

Synthesis and Characterization of Optically Active Zn-doped Silica-titania Nano-composites for Sensing Applications

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ABSTRACT

Zn-doped and undoped silica-titania nanocomposites are synthesized as matrices for the encapsulation of organic dyes through in-situ sol-gel procedure. The effect of Zn doping on silica-titania composite is investigated by Field Emission Scanning Electron Microscope (FE-SEM), Energy Dispersive Spectroscopy (EDX), Atomic Force Microscopy (AFM), surface analysis i.e. Brunauer–Emmett–Teller (BET), and UV–Vis Spectroscopy. The mixture of organic dyes (bromophenolblue, phenol red, cresol red and phenolphthalein) is used for the evaluation of sensing activity of the synthesized material for dynamic pH range. Experimental findings showed that the uniform coating with 92-62 % transparency in the visible range with low refractive index 1.33-1.39 and low roughness value 9.7–7.6 nm is promising for sensing applications. The response of the sensor is optimum at pH 12. The observed sensitivity is around 36 counts/pH with repeatability of 96 % at 447nm.

1. INTRODUCTION

Heterogeneous nano-composites are of great interest in chemical, optics, biomedicine, photocatalyst and sensing fields (Pawar et al. 2015, Islam et al. 2015, Islam et al. 2016). Silica-titania nano-composite as a host material offers unique properties such as smooth morphology with high surface areas, a porosity-dependent desorption behavior and the ability to act as a compatible host for multitude of different materials and molecules. In terms of nanostructured candidates, zinc oxide nanoparticles are of widespread interest in

gas sensing and as photocatalyst (Nenova et al. 2015, Qinqin et al. 2015). The nanocomposites were synthesized by sol-gel technique, which is well known for providing homogeneous and uniform nano-coatings with good optical properties at low temperatures. Furthermore, encapsulation of indicators within the nanocomposite matrix allows continued sensing without contamination and easy for concentration measurements with species detections (Islam et al. 2016). It also gives good adhesion with direct coating on silica fibers without the use of additional membrane. Moreover, the encapsulation of indicators into sol-gel based nanomatrix reduced the cracks and leads to stable morphology. The activity of entrapped compounds into a nanocomposite matrix remain accessible to external reagents by diffusion through the porous matrix, so it is possible to coupling optics and natural process make photonic devices and detectors. Indicators such as bromophenol blue ($C_{19}H_{10}Br_4O_5S$), phenol red ($C_{19}H_{14}O_5S$), cresol red ($C_{21}H_{17}NaO_5S$) and phenolphthalein ($C_{20}H_{14}O_4$) choose to stimulate the behavior of the sensor, such as its mechanical stability, selectivity, suitability for reagent immobilization and permeability of the analyte. The proposed work is a detailed structural and optical analysis of undoped and doped ZnO nanoparticle into silica-titania nanocomposite system for sensing applications. For good sensing system, there are certain properties that must be fulfilled such as crack-free morphology with low roughness, high surface area, low refractive index and nanoparticle size. Therefore, structural and optical properties of ZnO nanoparticles in nanostructured porous silica-titania host matrix, is investigated. To the authors' best knowledge, the synthesis of Zn-functionalized ST nanomatrix by sol-gel route as well as their pH sensor applications with broad dynamic range has been rarely reported.

2. EXPERIMENTAL

2.1. SYNTHESIS OF THE SOLS

To prepare silica-titania hybrid sol, the two sols SiO_2 and TiO_2 were mixed in 1:1 volume ratio of silica to titania. The details of synthesis of hybrid sol can be found in our previous paper (Islam et al. 2014). ZnO nanoparticles sol was synthesized by dissolving 0.2 g of 99.8% pure zinc acetate [$Zn(CH_3CO_2)_2 \cdot 2H_2O$] in 10 mL of de-ionized water, 30 mL of isopropyl alcohol and 1mL of isopropyl. After mixing, the solution is stirred at a temperature of 70 °C for 60 min. For doped sol, 10mL ZnO sol, 5ml of 0.5M concentration of co-indicators and 1ml of 0.5M concentration of CTAB solution were mixed into hybrid sol. This mixture was stirred and heated at 80 °C to ensure proper combination of the constituents. The mixture was left for several days for appropriate aging cycles and removal of volatile components at room temperature.

