



A convenient sol–gel route for the synthesis of salicylate–titania nanocomposites having visible absorption and blue luminescence

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ABSTRACT

Syntheses of titania-based nanomaterials by simple sol–gel route using a mixture of CTAB and salicylate as well as salicylate ions as templates have been reported. The materials are characterized by the powder X-ray diffraction (XRD), thermal analysis, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and spectroscopic (FT IR, UV–VIS) analyses. A disordered mesoscale orientation of nanoparticles (ca. 2–4 nm) composed of TiO₂–salicylate surface complex has been obtained when 1:1 mixing ratio of CTAB and salicylate at the CTAB concentration of 0.001 M was employed as a template. All these nanocomposites exhibit a considerable red shift at the onsets of their absorption band compared to pure (organic-free) nanocrystalline TiO₂ and show blue luminescence at room temperature. This assembly of nanoparticles is highly interesting in the context of visible light sensitization and nanodevice fabrication.

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1. Introduction

Design and fabrication of the advanced nanodevices, one of the most fascinating technological challenges of the 21st century require the synthesis of building blocks in nanoscale and their assembly into desired length scale. New and improved properties through the collective behavior of the individual units can be expected through such complex nanostructured composites of nanoparticle assembly [1]. As a result of these constant efforts highly organized monodispersed particles of metals, metal oxides, semiconductors, organic–inorganic hybrid materials, biominerals, etc. have been fabricated using various synthetic strategies [1–7]. Among various methods the chemical synthetic approach using soft template has been recognized as a favorite protocol to fabricate the nanostructured materials because of its huge potentiality to control the architecture of nanomaterials by changing the reagents, synthesis conditions, etc. In this aspect there is a constant demand to innovate new templating system, which can direct the synthesis of novel nanomaterials with new and improved properties.

Since the discovery of the M41S family of mesoporous silicates [8], self-organizing surfactant assemblies have been widely

employed as a template to direct mesostructured inorganic oxide formation through sol–gel processes. Addition of hydrotopes like sodium salicylate [9] in the CTAB solution causes spherical micelles to undergo a transition to wormlike micelles and the solutions exhibit viscoelastic behavior as a result of micellar entanglement. The detailed microstructure and other interesting properties of such colloids have been reported [9–13]. The cryo TEM observation revealed that the mixture of CTAB and salicylate in 1:1 mole ratio forms the cobweb structure [9]. So far this template has been employed to the synthesis of only silica-based materials [14]. Synthesis of transition metal oxide nanocomposites by using such template should be very interesting because in contrast to Si, the transition metals have ability to form complex with salicylate ion by utilizing its coordination sphere. In this context titania based nanomaterials [15–19] has attracted an extensive research interest owing to their numerous applications in various fields including photocatalysis, solar energy conversion, sensors, etc. But large band gap (3.2 eV) of TiO₂ allow absorption of only the UV region of the solar spectrum resulting in low conversion efficiency. To overcome such limitation number of attempts in which dye molecules or narrow band gap semiconductor nanocrystals were incorporated onto titania matrix have been reported in literature [20–23]. The modification of TiO₂ surface with organic molecules containing suitable donor ligands can form a charge transfer (CT) complex that absorbs radiation at a lower energy than either the molecule or the TiO₂ nanoparticles. And thus sensitization occurs by direct injection of an electron from the ground state of the molecule into the conduction band of

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the particle without involvement of an excited molecular state. This sensitization in turn enhance the ability of TiO₂ particles to absorb photons in the visible spectrum which is essential for many optical applications [24,25]. Thus TiO₂-ligand nanoscale assembly of particles having smaller band gap is highly desirable [26].

We described herein, a mixture of cationic surfactant CTAB and salicylate (in 1:1 molar ratio) as a template to fabricate novel titania-based nanostructured materials. Interestingly here ca. 2–4 nm particles of TiO₂-salicylate surface complex assembled in the CTAB-salicylate matrix have maintained the nanoscale arrangement. The as-synthesized samples were characterized by the powder X-ray diffraction (XRD), thermal analysis, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and spectroscopic tools (FT IR, UV-vis and PL).

