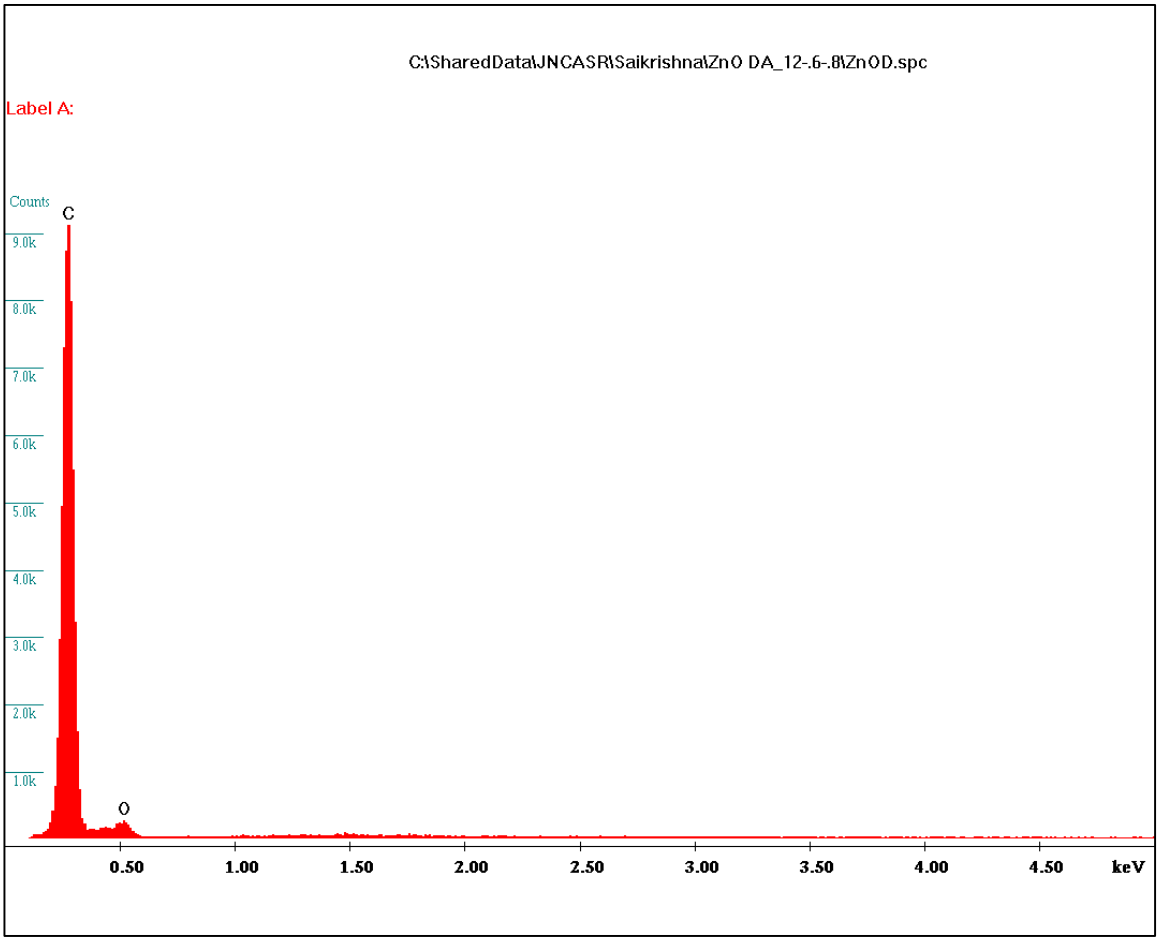
Supplementary Information 2: FESEM images of the morphologies of ZnO obtained by hydrothermal treatment for (a) 1 day (b) 2 day and (c) 4 days respectively.