In order to fabricate the pH sensor, 30 cm long Plastic Clad Silica optical fiber 15 μ m core diameter ($NA = 0.37 \pm 0.02$) with 5 cm decladded region was washed with HNO_3 for 5min and rinsed several times with de-ionized water in order to ensure the constancy in the coupling behavior of the launched light into the fiber during the detection measurement; both ends of the fiber were polished carefully. Coating was done on fiber by dripping the sol onto the decladded region at the middle of the fiber. After coating, the fiber was dried at room temperature and left for several days in order to get a tough, inert, highly adhesive coating. For pH measurements, pH buffer solutions 3–12 were used.

3. CHARACTERIZATION:

A field emission scanning electron microscope FESEM SU8020 was employed to observe the interaction of doped particles into host matrix at the surface and for the study of grain sizes of undoped and Zn-doped nano-particles. EDX spectrum (Oxford Silicon Drift Detecto SDD) was used to know the percentage of elements present in the sample. Surface topography and roughness analysis was observed using Atomic Force Microscopy (AFM) equipment SPI 3800 N. The surface areas of the samples were determined from the Brunauer, Emmett and Teller (BET) multipoint method and the pore size distribution was obtained using the Barret, Joyner and Halenda (BJH) method. For calculation of the surface areas, the BET method was used to elaborate N₂ adsorption-desorption isotherms. Ultraviolet-visible (UV-Vis) transmission spectra were measured by a Shimadzu UV-3101PC spectrophotometer. The employed spectrum was in the spectral range of 400–700 nm with an accuracy of ±3 nm. The dynamic range of the sensor in various pH environments was investigated using a photospectrometer. The white light emitting diode was used as a light source and significant wavelength characteristics were detected by USB2000 miniature fiber optical spectrum analyzer.

RESULTS AND DISCUSSION

The FE-SEM micrograph of silica-titania in Fig. 1(a) reveals smooth surface morphology of silica-titania hybrid nanoparticles without voids. However, silica-titania after Zn-doping [Fig. 1(b)] shows aggregation of nanoparticles with pores. Nanoparticles agglomeration is probably due to the hydroxyls ions or adsorbed water molecules on the surface of the composite films as reported by other researchers (Falcao et al. 2003). In composite films, pores serve as active centers, which is valuable for improving the sensing properties as reported by other researchers (Singh et al. 2014). Therefore, porous material with enlarged specific surface area is proposed to produce better response of the device. In order to identify the elemental composition of undoped and Zn-doped silica-titania matrices and to check the indicator incorporation with matrix species, Energy Dispersive X-ray analysis was used. Fig. 1 (c, d) shows the EDX spectra obtained for both matrices. EDX analysis reveals that indicator is successfully incorporated into the host matrix. The values of elements are summarized in Table 1. The variations of Si, Ti, O along with Zn in doped sample shows good incorporation of Zn with hybrid silica-titania matrix lattice. The average surface roughness of silica-titania and Zn-doped silica-titania matrix was examined over a 1x1 μm² area. In the analyzed area through atomic force microscopy, silica-titania matrix [Fig. 1(e)] exhibits an average surface roughness of 9.7 nm with clusters. However, the average surface roughness slightly decreases to a value of 7.6 nm after Zn doping in silica-titania matrix [Fig. 1(f)]. Low roughness is highly appropriate for optical and sensing applications.

