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# Room Temperature Synthesized $TiO_2/Bi_2Se_3$ Bilayer Thin Film by Simple Chemical Route: Study the Effect of Deposition Time of Bismuth Selenide on Physical Properties of Film

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Simple chemical route namely Chemical Bath Deposition (CBD) has been successfully employed for deposition of Bismuth Selenide ($Bi_2Se_3$) nanoparticles on porous $TiO_2$ at room temperature. The effect of deposition time of $Bi_2Se_3$ on structural, surface morphological and optical properties of $TiO_2/Bi_2Se_3$ bilayer film has been systematically investigated. X-ray diffraction and energy dispersive X-ray spectra analysis was confirmed the $Bi_2Se_3$ nanoparticles are of effectively deposited on anatase $TiO_2$ film. Field Emission Scanning Electron Microscopy (FESEM) images shows the $TiO_2$ film uniformly covers by $Bi_2Se_3$ nanoparticles. Optical absorption spectrum is reflecting the considerable enhancement in absorption of visible light with increasing deposition time of $Bi_2Se_3$ on $TiO_2$ thin film.

**Keywords:** Bismuth Selenide, Titanium Dioxide, Nanoparticle, CBD, Thin films.

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## 1. INTRODUCTION

The transparent conducting metal oxide such as $TiO_2$, ZnO, CdO, and $SnO_2$ earned the considerable interest by research community since from last few decades due to its novel physical and chemical properties. Among them $TiO_2$ is one of the excellent metal oxide semiconducting material which is abundantly available, non-toxic, low cost, and chemically stable. As these consequences $TiO_2$ has been extensively used in number of applications such as in photoelectrochemical cells [1-4], gas sensors [5-6], supercapacitor [7-8] display devices [9-10], photocatlyst [11] etc.

The ideal physical and chemical characteristics of $TiO_2$ established him as promising candidate for the applications of solar energy conversion devices. But it is not functionalise ideally due to its wide energy band gap ($E_g$ = 3.2 eV) which is weaker its light harvesting ability in visible region [12]. Band gap modulation of $TiO_2$ by using of appropriate narrow band gap material is one of the convenient approach for enhancing optical absorption toward lower wavelength. With this consequences number of efforts has been taken by research community to improved optical properties of $TiO_2$ by using dyes, metal nanoparticles and metal chalcogenide materials. Compare with dyes and metal nanoparticles, semiconducting metal chalcogenides are prominent materials due to its easy band gap tuning by optimizing preparative parameters during synthesis. In this context some of the papers was reported were narrow band gap metal chalcogenide semiconductors such as CdS [13], CdSe [14], $Bi_2S_3$ [15], $Sb_2S_3$ [16], etc. used as sensitizer with metal oxide for effective trapping of visible light.

In this paper attempt has been made to extend the optical absorption response of $TiO_2$ towards lower wavelength region through the deposition of group V-VI compound inorganic semiconductor material such as Bismuth selenide consisting narrow optical band gap which is tuneable in the range of 0.91 to 2.3 eV [17, 18] by simple chemical route. The effect of deposition time on structural, surface morphological and optical properties of resulted $TiO_2/Bi_2Se_3$ bilayer film was systematically presented.

## 2. EXPERIMENTAL

### 2.1 Chemicals and Materials

For the fabrication of $TiO_2/Bi_2Se_3$ bilayer system, $TiO_2$ powder (P-25 Degussa, Germany), titanium isopropoxide (Aldrich, India), acetyl acetone (Sigma Aldrich), ethanol absolute, triethanolamine (TEA) (Merck, Germany) and bismuth nitrate, sodium sulphite, selenium (Loba chemie) were analytical reagent (AR) grade and used without further purification. All precursor solutions were freshly prepared with ultrapure deionized water.

The fabrication of $TiO_2/Bi_2Se_3$ bilayer system is a two-step process namely; coating of $TiO_2$ on pre cleaned glass substrate by using spin coating technique and then $Bi_2Se_3$ nanoparticles decoration on porous $TiO_2$ thin film by using simple chemical route.

