Study of Structural, Optical, Morphology and Photoelectrochemical Properties of Melanin Sensitized TiO₂ Thin Films Prepared by Chemical Bath Deposition Method

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Abstract

TiO₂ thin films were synthesized using simple, inexpensive, low-temperature chemical bath deposition (CBD) method and annealing at 300, 400, and 500 °C. The obtained TiO₂ thin films were sensitized with melanin. Influence of annealing temperature on structural, optical, morphology, and photoelectrochemical cell properties were investigated using a variety of techniques such as low angle X-Ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), UV-Visible spectroscopy, linear sweep voltammetry (LSV), Mott-Schottky (MS), electrochemical impedance spectroscopy (EIS), etc. We found that sensitization of TiO₂ with melanin changed its phase from pure rutile to rutile-anatase mixed-phase and the average crystallite size of melanin sensitized TiO₂ films is lower than TiO₂ films over the entire range of annealing temperature studied. SEM analysis showed the development of microcracks when TiO₂ was sensitized with melanin. UV-visible spectroscopy analysis showed that TiO₂ films absorbed mainly in the UV region whereas melanin sensitized TiO₂ thin films absorbed significantly in the visible region. Upon melanin sensitization, TiO₂ films showed a decrease in current density and flat band potential besides an increase in depletion width when annealing temperature was increased from 300 to 500 °C. Furthermore, EIS analysis revealed that melanin sensitized TiO₂ had a high charge transfer resistance. The obtained results showed that the sensitization of TiO₂ with melanin was not advantageous for the photocatalytic water splitting.

Keywords: Chemical bath deposition; Melanin sensitization; XRD; Raman; PEC properties

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1. Introduction

The photoelectrochemical (PEC) process is a clean and green method used for the production of hydrogen and oxygen via catalytic water splitting. This method was introduced by Fujishima and Honda in 1972.^[1] Now it is recognized as a feasible substitute for non-renewable energy sources.^[2] In a PEC cell, the semiconductor material is of immense importance. A large number of metal oxide materials such as TiO₂,^[3] Fe₂O₃,^[4] BiVO₄,^[5] WO₃,^[6] Cu₂O,^[7] ZnO,^[8] etc. have been investigated for realizing efficient photoanodes for water

splitting. Among these, TiO₂ has been extensively explored owing to its physical, chemical, and optical properties in the visible and near-infrared regions and high refractive index and high dielectric constant.^[9] These properties make TiO₂ one of the potential candidates for applications in PEC water splitting cells,^[10] supercapacitors,^[11] rechargeable batteries,^[12] photocatalysis,^[13] gas sensors,^[14] dye-sensitized solar cells,^[15] etc. Properties of TiO₂ strongly depend on their crystallinity, purity, structure, chemical composition, size- and/or shape-distribution, dimensionality, and defect centers, which can be easily tailored by changing the process parameters during preparation methods.

The material has been synthesized using various methods. These includes chemical bath deposition (CBD),^[16] chemical vapor deposition (CVD),^[17] hydrothermal,^[18] spin coating,^[19] pulsed-DC magnetron sputtering,^[20] dip coating,^[21] sol-gel,^[22] spray pyrolysis,^[23] successive ionic layer adsorption and reaction method (SILAR).^[24] Among these, CBD is an

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effective method to prepare TiO₂ films at low temperatures. It is a simple, cost-effective, and low-temperature solution processing technique, which can be used to deposit TiO₂ thin films on a large area and any kind of substrates. The advantage of the CBD method is that the properties of deposited films can be tuned by simply changing various growth parameters such as precursor, pH of the solution, the concentration of the precursor, additives, bath temperature, and bath time.^[25] To the best of our knowledge, only very few reports exist in the literature for the preparation of uniform TiO₂ films at low temperatures using CBD method.