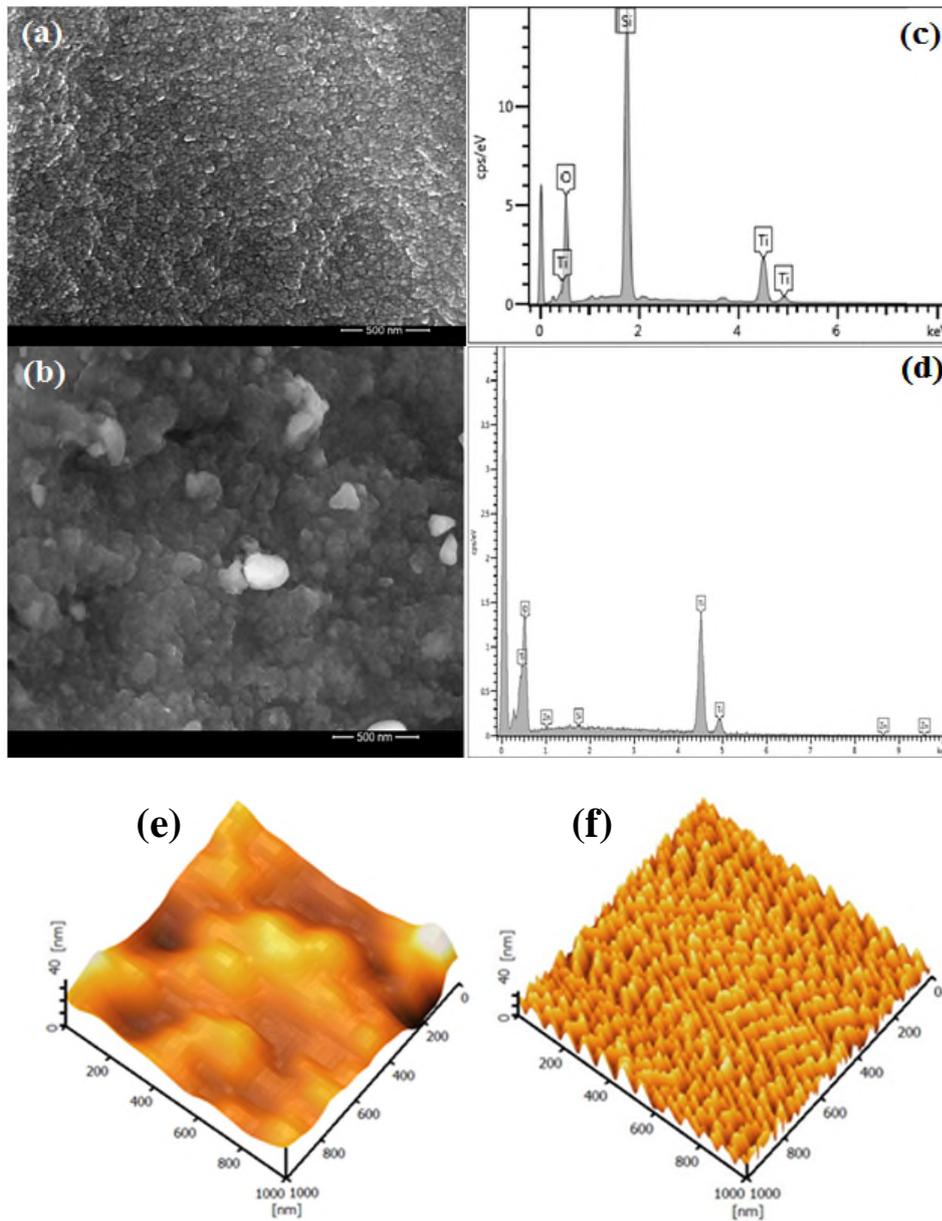


Fig. 1 FE-SEM micrographs of (a) silica-titania hybrid (b) Zn-doped silica-titania matrix (c, d) corresponding to the EDX spectra of (a) and (b). While, (e) and (f) corresponding to the AFM patterns of (a) and (b) respectively.

Table 1. EDX analysis of silica-titania and Zn-doped silica-titania matrix

| Elements wt. (%) | Ti | Si | O | Zn |
|-------------------------|-------|-------|-------|-----|
| Silica-titania | 22.47 | 35.87 | 41.66 | - |
| Zn-doped silica-titania | 34.3 | 30.1 | 28.9 | 6.7 |

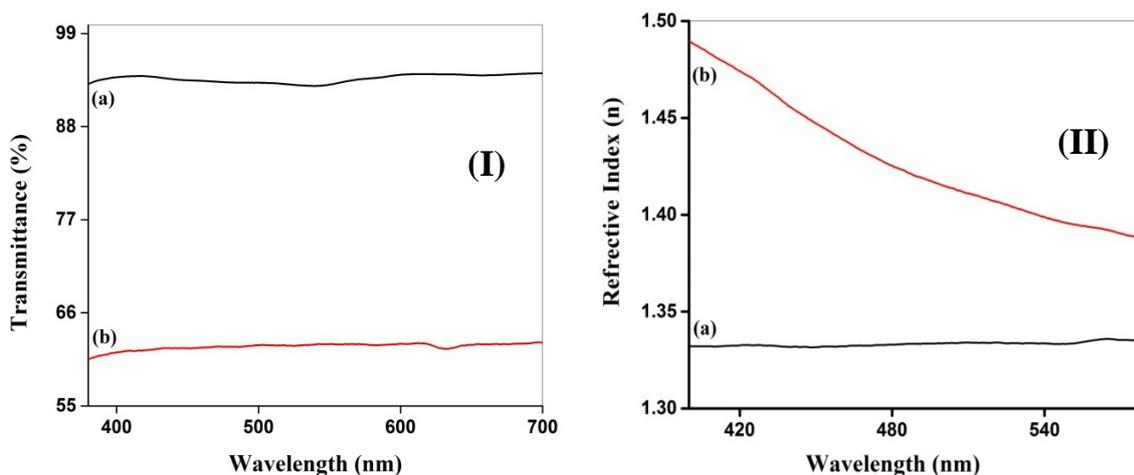


Fig. 2(I). Optical transmission spectra of the phph immobilized (a) ST nanoparticles (b) ZST nanoparticles, (II) refractive index dispersion (a) ST nanoparticles (b) ZST nanoparticles