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### 2.2 Deposition of $TiO_2$ Thin Film

The amorphous glass was used as a substrate for the deposition of porous $TiO_2$ thin film. Preliminarily glass substrates well cleaned with labolin soap solution and then proceed for ultrasonic cleaning treatment in double distilled water (DDW) followed by acetone. Finally cleaned glass substrates were dried in nitrogen environment before the deposition of $TiO_2$ thin film.

Initially $TiO_2$ gel prepared by adding 2 gm of P-25 $TiO_2$ powder in the 10 ml mixture of ethanol and acetyl acetone followed by addition of 1 ml titanium isopropoxide. The resultant mixture was well stirred at room temperature and subjected in ice bath for ultrasonic probe sonication at an frequency (20 kHz) for 30 min. The sol-gel spin coating route followed for the preparation of $TiO_2$ thin films onto glass substrate by injecting 1 ml of prepared $TiO_2$ gel one time onto the centre of glass substrate. The spin coater was rotated with the different r.p.m. from 500 to 2000 rpm for 1 min. and finally a uniform film was obtained. In order to avoid agglomerations of $TiO_2$ nanoparticles in $TiO_2$ gel, it is mandatory to keep it inside the ultrasonic bath till end of the deposition process. The synthesized films were annealed at 450 °C for 30 min. to eliminate organic ingredients and to enhance the adherence as well as porosity of film with surface of the substrate. Lastly, the annealed $TiO_2$ thin film was used as a substrate to for further deposition of $Bi_2Se_3$ nanoparticles carefully store in vacuum desiccator.

### 2.3 Deposition of Nanocrystalline $Bi_2Se_3$ on Porous $TiO_2$ Thin Film

The experimental set up used for the preparation of $TiO_2/Bi_2Se_3$ bilayer system is shown in Fig. 1. Simple and low cost CBD method employed for the deposition of nanocrystalline $Bi_2Se_3$ on porous $TiO_2$ thin film at room temperature. The cationic precursor for $Bi_2Se_3$ was 1 mM bismuth nitrate ($Bi(NO_3)3.5H_2O$) complexed with optimised amount of triethanolamine (TEA) at a $pH \approx 9$. The source for selenium is a sodium selenosulfate serve as a anionic precursor prepared by adding elemental selenium powder and sodium sulphite ($Na_2SO_3$) in 60 ml deionized water followed by magnetic stirring at 65 °C for 6 h consisting $pH \approx 11$. The cationic and anionic precursors were taken in 1:1 volumetric ratio in beaker and earlier coated porous $TiO_2$ thin film was immersed in chemical bath and kept inclined to the wall of the beaker in such manner that deposited surface towards the mixture. The films were taken out with specific time intervals i.e. after 15, 20 and 25 min. and rinsed with DDW to remove loosely bounded particles. $TiO_2/Bi_2Se_3$ films exhibiting variation in colour from faint brown to dark brown as increasing deposition time from 15 to 25 min. Finally deposited films were dried in air at room temperature and used for further characterizations.

### 2.4 Reaction Mechanism

The solution growth is the proposed route for the deposition of $Bi_2Se_3$ thin film onto porous $TiO_2$ majorly involved ion by ion mechanism. The cationic precursor is a source of $Bi^{3+}$ ions consist Bi-TEA mixture where TEA used as complexing agent. The complexing agent having two important aspect first to prevent dissociation of cations and suitably releasing them for further reaction. The dissociation of selenide anions by the hydrolysis of sodium selenosulfate in alkaline solution containing soluble complexes of bismuth. The ionic product of cations and anions in precursor solution exceed the solubility product they lead to formation of embryos by coagulation of atoms. Once these embryos attain the critical size initiated the nucleation which serve as a seed for further growth of $Bi_2Se_3$ nanoparticles on the surface of substrate. In this way the thin film formation is proceed on porous $TiO_2$ substrate by ion by ion condensation which facilitated us to easily tuning particle size by controlling preparative parameters. Here growth of $Bi_2Se_3$ thin film controlled by varying the deposition time of film in precursor solution and the resultant effect on physical properties of $TiO_2/Bi_2Se_3$ film are systematically presented. The overall reactions proceed in precursor solution are as follow

$$\text{Bi-TEA} \longrightarrow Bi^{3+} + \text{TEA}$$
$$Na_2SeSO_3 + OH^- \longrightarrow Na_2SO_4 + HSe^-$$
$$HSe^- + OH^- \longrightarrow H_2O + Se^{2-}$$
$$2Bi^{3+} + 3Se^{2-} \longrightarrow Bi_2Se_3$$