2. Experimental

The TiO₂ nanocomposites are synthesized by using a mixture of cetyltrimethyl ammonium bromide (CTAB, Sigma Aldrich) and sodium salicylate (Sigma Aldrich) as a template and titanium (IV) butoxide (TB, Sigma Aldrich) as a titanium source. The four nanocomposite samples are prepared keeping the overall mole ratio of template to TB 1:2. The detailed mole ratio of CTAB, salicylate and TB are (1:1:4), (3:1:8), (1:3:8) and (0:1:2) and these samples are designated as sample 1, 2, 3 and 4, respectively. In a typical synthesis procedure, initially the templating gel is prepared by mixing the aqueous solutions of CTAB and sodium salicylate with desired mole ratio. Then ice-cooled titanium butoxide is added quickly into the viscous solution of CTAB-salicylate mixture (or only salicylate solution for sample 4) and the whole reaction mixture is left under vigorous and constant stirring in the ice-bath for 1 h. The mixture was then aged at 353 K for 72 h in the autoclave. The yellow precipitate was filtered and washed with water several times and dried by a freeze-drier.

All the samples were identified by powder XRD using a Bruker AXS D8 Advanced X-ray diffractometer on which the small and wide-angle goniometers are mounted. The X-ray source was CuK α radiation ($\lambda = 0.15406$ nm) with an applied voltage and current of 40 kV and 20 mA, respectively. Carbon, hydrogen and nitrogen contents were analyzed using a Perkin Elmer 2400 Series II CHN analyzer. Particle size and mesoscale assembly of different samples were observed using a JEOL, JEM 2010 TEM at an accelerating voltage of 200 kV. Jeol JEM 6700F field emission Scanning Electron Microscopy with an EDS attachment was used for the determination of surface morphology and chemical composition. UV-visible diffuse reflectance spectra of different samples were recorded on a Shimadzu 2401PC UV-visible spectrophotometer with an integrating sphere attachment using BaSO₄ as background standard. For the Fourier transform infrared (FT IR) measurement a Nicolet Magna IR 750 Series II was used. The luminescence excitation and emission spectra were measured at room temperature on a Hitachi 9000F spectrofluorometer with a xenon lamp as the excitation source. Photocurrent measurements were recorded in air on a tailor made setup at room temperature (298 K). The dark current-voltage (I-V) measurements were done by keeping the sample in dark for several hours and measuring the DC current between the two contacts using a Keithley 2400 source meter. For the photoresponse measurements, the photocurrent was measured at a fixed bias voltage by illuminating the sample (pelletized and making two silver contacts) with the light using a spectral illuminator with a 150 W Xenon lamp source (Newport Corp. USA; 96000 Oriol solar simulator).

3. Results and discussion

The small angle XRD pattern of sample 1 is shown in Fig. 1. The presence of this broad peak corresponding to a repeat distance of ca. 4.0 nm and the absence of any other low angle peaks indicate that the TiO₂ composite possess disordered mesophase with no long-range order. No such low angle XRD peak has been observed for other nanocomposites (samples 2–4). This result suggested that in the presence of CTAB:salicylate at 1:1, a new TiO₂-salicylate surface complex is formed which possess mesoscale arrangement within the nanoparticles. HR TEM micrograph of sample 1 (Fig. 2) clearly shows that almost spherical particles (the dark contrast vis-à-vis lighter wormhole-like matrix) of 3 ± 1.0 nm size are dispersed in the organic matrix (the continuous gray part of the TEM micrograph). Interestingly, from TEM images one can note that the interparticle distances are almost similar throughout the micrograph and the distance between two particles center is ca. 4 nm. So the TEM observations are in agreement with the low angle XRD results of this nanocomposite. The TEM observations for other salicylate-TiO₂ nanocomposites (samples 2 and 3, synthesized in the presence of CTAB) also illustrate that all those composites are composed of ca. 2–4 nm titania nanoparticles embedded in the CTAB-salicylate matrix. However, these particles are very close to each other and there is no regular arrangement among the particles. On the other hand sample 4 synthesized with salicylate alone (no CTAB) displayed no significant nanostructure (Fig. 2). In Fig. 3 FE SEM image for the sample 1 is shown. Very tiny particles having nanoscale dimensions are seen throughout the specimen.