For PEC applications, major problems associated with TiO₂ are poor visible light absorption, fast electron-hole recombination, and slow transfer kinetics of the charge carriers to the surrounding media.^[26] To overcome these problems and to enhance the PEC performance, various strategies such as energy band regulation, morphology control, doping, construction of heterogeneous junctions,^[27] surface plasmon resonance (SPR),^[28] quantum dots sensitization^[29] have been tested. Dye sensitization is the commonly used technique to increase visible light absorption to enhance PEC performance of TiO₂. For example, Youngblood *et al.*^[30] and Swierk *et al.*^[31] have carried out extensive studies on dye-sensitized semiconductor-based PEC water splitting. They obtained 1 % and 2.3 % quantum yield when [Ru(bpy)₃]²⁺ and ruthenium polypyridyl were used as a sensitizer in metal oxide semiconductors respectively. Gao *et al.*^[32] also worked on Ru-based PEC cells and achieved a photocurrent density of more than 1.7 mA/cm² under an applied potential of 0.2 V. Reisner and coworkers^[33] incorporated Ru-based dye on TiO₂ by adsorption method and achieved very an efficient sunlight conversion without precious metals. Dhanalakshmi *et al.*^[34] prepared sensitized TiO₂ by using electrostatic adsorption of the ruthenium complex. However, they reported that an optimum concentration of dye molecules on the surface of TiO₂ enhanced H₂ production, and a further increase in dye concentration decreased the activity due to the saturation in photocatalytic sites on TiO₂. Besides, Le *et al.*^[35] showed an enhancement of 6 times H₂ evolution onto Co-doped TiO₂ without dye. Recently, Lee *et al.*^[36] reported that the melanin-based organic/inorganic hybrid photoanodes had remarkably improved the photocurrent density for solar water oxidation.

Recently, we investigated the effects of synthetic melanin dye on the nanostructured ZnO for the PEC and showed that

the melanin incorporated ZnO photoanodes had a photocurrent density of about twice that of pristine ZnO photo-anode under one sun illumination. With this motivation, an attempt has been made to investigate the effect of synthetic melanin dye on TiO₂ for the PEC application. In the present paper, the TiO₂ thin films were synthesized by using the CBD method and annealed at 300, 400, and 500 °C. These TiO₂ thin films were then sensitized with melanin. The structural, optical, and morphology properties of as-annealed and melanin synthesized TiO₂ films were discussed as a function of annealing temperature. Finally, PEC properties of as-annealed and melanin synthesized TiO₂ films were also examined.

2 Experimental section

2.1 Preparation of TiO₂ films

For the deposition of TiO₂ thin films by CBD method, initially, precursor solution was prepared by mixing 10 mL distilled water (DW) with 10 mL of concentrated hydrochloric acid (HCl) [99.9 % Pure, Sigma Aldrich]. 2 mL titanium tetra isopropoxide (TTIP, 99.9 % pure, Sigma Aldrich) was added drop-by-drop in the mixture of DW and HCl. The solution was stirred for 15 min. To dilute the precursor solution, 100 mL DW was again added. The solution was again stirred for 30 min rigorously at room temperature. Finally, a muddy transparent precursor solution was obtained. To prepare TiO₂ thin films, the cleaned fluorine-doped tin oxide (FTO) substrates (2 cm × 2 cm) were dipped vertically in the precursor solution bath for 3 hr. The temperature of the precursor solution and bath was maintained at 80 °C. After completion of the process, the films were taken out from the bath and rinsed with DW, and allowed to dry. The as deposited TiO₂ films were then annealed at 300, 400, and 500 °C for 1 hr and then various characterizations were carried out.

2.2 Preparation of melanin sensitized TiO₂ films

For the synthesis of melanin sensitized TiO₂ thin films, initially, a melanin solution was prepared. For the preparation of melanin solution, 10 mg of melanin powder (99.9 % pure, Sigma Aldrich) was dissolved in 4 mL of dimethyl sulfoxide (DMSO) and 7 mL of ethanol (C₂H₅OH). Then annealed TiO₂ films deposited on FTO were immersed in a beaker containing melanin solution. After 20 hr, the films were taken out from the melanin solution bath and rinsed with DW and allowed to dry at room temperature, and then various characterizations were carried out.

