Optical absorption enhancement of CdS nanoparticles by SILAR method and it's physical characteristics

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Abstract

TiO_2 nanostructure electrodes with CdS surface treatment were synthesized with simple and cost-effective chemical deposition method. Pristine TiO_2 deposited by CBD. Chemical solution process and CdS in different SILAR cycles. The structural and morphological changes were confirmed from the XRD, SEM, and EDAX measurements. The XRD patterns of the TiO_2 nanostructures after CdS deposition for 10, 20 and 30 SILAR cycles, called as B-D, were obtained. electrode material was confirmed using JCPDF files no. 46-1238. The diffraction peaks were corresponding to the (100), (101), (111), (211), (002) and (310) planes. To confirm the CdS surface treatment we carried out EDX analysis of TiO_2 with CdS surface treatment for 20 SILAR samples. Optical density was a function of CdS loading cycles i.e. with cycles optical density of TiO_2 was increased. We got maximum optical for the 20 SILAR cycles of CdS doping on TiO_2 sample

Keywords: optical absorption, SILAR method, Surface treatment

1. Introduction

In last few decades due to the need of various demands of humans the rise of nanomaterials has led to substantial advances in a expansive range of (photo)electrochemical and (photo)- catalytic applications where high surface areas are decisive factor for high rate of chemical reaction.[1-3] Recently, number of synthesis routes have developed for the controlled synthesis of various nanoparticles with control over the size, crystallinity, faceting, and surface functionality.[4] metal oxide nanoparticles are diverts attention of many scientist due to wide range of applications including batteries, fuel cells, supercapacitors, and photovoltaics. Amongst all metal oxide Titanium dioxide (TiO_2) is prominent choice for such applications. Titanium dioxide also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium, with a chemical formula TiO_2. TiO_2 is a wide 3.2 eV band gap semiconductor that can be found in nature as Anatase, Rutile and seldom or Brookite crystalline structures. Anatase is the most common structure used in high performance solar cells [5]. TiO_2 has been extensively studied because of its unique optical and chemical properties in photocatalysis,[6] photovoltaic cells,[7] sensors [8], water splitting [9], lithium ion batteries [10], direct methanol fuel cells (DMFCs) [11] and so on. For utilization of TiO_2 for various applications we need to modify the TiO_2 electrodes by using various approaches. Generally, various surface treatments are used to modify the structure for wide ranges of applications [12-15].

In continuation to our ongoing metal oxide thin film-based research [16-28]. In present paper, we are investigating optical properties of CdS-TiO_2 nanostructures for different deposition cycles (10, 20, 30) of CdS by SILAR method. we are synthesizing TiO_2 by chemical deposition method and modify TiO_2 surface by treatment of CdS. Use these films for structural elucidation, morphology evolution and optical mesurements.

2. Experimental Details

Pristine TiO_2 and CdS surface treated TiO_2 nanostructure thin films were synthesized by using titanium tetra chloride ($TiCl_4$), Cadmium chloride ($CdCl_2$), sodium sulfide (Na_2S), ammonia solution (NH_4OH), double distilled water all the films were deposited on the fluorine doped-tin oxide (FTO) substrates. All chemicals used in this experiment were of analytical grade and used without further purification. FTO substrate sheets purchased from SAMSUNG electronics were used on account of their good stability at high temperature and transparency. FTO substrates were cleaned with soap, distill water (20 min), acetone (20 min) and isopropanol (20 min) and finally, dried in air flow at room temperature for 30 min and dried with a nitrogen (N_2) air stream. The concentration of $TiCl_4$ was changed by adding deionized water in stock $TiCl_4$ solution. For preparation of TiO_2 nanostructured initially, reduce $TiCl_4$ Solution in 20% HCl by adding the calculated volume of HCl to triply distilled water to make 1M stock solution. This stock solution was kept at cool place before use. The yellow color of solution was slowly turned to colorless. In exact processes, 0.1 M thiourea was added into Appropriate amount $TiCl_4$ stock solution make the total solution 25 ml. A transparent solution with a reddish-yellow color was obtained after vigorous stirring for 30 min at room temperature. 25 ml of the resulting solution was poured into beaker. Make similarly in three more beakers. The reactions were allowed to proceed for 4 h at 328 K. Whitish Ti(OH)2 were removed, washed with distilled water, dried and annealed at 573 K for 1 h before further use. For further work use three TiO_2 nanostructured films out of four. Cadmium sulfide (CdS) nanoparticles were growing on to the mesoporous TiO_2 nanostructure by the SILAR method. Take 0.1M cadmium chloride ($CdCl_2$) aqueous solution whose pH was adjusted to ~11 by adding liquid ammonia solution and 0.1 M sodium sulfide (Na_2S) in water separately. It acts as cationic (Cd^{2+}) and anionic (S^{2-}) precursors to form CdS nanoparticles on to TiO_2 nanostructures. The deposition of CdS on/in to TiO_2 was carried out using four beakers system at room temperature. The beaker number one was containing the aqueous solution of 0.1M $CdCl_2$ solution whose pH was ~11 by liquid ammonia and beakers two and four with deionized water. The beaker three was of 0.1M sodium sulfide Na_2S solution.