### 2.5 Characterizations

The prepared $TiO_2/Bi_2Se_3$ bilayer architecture was characterized by using XRD, FESEM and UV-Vis spectroscopy. Crystallographic and structural studies are carried out using Bruker D8-Advanced X-ray diffractometer using a $CuK_\alpha$ radiation source ($\lambda = 1.54056$ Å). The surface morphology and chemical composition of the prepared $TiO_2/Bi_2Se_3$ film was determined by FESEM and energy dispersive X-ray spectroscopy (EDS) using S-4800 type-II (Hitachi High Technology Corporation Tokyo, Japan). The optical properties were investigated using UV-Vis. double beam spectrophotometer, Shimadzu (Model-1601) within the wavelength range 300 to 800 nm.

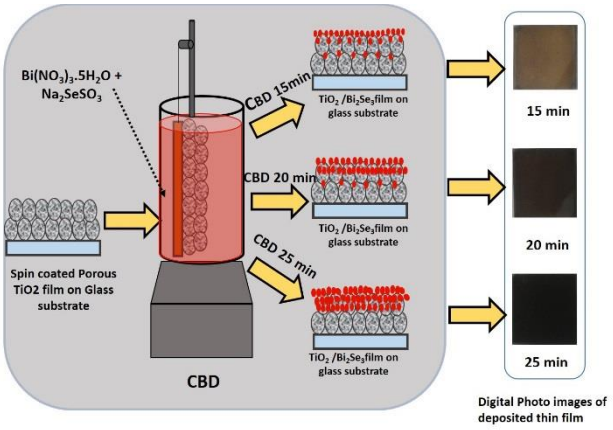


**Fig. 1 –** The schematic illustration of $TiO_2/Bi_2Se_3$

## 3. RESULTS AND DISCUSSION

### 3.1 Structural Studies

Fig. 2(a) and 2(b-c) shows the XRD pattern of a spin

coated bare $TiO_2$ and $TiO_2/Bi_2Se_3$ thin films respectively. Fig. 2(a) shows the XRD pattern of the bare $TiO_2$ synthesized on glass substrate which clearly reveals polycrystalline in nature. The most intense peak observed at $2\theta \approx 25.26°$ assigned to (101) plane, which is the characteristic peak of anatase phase with tetragonal crystal structure of $TiO_2$ [JCPDS card no. 84-1286]. While other low intense peaks at $2\theta \approx 37.87°$, 48.15°, 54.54° and 55.06° correspond to reflections from (004), (200), (105) and (211) planes respectively of $TiO_2$.

In Fig. 2(b-c) some additional low intense peaks are observed at $2\theta \approx 27.58°$ and 50.35° established the presence of another layer on $TiO_2$. The diffraction angles indexed to planes with orientation (121) and (351) correspond to formation of orthorhombic crystal structure of $Bi_2Se_3$ nanocrystals [JCPDS card no. 77-2016]. The XRD pattern confirmed the CBD method has been successfully utilized for synthesised $TiO_2/Bi_2Se_3$ bilayer architecture.

The crystallite size ($D$) for $TiO_2$ in the films has been evaluated by using Scherer's formula at an angle 25.26°.

$$D = \frac{k\lambda}{\beta \cos\theta}, \qquad (1)$$

where $k$ is constant (0.94), $\lambda$ is the wavelength of X-ray, $\beta$ is the full width at half of the peak maximum in radians and $\theta$ is Bragg's angle. Above equation established crystallite size of $TiO_2$ is found to be nearly 26 nm.