Table 1. Microstructural parameters of TiO₂ and melanin sensitized TiO₂ films annealed at different temperatures.

a) As-annealed TiO ₂ films								
T _{Annealing} (°C)	d _{X-ray} (nm)	d (nm)	a = b (Å)	c (Å)	V (Å) ³	ε (10 ⁻⁴)	δx10 ¹⁵ (line/m ²)	α (10 ⁻³)
300	28.73					1.47	1.81	4.72
400	23.72	3.2291	4.6675	2.9398	64.04	1.45	1.78	4.71
500	23.51					1.21	1.12	4.70
b) Melanin sensitized TiO ₂ films								
300	7.22					4.6	1.78	3.21
400	7.49	1.7306	4.8948	2.4490	58.67	4.7	1.91	3.25
500	6.22					5.2	2.28	3.23

2.3 Film characterization

Structural properties of TiO₂ and melanin sensitized TiO₂ films were studied by using low angle x-ray diffractometer using Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation source (Bruker AXS D8 Advance, Germany) over a 2θ scan range of 20–80°. Raman spectra were recorded with Raman spectroscopy (Horiba Jobin-Yvon's LabRAM-HR) in the range 100–800 cm⁻¹ for the TiO₂ films and in the range, 100–1800 cm⁻¹ for melanin sensitized TiO₂ films. Scanning electron micrographs (SEM) of samples were recorded using JEOL JSMS-6360, Japan scanning electron microscope. Absorption spectra of films were recorded using a double beam UV-Visible spectrophotometer (JASCO V-670, Japan) in the range 200–1000 nm.

2.4 Photoelectrochemical (PEC) cell assembly and measurements

Fig. 1 Schematic of photoelectrochemical (PEC) cell assembly employed in the present study.

Fig.1 shows the schematic of the PEC cell employed in the present study. Three electrodes were placed inside the cell; the synthesized TiO₂ or melanin sensitized TiO₂ on FTO acted as working electrode (WE), whereas, platinum foil and saturated calomel electrode (SCE) were used as counter electrode (CE) and reference electrode (RE), respectively. 0.1 M Na₂SO₄ was used as an electrolyte. Potentiostat (Metrohm Autolab: PGSTAT302N) and 150 W Xenon Lamp (PEC-L01) with an illumination intensity of 100 mW/cm² (AM 1.5) were used to record the I-V characteristics.

3 Results and Discussion

3.1 X-ray diffraction analysis

X-ray diffraction studies give information about the crystal structure, orientation, and crystalline size of the films. **Fig. 2** shows the XRD pattern of as-annealed and melanin sensitized TiO₂ thin films deposited by the CBD method. The presence of multiple peaks in the diffraction pattern indicates that all films are polycrystalline. As seen from **Fig. 2(a)**, major diffraction peaks are observed at $2\theta \sim 27.6^\circ, 36.3^\circ, 41.5^\circ, 44.0^\circ, 54.7^\circ, 56.7^\circ, 63.1^\circ$ and 69.7° , which are associated with (110), (101), (111), (210), (211), (220), (310) and (311) diffraction planes. These peaks are compared with the standard JCPDS data card # 73-1765 (Space Group: P4₂/mmn), which confirms the formation of polycrystalline rutile TiO₂ structure. No diffraction peaks due to anatase

or brookite phases are detected, suggesting the formation of pure rutile-TiO₂ phase. The diffraction is dominant along the (110) plane and its intensity increases with an increase in annealing temperature, suggesting that the crystallites of rutile-TiO₂ have preferred orientation along the (110) direction. A careful comparison of the standard 2θ values with the observed 2θ values shows a slight peak shift.

The average crystallite size ($d_{\text{x-ray}}$) was calculated using the Debye-Scherrer equation,^[37]

$$d_{\text{x-ray}} = \frac{0.9 \lambda}{\beta \cos \theta_B} \quad (1)$$

where λ is the wavelength of the Cu-K α line and β is the full width at half maximum (FWHM) of diffraction peak. The estimated values are listed in **Table 1**. The crystallite size decreases with an increase in annealing temperature. A decrease in the crystallite size may be due to the recrystallization of the film with an increase in annealing temperature.^[38]

Fig. 2 X-ray diffraction pattern for (a) as-annealed TiO₂ films, and (b) melanin sensitized TiO₂ thin films deposited by chemical bath deposition method. (*) indicate the XRD diffraction peaks of SnO₂:F, on which the TiO₂ layer is deposited.