Thermogravimetric analysis (Fig. 4) suggested the total weight loss for the samples 1–4 were ca. 50, 38.7, 31.2 and 25.6 wt%, respectively. In the case of sample 1, after a moisture removal step (up to ~ 125 °C), the decomposition of organic matrix (CTAB-salicylate) is started at ~ 200 °C. In the sample 4, a larger amount of moisture is removed (up to 10%) and the salicylate decomposition step is observed. The thermograph of sample 4 is rather different compared to the samples 1–3, this is reasonable because the template used for the synthesis of samples 1–3 is different due to the presence of the CTAB. CHN chemical analysis for sample 1 showed 30.6 and 2.4 wt% of C and H, respectively. Calculated experimental mole ratio of C:H agree well with the theoretical value in the salicylate moiety. The wide-angle XRD results of all

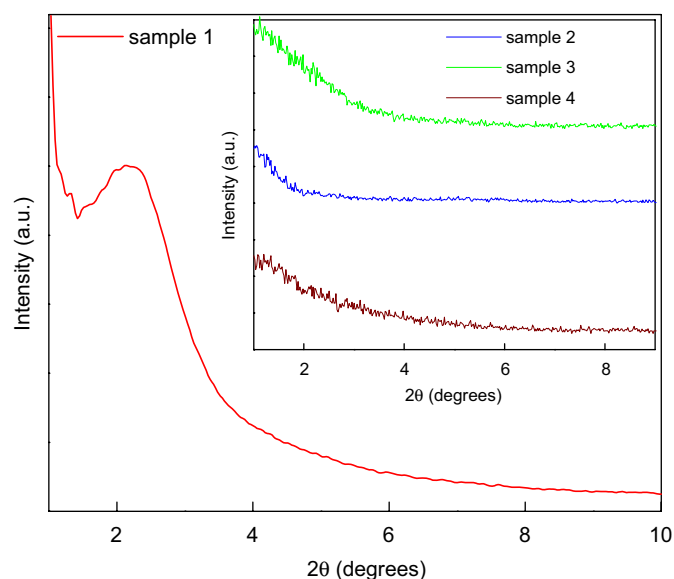


Fig. 1. Small angle XRD pattern of salicylate-TiO₂ nanocomposites.

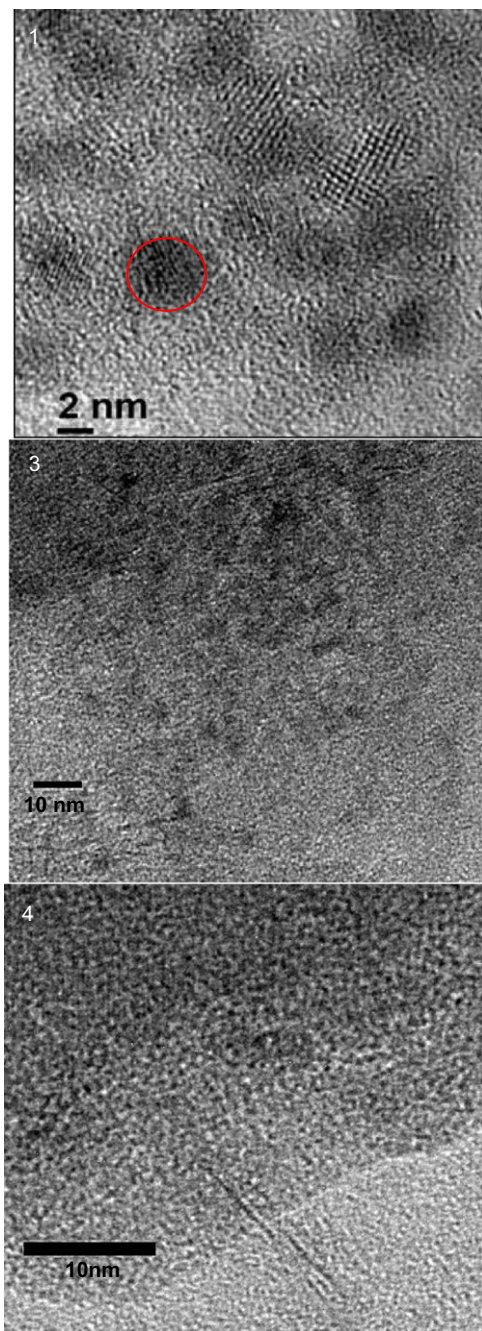


Fig. 2. HR TEM images of samples 1, 3 and 4. Single particles with an average diameter of about 3 ± 1 nm is shown in red circle. [For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.]