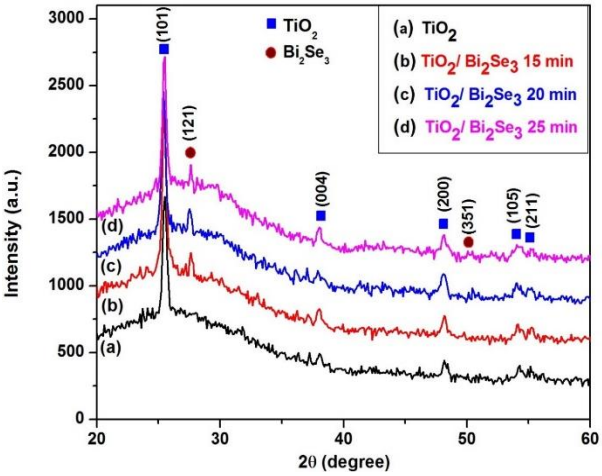


**Fig. 2** – XRD patterns of (a) bare $TiO_2$ (b) $TiO_2/Bi_2Se_3$ – 15 min (c) $TiO_2/Bi_2Se_3$ – 20 min (d) $TiO_2/Bi_2Se_3$ – 25 min

### 3.2 Surface Morphology and Compositional Studies

Fig. 3 shows the FESEM images were taken with scale bar of 200 nm for spin coated bare $TiO_2$ thin films and $TiO_2/Bi_2Se_3$ bilayer architecture. Fig. 3(a) depicted bare $TiO_2$ shows porous morphology constructed by small nanocrystals with average size 25 to 30 nm appears as agglomerated spherical clusters. This porous film provides large surface area for the further growth of $Bi_2Se_3$ nanoparticles. Fig. 3(b) gives the morphology of $Bi_2Se_3$ coated $TiO_2$ with 20 min. deposition time gives the pre deposited $Bi_2Se_3$ nanoparticles act as a secondary nucleation centres leading to coalescence formation.