The interplanar spacing between atoms (d-spacing) for TiO₂ thin films annealed at different temperatures is calculated using Bragg's law:

$$2d \sin \theta = n\lambda \quad (2)$$

The observed d-values of the deposited TiO₂ thin film were compared with JCPDS data card # 88-1175, which is in good agreement with the standard d-value (3.194 nm) of the rutile tetragonal TiO₂ phase.

The lattice constants ($a = b$ and c) and the unit cell volume ($V = a^2c$) of TiO₂ films have been determined from interplanar spacing (d-spacing) by using Equaiton (3&4):^[39]

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (3)$$

$$V = a^2c \quad (4)$$

The unit cell parameters obtained for the annealed TiO₂ thin films are $a = 4.6675 \text{ \AA}$, $c = 2.9398 \text{ \AA}$, and unit cell volume = $64.04 \text{ \AA}^3$. These results are also in good concurrence with previously reported values of lattice parameters and unit cell volume.^[40]

A dislocation is a crystallographic defect or irregularity within a crystal structure, which strongly influences the properties of the material. The dislocation density (δ) is the length of dislocation lines per unit volume of the crystal and is calculated using Equation (5):^[41,42]

$$\delta = \frac{n}{d_{x\text{-ray}}^2} \quad (5)$$

where n is the factor which is equal to unity for minimum dislocation density and $d_{x\text{-ray}}$ is the particle size.

Lattice microstrain (ϵ) in a crystal occurs due to the displacements of unit cells from their normal position. It arises in the TiO₂ crystal due to the presence of imperfections like dislocation, stacking fault probability and lattice distortion, etc. The microstrain is calculated using Equation (6),^[42]

$$\epsilon = \frac{\beta \cos\theta}{4} \quad (6)$$

Stacking fault probability (α) is the fraction of layers that undergo sequential stacking faults in a crystal^[43] and can be estimated using Equation (7):^[44]

$$\alpha = \left[\frac{2\pi^2}{45\sqrt{3}\tan\theta} \right] \beta \quad (7)$$

As seen, the stacking fault density decreases with increasing annealing temperature. The possible reason for the decrease in stacking fault density can be the slight shift in diffraction peaks when compared with standard JCPDS # 73-1765 data.

The estimated microstructural properties of as-annealed TiO₂ films, interplaner distance (d-spacing), dislocation density (δ), microstrain (ϵ), lattice constants (a , b , and c), unit cell volume (V), stacking fault probability (α), etc. are listed in Table 1. As seen, the dislocation density of TiO₂ decreases from 1.81×10^{15} to 1.12×10^{15} lines/m² when the annealing temperature is increased from 300 to 500 °C. At low annealing temperature (300 °C), the thermal energy and hence the surface mobility of atoms are low. As a result, the defects or lattice imperfection are developed in the growing film. However, with an increase in the annealing temperature, the atoms gain sufficient thermal energy and occupy the favorable lowest potential energy sites. This lessens the defects and lattice imperfections in the growing film. This helps in reducing the dislocation density with an increase in annealing

temperature. A decrease in crystallite size with an increase in annealing temperature further supports this conjecture. It is also seen that the microstrain of TiO₂ films decreases with increasing annealing temperature. The decrease in microstrain with an increase in annealing temperature may be due to a decrease in the crystallite size. The decrease in crystallite size increases the average grain size, which consequently reduces the grain boundaries. It has been reported that the reduction in grain boundaries lessens the microstrain in the film.^[45]

Fig. 2(b) shows the XRD pattern of melanin sensitized TiO₂ thin films. The major diffraction peaks are observed at $2\theta \sim 27.6^\circ, 33.7^\circ, 36.1^\circ, 41.3^\circ, 54.6^\circ, 62.8^\circ, 65.6^\circ$. Among these, the diffraction peaks at $2\theta \sim 27.6^\circ, 33.7^\circ, 36.1^\circ, 41.3^\circ, 54.6^\circ$, and 65.6° are associated with (110), (130), (101), (111), (211) and (221) diffraction planes respectively of rutile-TiO₂ phase (JCPDS data card # 73-1765). The diffraction peaks at $2\theta \sim 37.7^\circ$ and 62.8° are associated with (004) and (204) diffraction planes respectively of anatase-TiO₂ phase (JCPDS data card # 73-1764). No peaks associated with the brookite phase are detected. These results indicate that when TiO₂ is sensitized with melanin, the phase of TiO₂ changes from pure rutile to rutile-anatase mixed phase. The diffraction is dominant along the (004) plane and its intensity increases with an increase in annealing temperature, suggesting that the crystallites of anatase-TiO₂ have a preferred orientation along the (004) direction. Microstructural properties of melanin sensitized TiO₂ films are displayed in Table 1.