the samples exhibited mainly the amorphous structure of the TiO_2 nanoparticles. Further, the low intense and very broad peaks in the powder XRD patterns (Fig. 5A) reveal the presence of mostly anatase phase among all three phases, anatase, rutile and brookite of crystalline TiO_2 materials. Sample 1, which showed low angle powder XRD with a d spacing of ca. 4.0 nm (mesoscopic disordered assembly of nanoparticles) on calcination at 600°C resembles more closely to the crystalline anatase TiO_2 (Fig. 5B). However, the sample lost all surface bound organic salicylate moieties, becomes colorless and low angle diffraction peak disappeared after this high temperature calcination.

To examine the influence of salicylate ion in the preparation of titania nanocomposites, we have carried out a synthesis in the

presence of only CTAB as a template keeping all other reaction conditions similar. This as-synthesized sample is white in color and absence of any characteristic peak of CTAB in IR spectra suggested that the product was only TiO_2 (broad band at $500\text{--}700\text{ cm}^{-1}$ confirms the presence of Ti–O–Ti bond, curve a, Fig. 6). In contrast all the samples (sample 1–4) synthesized using CTAB–salicylate mixture and only salicylate as a template are yellow in color (but the intensity of the color increasing with the increasing ratio of salicylate ion to CTAB in the mixture) and IR spectra of all the composites exhibit the characteristic peaks of CTAB and salicylate (curve b and c of Fig. 6). The multiple bands between 1140 and 1600 cm^{-1} can be assigned to various vibration modes of salicylate ion. The characteristic bands such as the C–H stretching vibrations (of $-\text{CH}_2$ group) at 2921 and 2854 cm^{-1} indicate the existence of CTAB in the composites (curve b, Fig. 6). The broad band below 850 cm^{-1} confirms the presence of Ti–O–Ti bonds in composites 1 to 4. All the samples show the broad band centered at $\sim 3400\text{ cm}^{-1}$, which can be attributed to stretching vibration of surface hydroxyl groups. The results clearly indicate that presence of salicylate ion in the template-assembly is necessary for the interaction of template with the inorganic phase during the synthesis of all above composites.

The yellow color of the composites indicates the formation of the charge transfer titanium (IV) salicylate complex. Fig. 7 illustrates the UV–visible diffuse reflectance spectra of the different titania composites including the salicylate-free white TiO_2 sample. Organic-free TiO_2 gave no absorption features in the visible region (curve a, Fig. 7) and its band gap resembles to that in pure TiO_2 [24]. Composites exhibit significant amount of red shifts of the onsets of absorption spectra, compared to the bulk (organic-free) TiO_2 materials. The band edge for each sample has been calculated by extrapolating the steep slope of individual absorption spectra [27]. The band edge for only CTAB templated white TiO_2 sample is around 340 nm (3.64 eV) and the absorption red shift for composites 1, 2, 3 and 4 are nearly 170 nm (1.21 eV), 154 nm (1.13 eV), 190 nm (1.30 eV) and 262 nm (1.58 eV), respectively. So the absorption shifts for the composites, compared to pure TiO_2 sample increases with the increase of the salicylate content. In fact these CTAB–salicylate–titania nanocomposites show interesting hybrid properties, which includes charge transfer (significant red shift of the onset of the absorption spectra) [28] and the optical properties of semiconductor (continuous rise of absorption). Similar kind of hybrid properties of nanocrystalline TiO_2 has been observed, where the surface has been modified with different kinds of ligands like calixarenes [26] or enediol [29,30]. However, such kind of optical behavior was not seen in the earlier studies related to the aqueous titanium (IV) salicylate complex [31] and also the same surface complex in solid state [32].