Fig. 2 (I) Transmission spectra of (a) silica-titania matrix (b) Zn-doped silica-titania matrix, (II) Dispersion of refractive index (a) silica-titania matrix (b) Zn-doped silica-titania matrix

Fig. 2(I)(a, b) shows the transmittance spectra of the silica-titania matrix and Zn-doped silica-titania matrix respectively at room temperature. The absorption band ~ 545 nm in silica-titania matrix is shifted ~ 631 nm in Zn-doped silica-titania matrix due to particles cluster formation. Transmission is $\sim 92\%$ in silica-titania matrix which is reduced to $\sim 62\%$ at wavelength of 550nm. Furthermore, the refractive indices for nonocomposites were calculated by the Fresnel equation. The dispersion of the refractive index is shown in Fig. 2(II). The calculated refractive index of silica-titania matrix is 1.33 at 550 nm, which is increased up to 1.39 at 550 nm after ZnO nanoparticles doping. The refractive index of both samples is much lower than that of titania $n = 2.5$ and zinc oxide $n = 2$, meaning that the fabricated samples have a porous structure. This allows light to be drawn from the evanescent field, when used with waveguides and photonic sensors. Hybrid silica-titania matrix has a high surface area, pore diameter and pore volume which are advantageous for photocatalytic and sensing applications. However, in Zn-doped silica-titania matrix sample, the pore diameter, pore volume and surface area values reduced which is tabulated in Table 2. The reduction in values after Zn-doping and encapsulation of

indicators is due to blocking of the silica-titania matrix pores by the encapsulation of indicator dyes. In addition, the average pore diameter, determined through the Barrett–Joyner–Halenda (BJH) method using desorption isotherm was also found to decrease after doping and encapsulations.

Table.2 Surface area, pore volume and pore diameter distribution of ST matrix and ZST matrix

| Samples | Surface area (m²/g) | Pore Volume (cm³/g) | BET Pore diameter (Å) | BJH Pore diameter (Å) |
|-------------------------|---------------------------------------|---------------------------------------|------------------------------|------------------------------|
| Silica-titania | 441 | 0.69 | 62.97 | 58.53 |
| Zn-doped silica-titania | 283 | 0.23 | 33.20 | 32.87 |

The intensity variations within different pH solutions 3-12, of coated thin film on 5cm length of optic fiber with 0.5M concentration is shown in Fig. 3(I). The transmission in terms of intensity increases after coating resulting in good interaction of light with coating. The mechanism of fiber optic pH sensor is based on the evanescent field, generated by total internal reflection of transmitted light inside the fiber. The light is guided by the core (inner medium) of higher reflective index, with a small percentage of the evanescent field traveling outward beyond the core boundary radially to a little distance. This evanescent field can interact outside the core with active cladding (coating) that interacts with that pH solutions. When pH molecules come into contact with the coated species, it leads to change in its optical properties (Islam et al. 2016). Moreover, refractive index and film porosity determines the character of evanescent wave and its attenuation; the propagation of the evanescent wave is influenced by refractive index of coating. The value of the refractive index of Zn-doped silica-titania matrix was estimated to be 1.39. Furthermore, it is evident from the spectra [Fig. 3(II)] that the sensitivity increases with pH. Sensitivity varies in the present sensor at wavelength 447 nm. The value of sensitivity is calculated as 36 counts/pH with repeatability of 96 % and response is found to be linear for pH 3-12 as shown in Fig. 3(II). So, the useful linear range of this sensitive film is limited to a dynamic range of pH 3 – 12. For color determination, it can be seen visually that the coatings turn into yellow color in acidic solution pH 3 and it changes into blue color by increasing the pH values upto 12; this refers to Fig. 5 inset (III). Basically, the variations in color in different pH solutions are due to the hydrogen ion (H⁺) or hydroxide ions (OH⁻) attached or detached from the electrons that are confined in a molecule. So, present observations show that the interconnectivity between indicators molecules and Zn-doped silica-titania matrix has a significant role in the increased sensitivity of the present fiber optic pH nanosensor.