3.2 Raman spectroscopy Analysis

Raman spectroscopy is widely employed for the study of the chemical structure and the characteristic molecular vibration by the interaction of laser light with the material. Fig. 3 shows the Raman spectra of as-annealed and melanin sensitized TiO₂ thin films deposited by CBD at the excitation line of wavelength 514 nm at room temperature. Raman spectra of as-annealed TiO₂ films show four shoulders, two weak shoulders at ~ 140.1 and $\sim 232.2 \text{ cm}^{-1}$ and two strong shoulders at ~ 443.9 and $\sim 606.6 \text{ cm}^{-1}$ associated with the rutile phase of TiO₂.^[46,47] It has been reported that the Raman peak at 140.1 cm^{-1} is for the mode of B_{1g} symmetry, 232.2 cm^{-1} is for second-order scattering, 443.9 cm^{-1} is for E_g mode while 606.6 cm^{-1} is for A_{1g} mode.^[48] The A_{1g} mode at $\sim 606.6 \text{ cm}^{-1}$ corresponds to the symmetric stretching of the O–Ti–O bonds as a result of the opposite moving of the O atoms in the adjacent O–Ti–O bonds. A blue shift of 5.4 cm^{-1} is observed from the bulk value of 612 cm^{-1} to 606.6 cm^{-1} .^[49] The E_g mode $\sim 443.9 \text{ cm}^{-1}$ is mainly due to the asymmetric bending of the O–Ti–O bonds as a result of the opposite moving of the O atoms across the O–Ti–O bond, which suffers a softening of 3.1 cm^{-1} by decreasing from the bulk value of 447 to 436 cm^{-1} .^[49] No additional peaks were found in the acquired Raman spectra, suggesting the formation of pure rutile-TiO₂ phase in the present work. These results are in consistence with the x-ray diffraction analysis. The intensity ratio between Raman vibrational modes (A_{1g}/E_g) for annealed rutile-TiO₂ was found

quite similar (0.95, 0.97, and 0.99 for 300, 400, and 500 °C, respectively), indicating the good degree of crystallinity of TiO₂.^[50]

Fig. 3 Raman spectra of (a) as-annealed TiO₂ films and (b) melanin sensitized TiO₂ thin films deposited by CBD method.

Fig. 3(b) shows the Raman spectra of melanin sensitized TiO₂ thin films deposited by the CBD method. The Raman spectra show the shoulders at ~ 140.3 cm⁻¹, ~ 444.2 cm⁻¹, ~ 606.9 cm⁻¹ and ~ 1601.6 cm⁻¹. The Raman peak at ~ 140.3 cm⁻¹ can be indexed to the anatase phase of TiO₂,^[51,52] whereas the peaks at ~ 444.2 cm⁻¹ and ~ 606.9 cm⁻¹ are associated with the rutile phase of TiO₂.^[53] The Raman shoulder observed at ~ 1601.6 cm⁻¹ can be assigned to the melanin.^[54] These results further confirm that after melanin sensitization, the pure rutile phase of TiO₂ changes to the rutile-anatase mixed phase. It is worthy to note that the intensity of all Raman peaks is drastically reduced when TiO₂ films are sensitized with melanin.

3.3 Surface morphology analysis

The surface morphology of TiO₂ and melanin sensitized TiO₂ thin films was studied by scanning electron microscopy (SEM). Fig. 4 shows SEM images of as-annealed and melanin sensitized TiO₂ films. Before imaging, the samples were coated with platinum by the sputtering method. We observed that annealing and sensitization invoke a distinct change in the surface morphology. Top view of SEM micrograph of TiO₂

films annealed at 300 and 400 °C [Fig. 4(a1) and (a2)] clearly shows well defined randomly oriented TiO₂ spherical crystallites distributed over the entire substrate surface. The average diameter of TiO₂ crystallites is ~ 1-2 μm. However, with an increase in annealing temperature, these crystallites coalesce to form larger crystallites growing perpendicularly to the substrate surface, Fig. 4(a3).