From the UV–visible absorption spectra it is clear that the electronic structure and properties of TiO_2 nanocrystal surface have been engineered by the salicylate ions. Here it acts as organic capping agent to manipulate its band edge absorption. Organic-free pure TiO_2 absorb UV light only (band gap 3.2 eV), but salicylate– TiO_2 hybrid organic–inorganic nanocomposites absorb light at significantly lower energies in the visible range ($2.06\text{--}2.51\text{ eV}$), indicating ligand-to-metal charge transfer (LMCT) between salicylate and Ti centers on surfaces of TiO_2 nanoparticles. Presence of calixarenes at the surface of mesoporous TiO_2 have shown similar red shift in the absorption spectra due to LMCT band [26]. Here the salicylate molecules form a strong charge transfer complex with the surface of titania oxide nanoparticles and a different type of sensitization in comparison to unmodified titania occurs. In this mechanism electron transfer occurs from the ground state of the salicylate molecule to the conduction band of the titania particle without involvement of

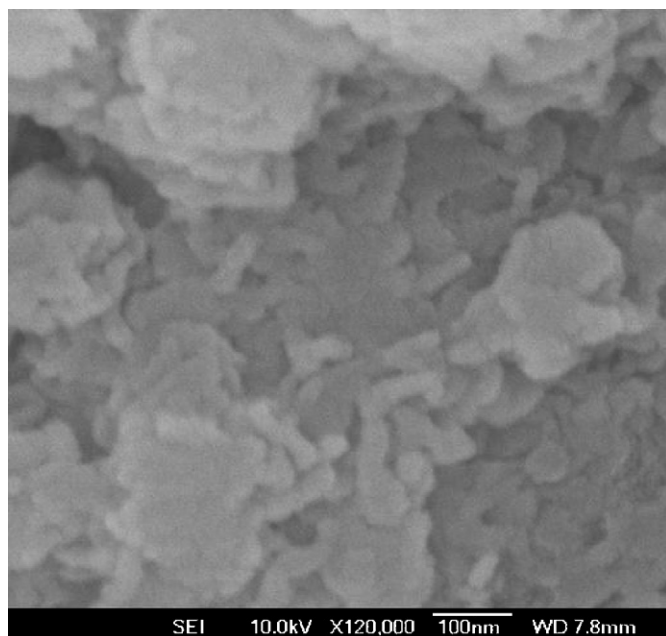


Fig. 3. Representative SEM micrograph of sample 1.

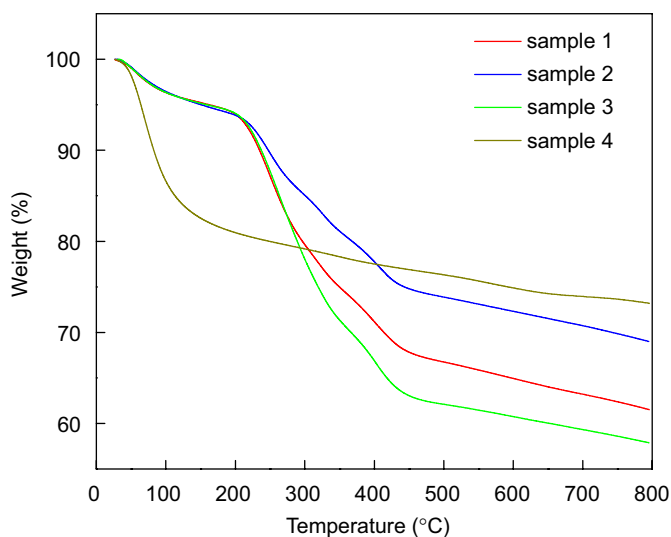


Fig. 4. Thermogravimetric curves (TG) for samples 1–4.

excited molecular state of salicylate (the UV absorption peak of the salicylate solution is at high energy 250 nm, which is absent in the absorption bands of the salicylate–TiO₂ composites) and this is the possible reason for significant red shift at the onset of absorption spectra (or reduction in band gap) observed in the case of our nanocomposites. In fact when we have plotted the band gap of different nanocomposites with respect to the concentration of salicylate concentration (Fig. 8) we observe a progressive decrease in band gap with the increase in salicylate concentration. This result suggested that sensitization of the TiO₂ surface with salicylate anions via LMCT complex in turn enhance the ability of TiO₂ particles to absorb photons in the visible spectrum.

