Deposition of Zinc Oxide Nanomaterial on different substrates for useful applications

Chanchal Mondal,† Arun Kumar Sinha, † Mainak Ganguly, † Jaya Pal, † Santanu Dhara,§ Yuichi Negishi # and Tarasankar Pal*,†

†Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, India
§School of Medical Science and Technology, Indian Institute of Technology, Kharagpur-721302, India

#Tokyo University of Science, Shinjyuku-ku, Tokyo 162-8601, Japan

E-mail: tpal@chem.iitkgp.ernet.in
Supporting Information

Supporting information S1:

Materials:
All the reagents were of AR grade. Zinc acetate \([\text{Zn(CH}_3\text{COO)}_2\cdot\text{2H}_2\text{O}]\) and ammonia were purchased from E-Merck. Glass slides, beakers and screw capped test tubes (capacity 15 mL) were obtained from Blue Star India and they were properly cleaned with aqua regia, water and dried prior to their use.

Analytical Instrument:

Powder X-ray diffraction (XRD) was done in a PW1710 diffractometer, a Philips, Holland, instrument. The XRD data were analyzed by using (JCPDS) software.

Reflectance spectra were measured using DRS (Diffuse Reflectance Spectra) mode with a Cary model 5000 UV-vis-NIR spectrophotometer.

Photoluminescence was measured using a He–Cd laser as an excitation source, operating at 325 nm with an output power of 45 mW and TRIAX 320 monochromator fitted with a cooled Hamamatsu R928 photomultiplier detector.

Raman spectra were obtained with a Renishaw Raman Microscope, equipped with a He-Ne laser excitation source of emitting wave length 633 nm and a peltier cooled (-70°C) charge coupled device camera (CCD).

Fourier Transform Infrared Spectroscopy i.e., FTIR measurements of the samples were done in KBr pellets in reflectance mode with a Nexus 870 Thermo-Nicolet instrument coupled with a Thermo-Nicolet Continuum FTIR microscope.

Field emission scanning electron microscopy (FESEM) was performed with a supra 40, Carl Zeiss Pvt. Ltd. instrument.

Transmission electron microscopy (TEM) was performed with an H-9000 NAR instrument, Hitachi, using an accelerating voltage of 300 kV.

The chemical state of the element on the surface of the nanomaterial was obtained X-ray photoelectron spectroscopy (XPS) measurements, carried out by a VG Scientific Escalab MK II
spectrometer equipped with a Mg Kr excitation source (1253.6 eV) and a five-channeltron detection system.

Water droplets (5 to 20 μL) were dispensed carefully onto the ZnO thin film by the use of a micropipette. The average contact angle was evaluated at five different positions from the side face of the same film using a digital still camera (Sony Cyber-shot 8.2 megapixels). During this experiment there was no disturbance such as change in air flow or mechanical vibration.

Supporting information S2:

Cytotoxicity measurement:

For evaluations of cytotoxicity of ZnO nanomaterials, the samples palettes of diameter 10.5 mm were made and both the sides of the palettes were sterilized under UV light for 15 mins individually. Then the samples were made aseptic using 70% ethanol in 2 h time. Prior to cell seeding, the samples were washed in 50 mg/mL phosphate-buffered saline solution (PBS) thrice with one min interval and incubated in complete cell culture media at 37°C for 24 h. Mouse fibroblast cell line (3T3) (NCCS, Pune, India) were seeded with a cell density of 10^5 cells per well in Dulbecco’s modified Eagle’s medium (DMEM, HiMedia) with 10% fetal bovine serum (FBS, HiMedia), 4 mM L-glutamine and 1% penicillin–streptomycin (A002A, Himedia, Mumbai, India) in tissue culture 12 well plate at 37 °C with 5% CO₂. The culture medium was changed every alternate day. MTT assay was carried out on 3rd day by detaching cells from the flasks/samples using trypsin–EDTA solution followed by splitting at 1:4 ratio. The cells seeded in TCP without any samples were used as the control. The proliferation of 3T3s on the samples and TCP was quantified after 3 days by MTT assay following the procedure described below. Briefly, the cells attached to the well were washed with sterile PBS and incubated in a mixture of 720 μl of PBS and 80 μl MTT solution (5 mg/ml) in PBS for 4 h at 37°C and 5% CO₂. The intense purple colored formazan derivatives formed were dissolved with 400 μl dimethyl sulfoxide for 15 min and the absorbance was measured at 590 nm with a micro plate reader Recorders and Medicare Systems, India).
Supporting information S3.

Cytotoxicity of ZnO nanomaterial:

We have carried out the cytotoxicity of ZnO nanomaterial for possible toxicity during human exposure. MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazoliumbromide) assay result for relative activity levels of mouse fibroblast cells after incubating with ZnO samples and standard TCP (tissue culture plate) are shown in fig. S5. The MTT assay result indicates that the cells remain viable in a culture containing ZnO samples after three days of incubation. However, the cell viability on ZnO nanomaterials was found to be slightly lower when compared with TCP. This may be indicative of the minimal cytotoxicity induced by ZnO nanomaterials. Further, leaching of ammonia and acetate ions which are used as hydrolyzing agent and precursor salt, respectively, during synthesis of ZnO nanoflowers may be the origin of cytotoxicity. Further repeated washing or biocompatible carbon coating on the ZnO can be an effective strategy for minimizing cytotoxicity as suggested by Guo et al.\(^1\)
Supporting information S4

FTIR Study:

FTIR spectrum (Fig. S6) shows a strong peak at 505 cm\(^{-1}\) for Zn—O bond. The appearance of the bands at 1394 cm\(^{-1}\) and 1507 cm\(^{-1}\) are due to C=O vibration of the acetate ligand from the bridging type metal-acetate bonding present in the ZnO nanoarchitectecture. These corroborate the wrapping of trace acetate ions in the as-synthesized nanoarchitecture and could not be washed out easily. The broad band at 3406 cm\(^{-1}\) is assigned for the O-H moieties in the sample. The band at 907 cm\(^{-1}\) and 1041 cm\(^{-1}\) are ascribed as stretching vibrations of C-O group which also authenticates the surface attachment of acetate ligand to ZnO nanoparticles. The band at 1656 cm\(^{-1}\) is assigned as the bending vibrational mode of surface trapped or adsorbed water molecules.\(^2\)
References


Fig. S1: XRD patterns of ZnO nanoflower deposited on various substrates.
Fig. S2: FESEM images of ZnO nanoflower on different substrates cotton wool (a), indium tin oxide coated glass (b), silicon substrates (c), and transparency sheet (d).
Fig. S3: Variation of water Contact angle with different volumes of water.
Fig. S4: XPS spectra of O 1s level of ZnO thin film before and after UV light irradiation.
Fig. S5: MTT reduction assay for (a) palette made using ZnO nano-flower and (b) TCP were compared after 3 days 3T3 cell culture study.
Fig. S6: FTIR spectrum of ZnO nanoflower produced from Zn(CH₃COO)₂·2H₂O and NH₃.
Fig. S7: Digital images of the stepwise separation procedure of water-kerosene mixture.