One SILAR cycle was of four steps; (1) for adsorption of cadmium species deep TiO_2 film in beaker 1 for 10 s, (2) then rinsing the film with distilled water for 5 s to remove excess adsorbed or loosely bounded cadmium species, (3) after that deep the film in to Na_2S solution for 10 s to form stable CdS, and (4) rinsing with purified water for 5s to remove excess or unreacted species or powdery CdS. The CdS adsorbed TiO_2 films were completed by drying with air stream after the washing process. These four steps preferred one 'SILAR cycle'. The TiO_2 films loaded with CdS nanoparticles by 10 cycles, 20 cycles and 30 cycles were named as B, C and D respectively. Pristine TiO2 film named as A. Finally, all the films were annealed in air at 523k for 1 hr and use these resultant films to further analysis. Crystal structure of A to D films were studied by using X-ray diffractometer (XRD, Rigaku D/MAX 2500 V, Cu Kα, λ = 0.15418 nm). Surface morphology of the A to D nanostructured electrodes was confirmed with a field-emission scanning electron microscope (FE-SEM, Hitachi S-4200). The optical analysis was carried out by using a carry 100 UV–vis spectrophotometer.

3. Results and discussion

3.1 Structural analysis

X-ray diffraction (XRD) is essential in the determination of the crystal structure and the crystallinity of deposited thin films. Figure 1 represents the XRD analysis patterns for pristine TiO_2 (A) and CdS deposited on to TiO_2 nanostructure for different deposition cycles of CdS like 10 (B), 20 (C), and 30 (D) SILAR cycles. In the XRD spectra all the XRD peaks are well matches with JCPDS file no. 46-1238 which confirmation of TiO_2 nanostructures. Diffraction patterns show peaks corresponding to (100), (101), (111), (211), (002) and (310) planes.

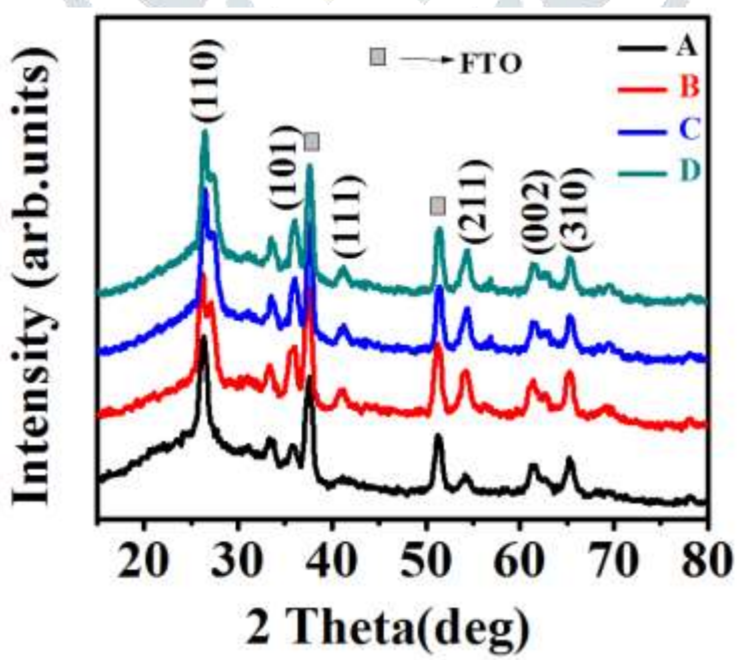

Fig. 3.1 XRD spectra for Pristine TiO_2 (A) and CdS surface treatment for 10 (B), 20 (C), and 30 (D) SILAR cycles.