The photoluminescence emission properties of all the nanocomposites are studied in solid state at room temperature. Illumination of alcoholic suspension of all titania nanocomposites

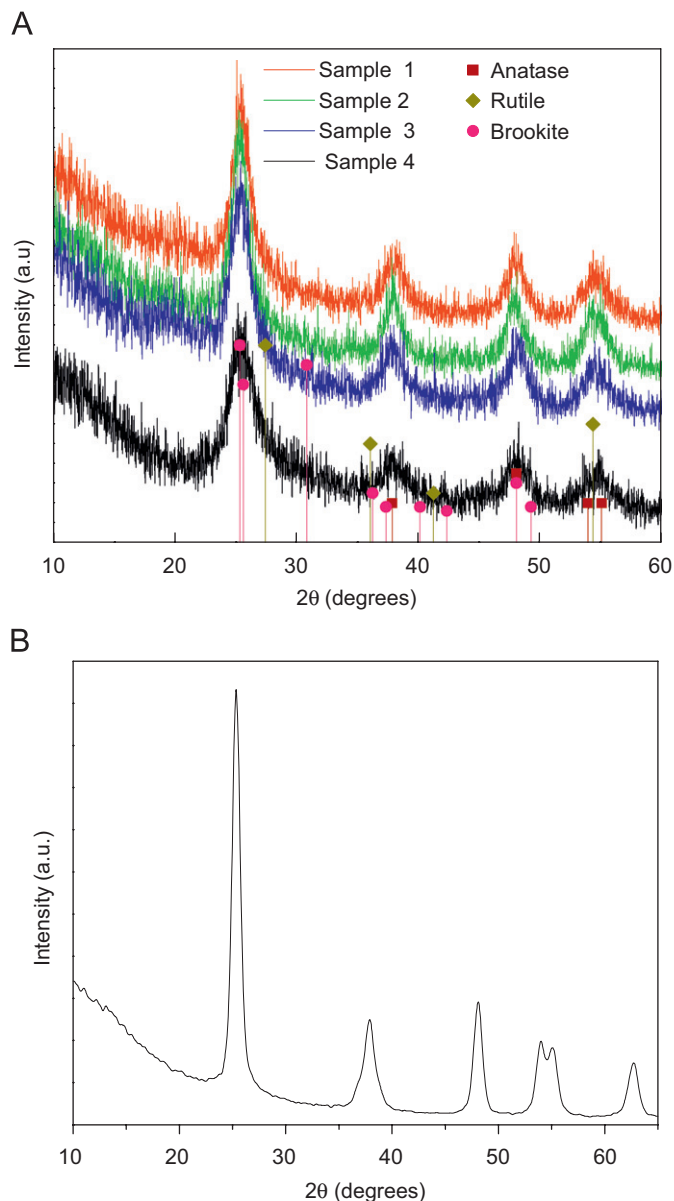


Fig. 5. (A) Wide-angle X-ray diffraction patterns for samples 1–4 and (B) sample 1 calcined at 600 °C.

(samples 1–4) with a UV lamp leads to blue luminescence at room temperature (inset, Fig. 9). Emission spectra of samples 1–4 are presented in Fig. 9. Excitation of the sample 1 at 290 nm results principal emission band centered around 467 nm along with other blue emission bands with maxima at ca. 449, 480 and 490.5 nm. Samples 2 and 3 followed similar emission behavior, although the PL intensity was much lower. This could be attributed to the low concentration of salicylate ions (TGA plot, Fig. 4). However, the emission peak for sample 4 synthesized in absence of CTAB was observed at high-energy ca. 425 nm. Previously we have reported similar multiple emission bands for titania–bidentate surfactant mesostructured composite materials centered at 425–428 nm [33]. Low-energy emissions (450–500 nm) in titania-based materials are generally associated with surface or bulk defect sites, including those intrinsic to isolated Ti atoms and titanates [34]. Multiple emission peaks in our salicylate–TiO₂ composites could be related to LMCT surface complex of Ti(IV) with the salicylate ion (covalent bonding), which leads to defect surface electronic