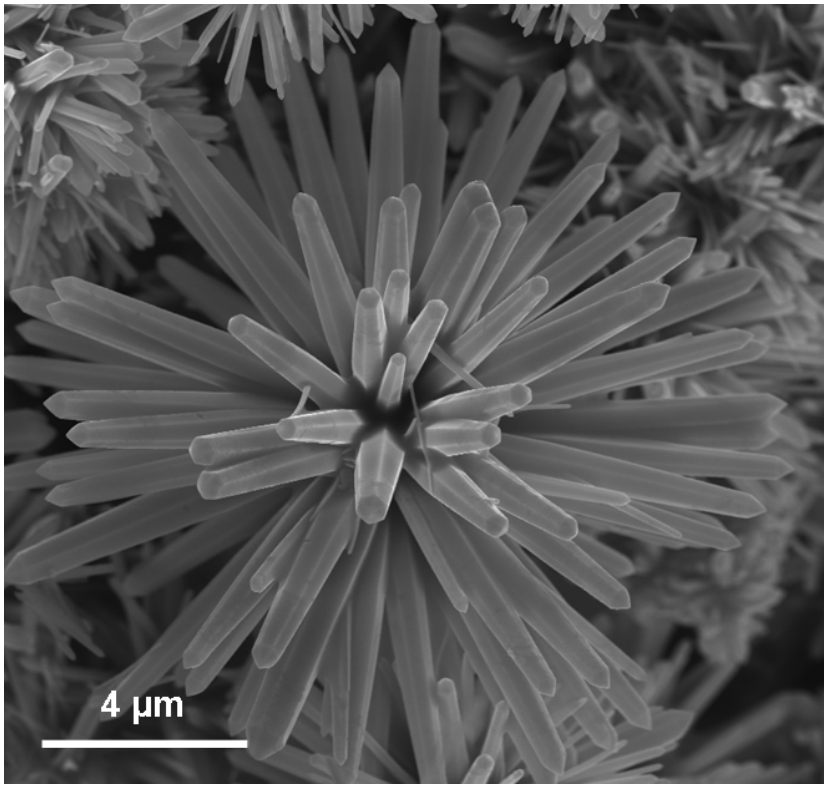
Supplementary information 3a: EDAX profile of the silica drums obtained after removing the ZnO template. The peak for carbon comes from the carbon tape substrate used for holding the sample during microscopy.



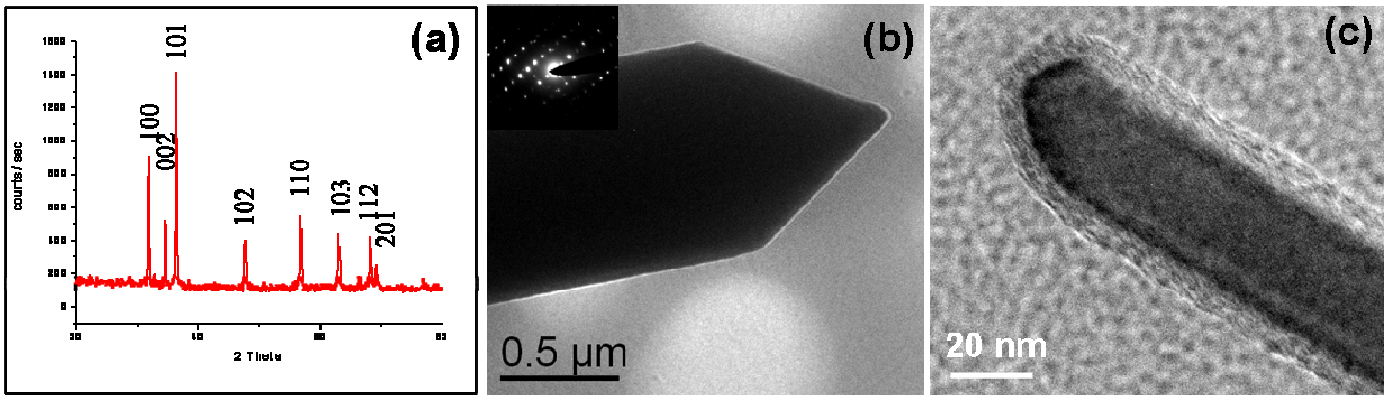
Supplementary information 3b: EDAX profile of the gold drums obtained after removing the ZnO template. The peak for carbon comes from the carbon tape substrate used for holding the sample during microscopy.