From XRD graphs we can calculate the grain size with the help of Debye Scherrer's formula by using full width at half maxima (FWHM). The crystallite grain size was calculated by using the Scherrer's formula [21,22]:

$$\textbf{Grain Size} = \frac{0.9\,\lambda}{B\ \mathrm{Cos}\ \theta}$$

Where, λ = X-ray wavelength, θ = Bragg diffraction angle, and B = FWHM of the XRD peak. The grain size calculates for all films by using (110) peak in the range of 27.84 to 38.42 nm. Lowest gain size 27.84 nm calculated for pristine TiO_2 and highest grain size 38.42 is for film C. Whereas, grain size of sample B and sample D is 31.62 nm and 34.57 nm respectively. As expected XRD spectra does not show any evidence for CdS doping so we take sample C for EDX analysis for confirming CdS doping. The results of EDX analysis for sample C is shown in figure 2. EDX analysis clear idea about CdS as Cd and S atoms are scanned.

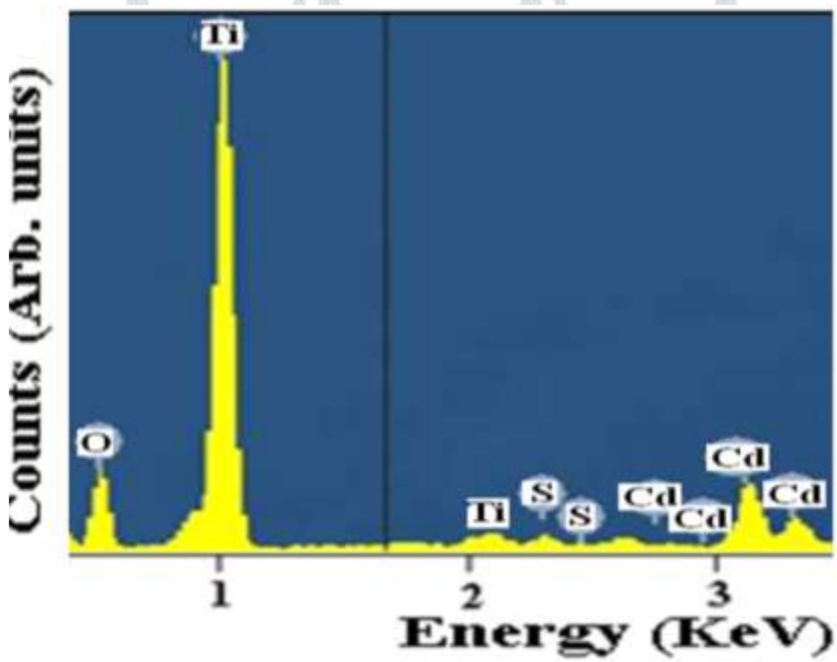

Figure 2 DEX analysis results for sample C

3.2 Surface morphological study

The surface morphology of pristine TiO_2 (a) and CdS (10 cycles (b), 20 cycles (c), 30 cycles (d)) surface treated TiO_2 nanostructure thin films were investigated using FE-SEM analysis and resulting FE-SEM images are shown in figure 3.

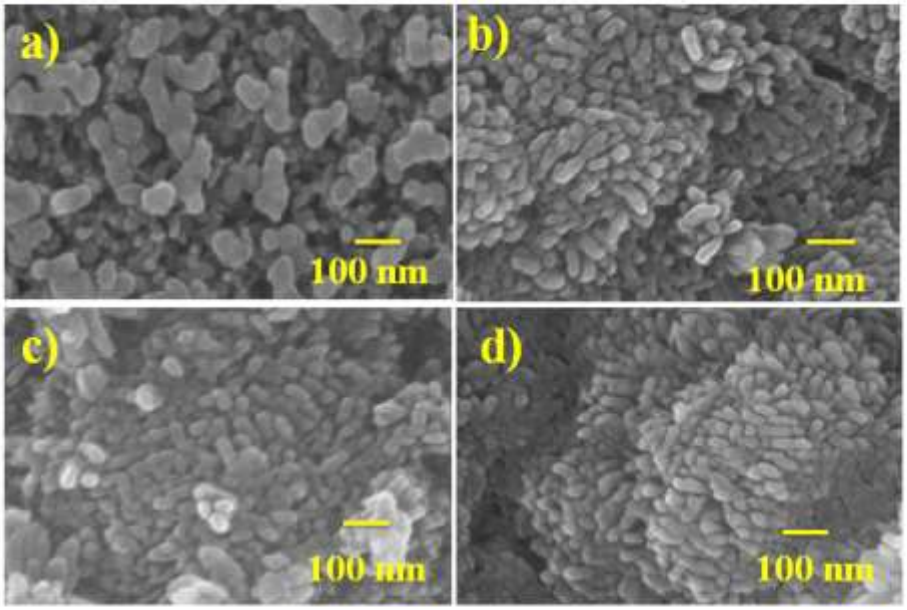

Figure 3 FE-SEM images of a) pristine TiO_2, b) 10 cycles, c) 20 cycles, and d) 30 cycles CdS on TiO_2 nanostructures.