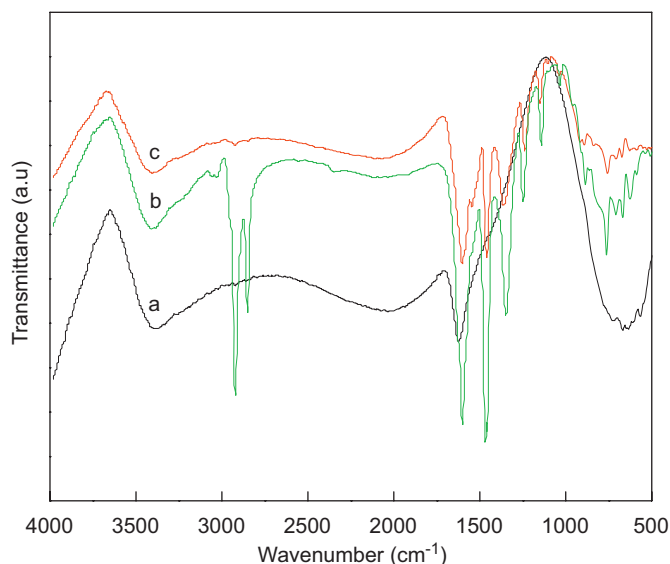


Fig. 6. FT IR spectra of different nanocomposites: (a) pure TiO₂ powder (white), synthesized in presence of CTAB template, (b) sample 1 and (c) sample 4.

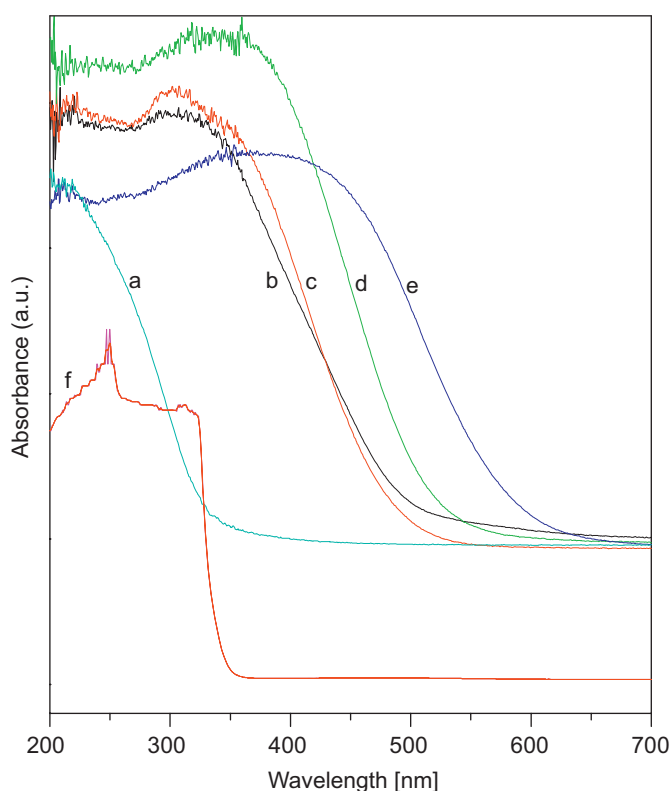


Fig. 7. UV–VIS absorption spectra of different nanocomposites: (a) TiO₂ powder (white) synthesized in presence of CTAB template, (b) sample 1, (c) sample 2, (d) sample 3, (e) sample 4 and (f) sodium salicylate (aqueous solution).

states [26,34]. Here the surface electronic states within the band gap can be created through charge transfer bands using salicylate as ligands, which capped the TiO₂ nanoparticles. The interface between the nanoparticle and CTAB–salicylate matrix introduces impurity states that alter carrier dynamics of the salicylate–TiO₂ nanocomposites and responsible for blue luminescence. Surface Ligand-mediated electron-transfer phenomena responsible for this blue luminescence could be particularly interesting in