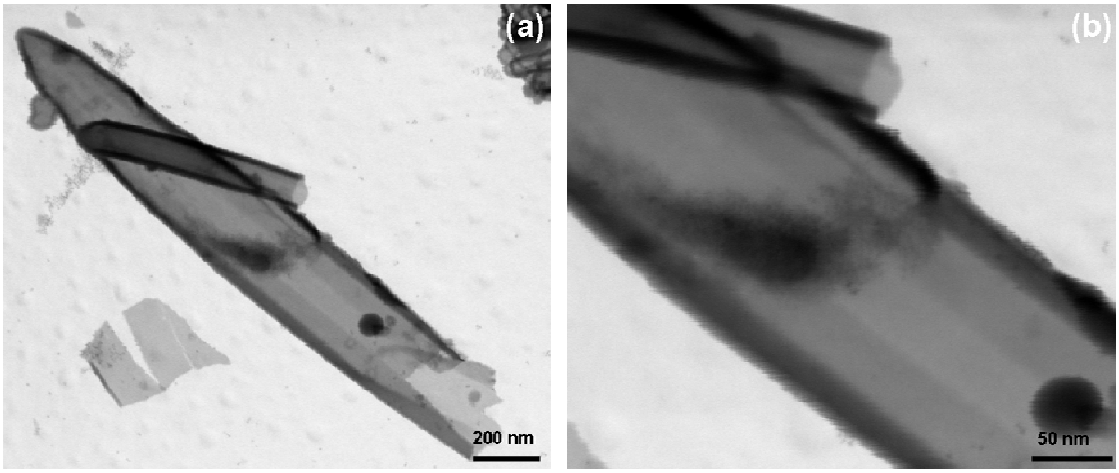
Supplementary information 3c: EDAX profile of the carbon drums obtained after removing the ZnO template.