Fig. 4(b1, b2 & b3) show the SEM images of melanin sensitized TiO₂ films. As seen in Fig. 4(b1), when TiO₂ is loaded with melanin, microcracks were developed over the entire surface of the film. The mismatch in the thermal expansion coefficients between TiO₂ and melanin may be responsible for the development of microcracks in the film. With an increase in annealing temperature, these microcracks are filled by the melanin and entire TiO₂ crystallites are covered by it.

3.4 UV-Visible spectroscopy analysis

The optical properties of TiO₂ and melanin sensitized TiO₂ thin films such as absorption bandgap were investigated by UV-Visible spectroscopy analysis. Fig. 5(a) and (b) shows the optical absorption spectra of as-annealed TiO₂ and melanin sensitized TiO₂ films. As seen in Fig. 5(a), the TiO₂ films annealed at 300, 400 and 500 °C absorb mainly in the UV region whereas the melanin sensitized TiO₂ films absorb significantly in the visible region, Fig. 5(b). This indicates that melanin incorporation with TiO₂ increases the absorption along with a shift in the absorption edge to the higher wavelengths.

In the direct transition semiconductor, the optical energy bandgap (E_{opt}) and the optical absorption coefficient (α) are related by Equation (8),^[55]

$$(\alpha h\nu)^{1/2} = B^{1/2}(E - E_{opt}) \quad (8)$$

where α is the absorption coefficient, B is the optical density of state, h is Plank's constant, and ν is the frequency of incident photon radiation. The α is calculated from the transmittance of the films using Equation (9),

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right) \quad (9)$$

where d is the thickness of the films and T is the transmittance. The optical band gap is obtained by extrapolating the tangential line to the photon energy ($E = h\nu$) axis in the plot of $(\alpha h\nu)^2$ as a function of $h\nu$ (Tauc plot). Fig. 5(c&d) shows the Tauc's plot for as-annealed and melanin sensitized TiO₂ films. The bandgap energy decreases from 3.04 to 2.98 eV when the annealing temperature increases from 300 to 500 °C (Fig. 5(c)). It has been observed that the estimated optical band gap values for annealed TiO₂ films match with reported values of band gap for rutile-TiO₂ in the literature.^[56] For melanin sensitized TiO₂ thin films, the bandgap energy also decreases from 2.69 to 2.63 eV [Fig. 5(d)]. We believe that the decrease in bandgap energy values may be due to an increase in the electron mobility upon melanin incorporation in the TiO₂ nanostructure.

Fig. 4 (a1), (a2) and (a3) SEM images of as-annealed TiO_2 and (b1), (b2) and (b3) Melanin sensitized TiO_2 films deposited by CBD method.

Fig. 5 (a) Optical absorption spectra of as-annealed TiO_2 films and (b) optical absorption spectra of melanin sensitized TiO_2 films (c) Tauc's plot for as-annealed TiO_2 films and (d) Tauc's plot for melanin sensitized TiO_2 films.

3.5 Photoelectrochemical (PEC) properties

Fig. 6 Variation of photocurrent density as a function of applied potential for (a) TiO₂ photoanodes (b) Melanin sensitized TiO₂ photoanodes.

The electrochemical behaviors of TiO₂ and melanin sensitized TiO₂ photoanodes were studied using linear sweep voltammetry under the illumination conditions. Fig. 6(a & b) shows the variation of photocurrent density as a function of applied potential for TiO₂ and melanin sensitized TiO₂ thin film photoanodes annealed at different temperatures. As seen in Fig. 6(a), with an increase in annealing temperature, the photocurrent density of TiO₂ photoanodes increases. A high degree of crystallinity and large particle size of TiO₂ photoanode (revealed from XRD and Raman analysis) may be responsible for the enhanced current density.^[57] The highest photocurrent density (8.0 μA/cm²) is observed for TiO₂ photoanode annealed at 500 °C for an applied potential 1.0 V. The increase in specific surface area of TiO₂ with an increase in annealing temperature facilitated the enhancement of catalytic sites and reaction centers for electrochemical reaction. This results in a significant improvement of photocatalytic behavior.^[58,59]