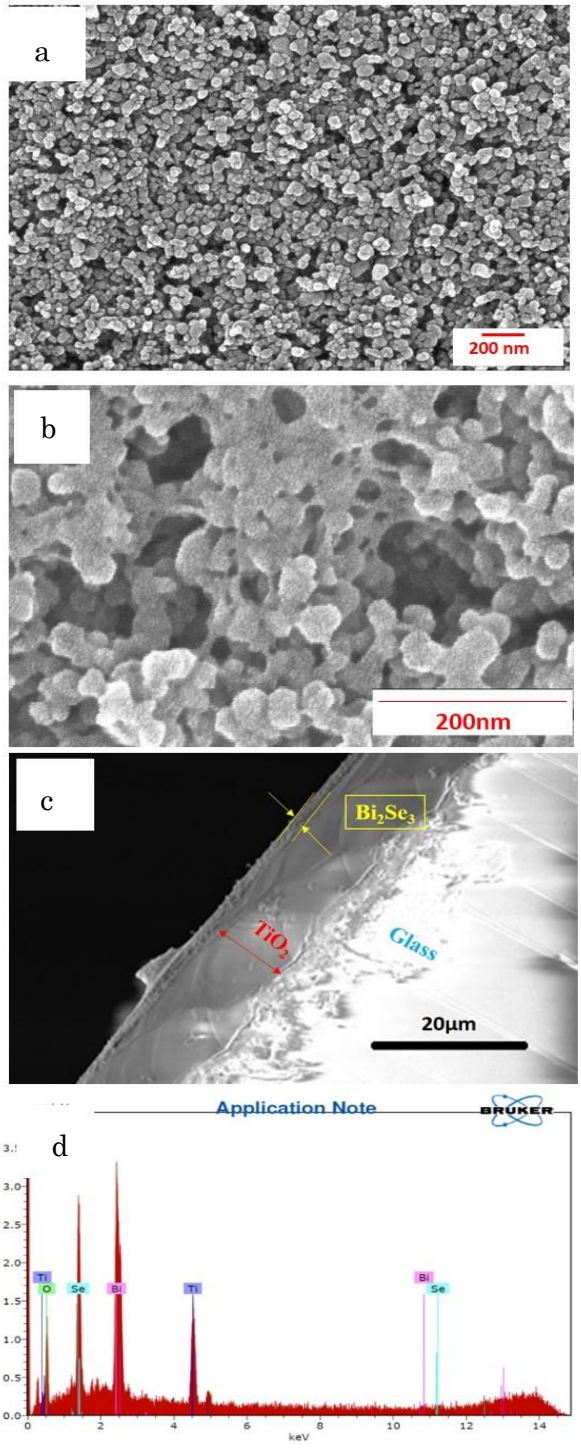


**Fig. 3 –** FESEM images of (a) bare $TiO_2$ (b) $TiO_2/Bi_2Se_3$ – 20 min. (c) Cross sectional image of $TiO_2/Bi_2Se_3$ (d) EDX spectra of $TiO_2/Bi_2Se_3$

The agglomerated $Bi_2Se_3$ nanoparticles enhancing the density of bridging result in minimizing porosity of resultant film. In this way by tuning deposition time in CBD is facilitated to optimise $Bi_2Se_3$ layer on porous surface of $TiO_2$. Fig. 3(c) for SEM cross sectional image clearly shows formation of another thin layer on bare $TiO_2$ recommended formation of $TiO_2/Bi_2Se_3$ bilayer thin film.

The compositional analysis was studied with the help of EDS coupled with FESEM unit. EDS spectrum

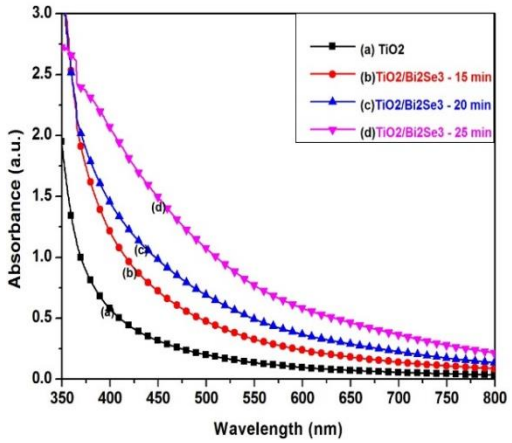


**Fig. 4 –**UV-Visible absorption spectra (a) bare$TiO_2$ (b) $TiO_2$/Bi2$Se_3$ – 15min (c) $TiO_2$/$Bi_2Se_3$ – 20 min (d) $TiO_2$/$Bi_2Se_3$ – 25 min

as shown in Fig. 3(d) consisted clear peak for Ti, O, Bi and Se strongly support to formation $Bi_2Se_3$ thin layer on bare $TiO_2$. In addition to XRD, this again confirmed the formation of $TiO_2$/$Bi_2Se_3$ bilayer architecture at room temperature by simple CBD method.

### 3.3 Optical Studies

The modification in light harvesting ability of $TiO_2$/$Bi_2Se_3$ architecture due to the chemically deposited thin layer of $Bi_2Se_3$ on bare $TiO_2$ film was studied by performing optical absorption studies in 300 to 800 nm wavelength range. The optical curve for bare $TiO_2$ as shown in Fig. 4(a) clearly revealed the sudden rise in absorption spectra at shorter wavelength (UV part) suggested the optical band edge would facilitate its application as window layer for visible spectrum. The enhancement in optical absorption is seen lower wavelength (visible region) with 15, 20 and 25 min. deposition time of $Bi_2Se_3$ as shown in Fig. 4(b-d) respectively. This might be due to as increasing in deposition time small particles get agglomerated to form bigger one, which is responsible to shifting optical properties towards the bulk materials. The optical absorption ability of bare $TiO_2$ is extended in lower wavelength region by depositing thin layer of $Bi_2Se_3$ nanoparticles.

## 4. CONCLUSION

In the present investigation we have successfully explored the simple chemical route for size controlled growth of $Bi_2Se_3$ nanoparticles on porous $TiO_2$ film at room temperature. The interaction between $TiO_2$ and $Bi_2Se_3$ significantly influences the surface morphological and optical properties of obtained $TiO_2$/$Bi_2Se_3$ bilayer thin film. The modulation in physical properties of as synthesised bilayer architecture will offer new opportunities in the field of optoelectronic, gas sensors and solar cell devices.

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