As can be seen, figure 1 (a) the surface morphology view of the pristine TiO_2 nanostructure shows show granular morphology in such a way that garnuls shows upward growth of nanostructure as well as nanostructure the granular structure grows. The nanostructure shows considerable voids in between garnuls. After CdS treatment for various cycles for i.e. 10, 20 and 30. Surface shows significant variations in surface morphology is represent in figure 3 b, c, and d respectively. After CdS deposited on TiO2 nanostructures the surface morphology changes to such a way those granules are starts to grow in upward directions. If we goes on increasing cycles after 20 the films showing starts to generation voids this leads to generation of cracks in the films so we stops deposition after 30 cycles.

3.2 *optical absorptions*

To investigate the optical absorption properties of pristine and CdS treated (A-D) TiO_2 nanostructure thin films the UV-Visible absorption spectra. The UV-Visible absorption spectrums were performed to measure optical absorption of TiO_2 nanoparticles after CdS loading as function of SILAR cycle number. UV-Visible absorption spectra were measured in the wavelength range of 350nm – 700 nm and results are demonstrated in figure 4.

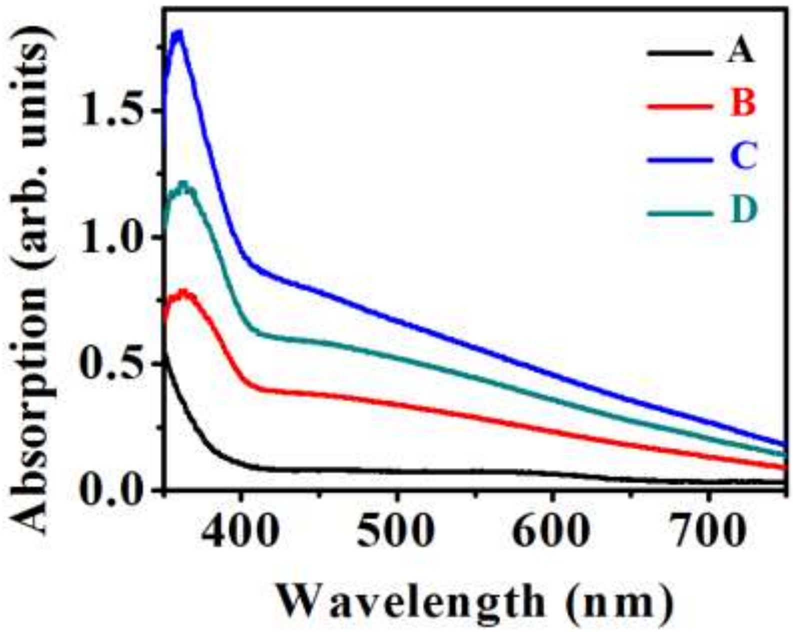

Figure 4 UV-Visible absorption spectrum of pristine TiO_2 (A) and CdSe treated TiO_2 nanostructures (A-D)

The variation in optical density of pristine TiO_2 (A) and the CdS-TiO_2 nanostructured electrodes (B-D) obtained for different SILAR cycles (10, 20 and 30 cycles) is observed in above figure 4. All the samples show strong band edge absorption in the range 350–420 nm wavelength region. After CdS treatment on the TiO_2 nanostructure the optical absorption of CdS doped film increased significantly. The TiO_2 electrodes exhibit different photon absorption activities because the optical density was different for each electrode, due to increasing SILAR cycles from 10 to 30, even though all of them were synthesized under the same conditions using the same method. The band gap of CdS corresponding to the absorption edge is about 2.38 eV. The absorbance gradually increased with the increase in the SILAR cycle number, indicating that more CdS have been deposited onto the TiO_2 thin film. We get highest optical absorption for electrode C which is for 20 SILAR cycles. In case of 30 SILAR cycle the optical absorption get decreased

Conclusions

In summary, pristine TiO_2 and CdS/TiO_2 nanostructured thin films were deposited on to the FTO substrate by chemical deposition method. Variations in optical absorption were studied for all samples. TiO_2 nanostructure and CdS doping were confirm by XRD and EDX analysis respectively. We get lowest optical absorption for pristine TiO_2 thin film and highest optical optical absorption for TiO_2 film with 20 SILAR cycles CdS treatment. This can be used in various optoelectronical applications like solar cell, supercapictors, etc

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