The variation of photocurrent density as a function of applied potential for melanin sensitized TiO₂ photoanodes is shown in Fig. 6(b). The photocurrent density of TiO₂ photoanodes is found significantly reduced when sensitized

with melanin. The highest photocurrent density (~ 4.61 μA/cm²) is observed for TiO₂ photoanode annealed at 500 °C for an applied potential of 0.2 V. These results indicate that sensitization of TiO₂ with melanin reduces the photocurrent density and hence sensitization of TiO₂ with melanin is not beneficial for water splitting for hydrogen production.

Table 2. Values of flat band potential (V_{fb}), charge carrier density (N_d), and depletion layer width (w).

Sample	Annealing temperature (°C)	V_{fb} (V)	N_d (cm ⁻³)	w (nm)
TiO ₂	300	-0.35	1.01×10^{19}	9.52
	400	-0.40	2.80×10^{19}	8.58
	500	-0.50	3.52×10^{19}	1.66
TiO ₂ /Melanin	300	-0.36	3.75×10^{19}	5.11
	400	-0.40	2.49×10^{19}	8.37
	500	-0.21	1.47×10^{19}	12.4

To critically determine the usefulness of semiconductors and sensitizer for photoelectrochemical (PEC) splitting of water, flat-band potential (V_{fb}) and charge carrier density (N_d) are important parameters. One of the reported simplest and reliable methods is the Mott-Schottky analysis. According to MS theory, the capacitance (C) at the electrode-electrolyte interface at different potentials (V) are related by Equation (10):^[60]

$$\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon_s A^2 q N_d} [V - V_{fb} - \frac{k_B T}{q}] \quad (10)$$

where ϵ_0 is the permittivity of free space, ϵ_s is the dielectric constant of semiconductor electrode, A is the effective surface area of semiconductor, q is the electronic charge, N_d is the free charge carrier density, k_B is the Boltzmann's constant, and T is the temperature in Kelvin. The extrapolation of tangents to MS curves to the x-axis gives flat band potential (V_{fb}) and from the slopes of tangents, the charge carrier density (N_d) can be determined. If the values of V_{fb} and N_d are known, the width of depletion region (w) can be determined by using the following Equations (10&11):^[61]

$$\text{Slope}(S) = \frac{2}{\epsilon_0 \epsilon_s A^2 q N_d} \quad (11)$$

$$w = \sqrt{\frac{2\epsilon_0 \epsilon_s}{q N_d} (V - V_{fb})} \quad (12)$$

Fig. 7(a&b) shows the M-S curves of as-annealed TiO₂ and melanin sensitized TiO₂ photoanodes, respectively. The estimated values of flat band potential, charge carrier density, and width of the depletion region are listed in Table 2. The flat band potential shifts from -0.35 to -0.50 V for the TiO₂ photoanodes when annealing temperature is increased from 300 to 500 °C. The shift of flat band potential to more negative values indicates a shift in the Fermi level towards the conduction band. This leads to an efficient charge transfer process across the electrolyte. The carrier density of TiO₂ photoanodes increases from 1.01×10^{19} to 3.52×10^{19} cm⁻³ when annealing temperature is increased from 300 to 500 °C. This increases the electrical conductivity and hence the PEC

performance. A decrease in depletion width (from 9.52 to 1.66 nm) of TiO₂ photoanodes with an increase in annealing temperature indicates an easier diffusion of photo-generated charge carriers, which is favorable for PEC activity.

However, when TiO₂ is sensitized with melanin, the Mott-Schottky analysis shows contradictory results. The flat band potential shifts from -0.36 to -0.21 V. It leads to the shifting of Fermi level away from the conduction band resulting in a incompetent charge transfer process across the electrolyte. The carrier density of melanin sensitized TiO₂ photoanodes is decreased from 3.75×10^{19} to $1.47 \times 10^{19} \text{ cm}^{-3}$. Furthermore, the depletion width is also enhanced from 5.11 to 12.4 nm. This hampers the easier diffusion of photo-generated charge carriers and hence electrical conductivity and the PEC performance. We believe that the change of phase from pure rutile-TiO₂ to rutile-anatase-TiO₂ may be responsible for the deterioration of PEC performance. However, the phenomenon of change of TiO₂ phase from melanin sensitization is not clear at this moment.