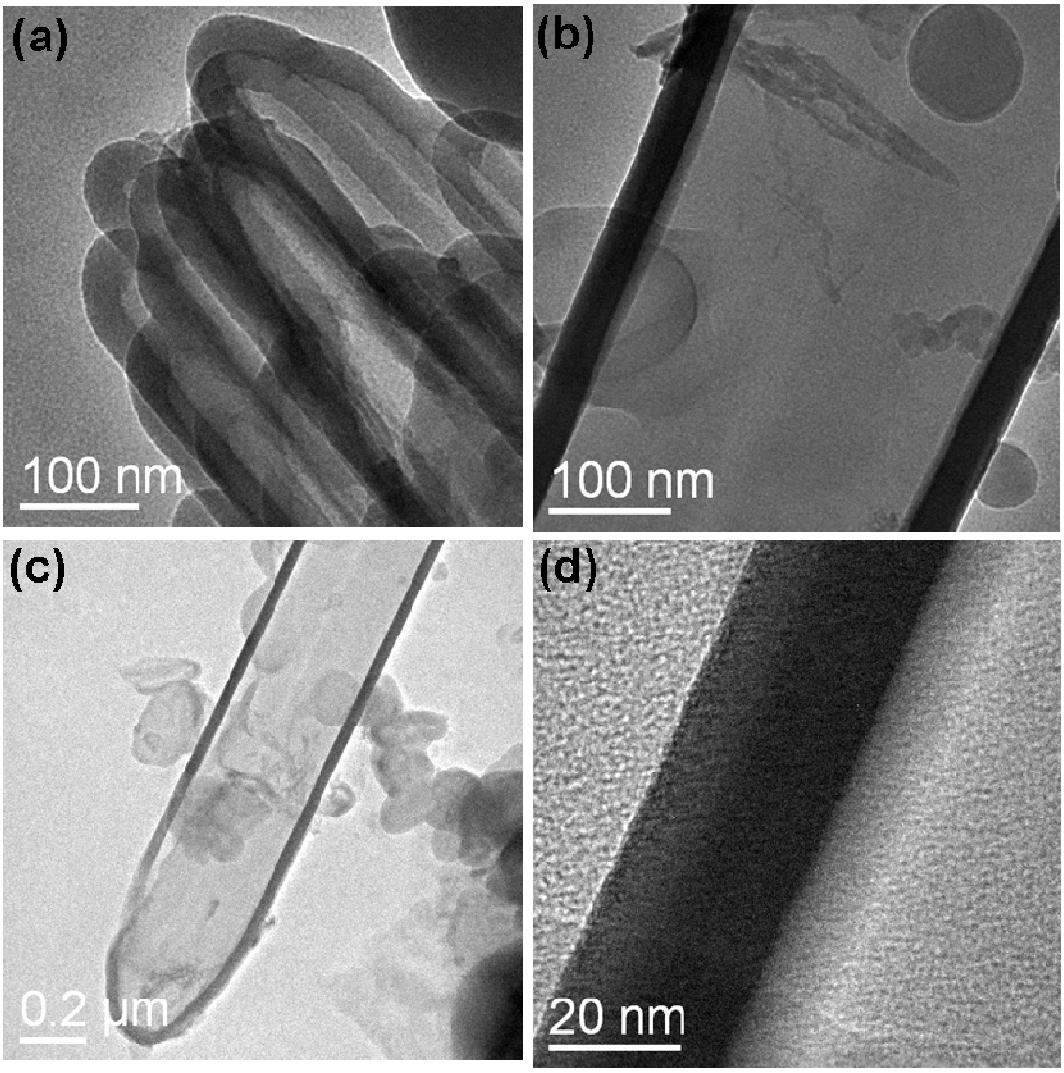
Supplementary Information 4: Dandelion-like ZnO structures (with pencil-shaped tips) obtained by hydrothermal reaction.



Supplementary Information 5: (a) Powder X-ray diffraction (PXRD) pattern obtained of pencil-shaped ZnO nanorods. (b) TEM image of a ZnO pencil-shaped nanorod. Inset shows the Electron Diffraction (ED) pattern. (c) TEM image of a silica coated ZnO nanorod with a coating thickness of ~ 10 nm.



Supplementary Information 6: (a) STEM image of a Ferritin protein encapsulated silica nanotube that is open at one end and closed at the other. (b) Higher magnification image of the encapsulated region.



Supplementary information 7a: (a) TEM image of Fe_2O_3 coated silica nanotubes (obtained from templating ZnO nanorods).(b) & (c) shows a single Fe_2O_3/SiO_2 core-shell nanotube. (d) Higher magnification image showing a coating thickness of ~ 30 nm.

Supplementary information 7b:

Synthesis procedure for the $SiO_2@Fe_2O_3$ hollow tubes:

0.55 g of $FeCl_3.6H_2O$ (S.D. fine-chemicals, India) and 0.77 g of citric acid (S.D. fine-chemicals, India) were dissolved in a mixture of 0.75 ml of water and 5.25 ml of ethanol (water–ethanol v/v = 1:7). To this solution, 1 ml of PEG (molecular weight = 600, S.D. fine-chemicals, India) was added as cross linking agent. The mixture was stirred for 1 h to form a solution and then the 65 mg of $ZnO@SiO_2$ nanorods sample was added under stirring. The suspension was further stirred for another 3 h, and then the product was separated by filtration. The samples were dried at 100 °C for 1 h immediately afterwards. The dried samples were annealed at 500 °C for 2 h in a furnace with a heating rate of 1 °Cmin–1. Then the preheated samples were annealed to 600 °C with a heating rate of 1 °Cmin–1. Due to the presence of citric acid in the medium, ZnO was etched during the synthesis and the products formed were $SiO_2@Fe_2O_3$ hollow tubes.