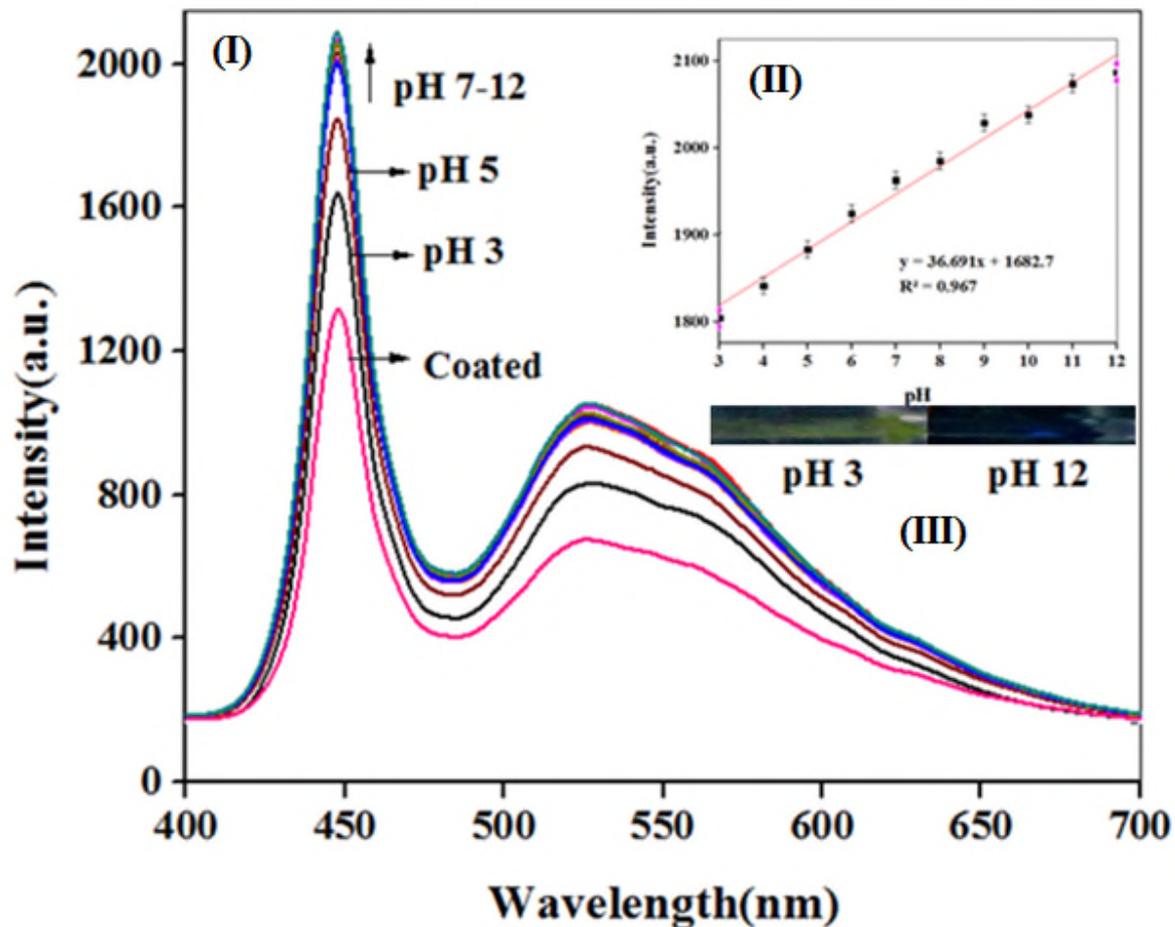


Fig. 3(I). Optical spectra of indicators encapsulated Zn-doped silica-titania nanocomposite coated thin films within different PH ranges 3-12, inset (II) Sensitivity response of coated fiber within different pH values 3-12 at 447 nm, inset (III) showing the color variations of coated fiber within two extreme pHs 3 and 12.

5. Conclusions:

Zn-doped and undoped silica-titania nanomaterials were prepared by sol-gel method. The microscopic analysis indicated that Zn-nanoparticles were uniformly distributed into silica-titania host matrix without any cracks or voids and showed good performance due to their physio-chemical properties. The Zn-doped silica-titania nanomatrix is encapsulated with mixture of indicators and deposited on PCS optical fiber for pH sensing. Coated nanosensor allowed good indicator's interaction with host matrix and improved signal sensitivity around 36 counts/pH with repeatability of 96 %, due to good incorporation between indicators and host matrix species. It is concluded that Zn-doped silica-titania nanomatrix is an excellent composite material for optical sensing in photonic field.

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