Fig. 7 Mott-Schottky plots for (a) as-annealed TiO₂ and (b) Melanin sensitized TiO₂ photoanodes.

All the photoanodes were further used to investigate charge transfer properties by the electrochemical impedance spectroscopy (EIS). EIS measurements were carried out at a fixed potential of 0.1 V in the frequency range from 100 kHz-100 MHz under the illumination of light. Fig. 8 shows the Nyquist plots of as-annealed TiO₂ and melanin sensitized TiO₂ photoanodes.

Fig. 8 Nyquist plots of (a) As annealed TiO₂ and (b) Melanin sensitized TiO₂ photoanodes.

In the Nyquist plots, the radius of the semicircle represents the charge transfer resistance and charge separation efficiency.^[62,63] As seen from Fig. 8(a&b), both TiO₂ and melanin sensitized TiO₂ photoanodes have semicircles with a large radii, suggesting high charge transfer resistance and hence low charge transfer efficiency. The charge transport in the as-annealed TiO₂ photoanode is found better than that of melanin sensitized TiO₂ photoanode. The formation of heterojunction between TiO₂ and melanin enhances the charge carrier recombination rate, which increases the charge transfer resistance. These results are contradictory to ZnO sensitized melanin photoanodes.^[54] The sensitization of TiO₂ with melanin is not favorable for the photocatalytic water splitting. Therefore, the investigations on sensitization of melanin with other photoanode materials such as gallium nitride (GaN), hematite ($\alpha\text{-Fe}_2\text{O}_3$), tungsten oxide (WO₃), bismuth vanadate (BiVO₄), zinc oxide (ZnO), perovskites, etc. should be undertaken for photocatalytic water splitting application. Some organic compounds/dyes like tannin, anthocyanin, betalain, carotenoid, chlorophyll, phenolic, etc. can also be explored with TiO₂ for PEC activity.

Conclusion:

In this study, thin films of TiO₂ and melanin sensitized TiO₂ were successfully prepared by a simple, inexpensive, low-temperature chemical bath deposition method. The influence of annealing temperature on the structural, optical, morphology, and photoelectrochemical cell properties were investigated using a variety of techniques. The formation of

TiO₂ and melanin sensitized TiO₂ was confirmed by low angle XRD and Raman spectroscopy. Low angle XRD patterns revealed that TiO₂ films were polycrystalline with a tetragonal rutile phase while melanin sensitized TiO₂ films had a rutile-anatase mixed phase. Furthermore, the average crystallite size of melanin-sensitized TiO₂ was found smaller than that of TiO₂ films. SEM analysis showed that when TiO₂ was sensitized with melanin, microcracks were developed over the entire surface of the film. UV-Visible spectroscopy analysis showed that the TiO₂ films annealed at 300, 400 and 500 °C absorbed mainly in the UV region whereas melanin sensitized TiO₂ thin films absorbed significantly in the visible region. The carrier density of TiO₂ photoanodes was increased from 1.01×10^{19} to $3.52 \times 10^{19} \text{ cm}^{-3}$, whereas it was decreased from 3.75×10^{19} to $1.47 \times 10^{19} \text{ cm}^{-3}$ for melanin sensitized TiO₂ photoanodes. For TiO₂ photoanodes, the flat band potential was increased from -0.35 to -0.50 V while the depletion width was decreased for the TiO₂ photoanodes when annealing temperature was increased from 300 to 500 °C. However, the melanin sensitized TiO₂ films showed the opposite trend. Electrochemical impedance spectroscopy (EIS) analysis revealed that melanin sensitized TiO₂ had a high charge transfer resistance. Finally, it is concluded that the sensitization of TiO₂ with melanin is not favorable for photocatalytic water splitting and further work still needs be done to obtain enhanced water splitting.

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Supporting information

Not applicable

Conflict of interest

There are no conflicts to declare.

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