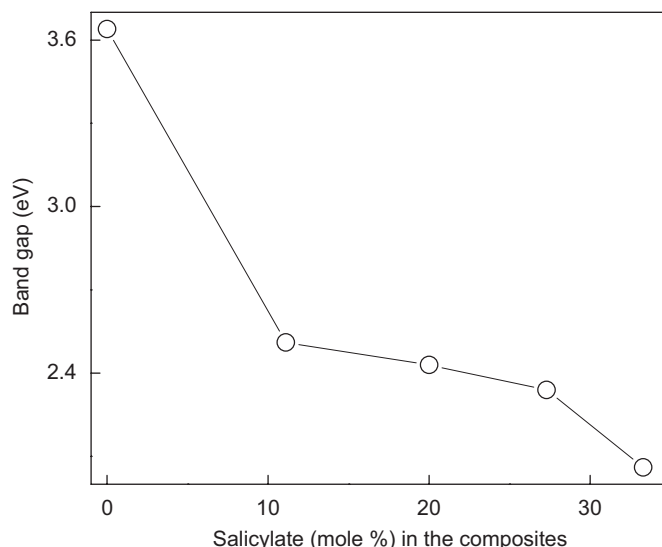


Fig. 8. Dependence of band gap with salicylate concentrations (mol% of salicylate in the mixture of salicylate+TB).

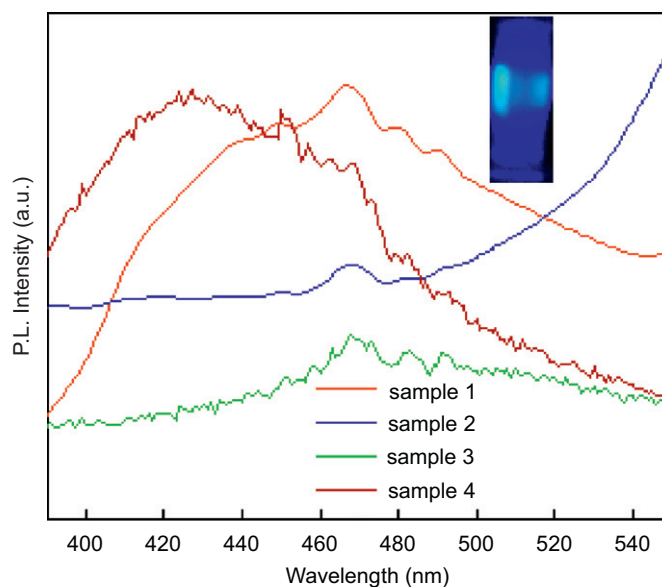


Fig. 9. Room temperature photoluminescence emission spectra from samples 1–4; Inset: an illumination photograph of sample 1.

optoelectronics and sensor applications [35] under visible light illumination.

Photoconductivity measurement is carried out on our salicylate–TiO₂ composites in the presence of sunlight to understand whether the conductivity increases compared to that in the dark. For sample 1, at an applied voltage of 0.75 V the current generated at dark is 0.011 μ A whereas after illumination the current increases to 0.0242 μ A after 15 min, which is the maximum value and it does not increase on further illumination. Thus we see that the current increases by about 2.2 times compared to that in the dark. On the other hand, when the photoconductivity of the material is compared with pure TiO₂ under identical condition, sample 1 is found to be 4 times more efficient. Thus we can conclude the salicylate–TiO₂ nanocomposite materials synthesized in the present work have photo-conducting behavior under visible light illumination.

4. Conclusions

In conclusion, here we have demonstrated that salicylate–TiO₂ nanocomposites can be synthesized by simple sol–gel route using low cost compounds CTAB–salicylate mixture and also salicylate ions as a template. The disordered mesoscale orientation of nanoparticles in the composite has been obtained for 1:1 mixing ratio of CTAB and salicylate at the CTAB concentration 0.001 M. The assembly of nanoparticles designed herein is highly interesting in the context of sensitization by LMCT bands under visible light illumination. All the nanocomposites exhibit a considerable red shift of the onsets of absorption spectra towards the visible region compared to organic-free nanocrystalline TiO₂. All the salicylate–titania nanocomposites show interesting blue luminescence, which could be utilized for their possible application in optoelectronics and sensors.

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