

# Optical performance of visible and near-infrared responsive TiO<sub>2</sub>/Ag doped-SiO<sub>2</sub>/TiO<sub>2</sub> thin films prepared by sol-gel spin-coating method

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The visible and near-infrared reflective thin film of TiO<sub>2</sub>/Ag-doped SiO<sub>2</sub>/TiO<sub>2</sub> hybrid structure was successfully deposited on glass substrate using sol-gel spin coating techniques. The prepared thin films were characterized by UV-visible spectroscopy (UV-Vis), X-ray diffractometer (XRD), Fourier transform infrared (FTIR) and Raman spectroscopy to investigate its reflectance, structural, functional elements and vibrational modes of the samples. The UV-Vis spectrum evidenced the highest reflectance at 640 nm. The FTIR and RAMAN spectral peaks exploring the various vibration modes and concerning elements of prepared thin films. The XRD diffraction pattern was endorsed the presence of silver, silica and titanium. Further, the crystallite size was calculated as 8.3 nm using Debye-Scherrer's formula.

(Received November 27, 2020; accepted October 7, 2021)

**Keywords:** Thin Film, FTIR, Raman, TiO<sub>2</sub>, Ag-SiO<sub>2</sub>, XRD

## 1. Introduction

Nowadays, metal doped-TiO<sub>2</sub> and SiO<sub>2</sub> thin films are useful in various optical applications such as heat reflection glass, self-cleaning, decorative glass, decorative windows, anti-reflective multilayer and photo-catalyst due to its higher refractive index contrast. This thin film has been developed using sol-gel, hydrothermal, chemical vapor deposition (CVD), sputtering, chemical bath deposition (CBD) and electrochemical deposition (ECD) methods. The homogeneous thin film is considering for the real challenges due to the cracks on the substrate surface and hydrophilic nature of SiO<sub>2</sub> thin film. Jeon et al. (2003) prepared silver (Ag) doped SiO<sub>2</sub> thin film on glass substrates by using sol-gel dip-coating method and used as an antibacterial materials. The deposited Ag-doped SiO<sub>2</sub> thin film calcination temperature was changed (400, 500 & 600°C) and studied their optical and morphological performance by using X-ray diffraction (XRD), UV-visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The results showed that the Ag completely trapped in to the SiO<sub>2</sub> matrix with their reduction could be achieved at 600°C calcination temperature. Further, antibacterial effects were investigated against Escherichia coli and Staphylococcus aureus using in film attachment techniques. Finally, the prepared coating achieved remarkable antibacterial performance [1]. Zhao et al. (2012) fabricated TiO<sub>2</sub>/Ag<sub>x</sub>-(SiO<sub>2</sub>)<sub>1-x</sub> nanocomposite thin films (bilayer) using sol-gel spin-coating method. The prepared thin film thickness was around 200 nm. It includes 60 nm of top-TiO<sub>2</sub> layers and spherical Ag nanoparticles diameter varied from 10 to 30 nm. Further, the surface plasmon resonance peak was confirmed by UV-Vis spectrum at 420 nm. The

photocatalytic performance was increased by the addition of silver content ~15at.% and further reduced due to highest Ag content. The optimal silver content yielded the maximum photocatalytic activity [2]. Junlabhut et al. (2013) demonstrated the optical absorptivity enhancement of silica (SiO<sub>2</sub>) thin films by adding titanium (Ti) and silver (Ag) thin films. Initially, Ti and Ag added SiO<sub>2</sub> thin film was coated on glass substrates by using sol-gel spin-coating (2500 rpm & 45 sec.) process. After the coating, the prepared samples were baked at 80°C for 5 minutes to remove the solvents and then thermal treatment was carried out such as 150, 350 and 550°C for 2 hours. The optical and physical properties of as-prepared samples were studied by UV-Vis, XRD and transmission electron microscopy (TEM). The XRD and TEM results were disclosing the existence of Ti and Ag nanoparticles. Overall, observed the enhancement of optical absorption in the UV and visible spectral region due to the Ti and Ag into the SiO<sub>2</sub> thin films [3]. Similarly, Junlabhut et al. (2016) experimentally fabricated for hybrid optical sensitive Ag-SiO<sub>2</sub>/TiO<sub>2</sub> thin film via sol-gel spin-coating method. The prepared thin film photo-induced by irgacure 784 photo initiator under helium (He) and cadmium (Cd) laser at 442 nm. The structural, morphological and existing elements of prepared photo-sensitive films were found by XRD, TEM, field-emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDS) techniques. The results showed the compatibility and the formation of photo-sensitive material. The periodically aligned silver ions in SiO<sub>2</sub>/TiO<sub>2</sub> photosensitive hybrid thin film and showed remarkable enhancement of optical absorption in the visible region by the reason of surface plasmon resonance [4].

Magdalane et al. (2019) explored the self-cleaning mechanism of SnO<sub>2</sub>/TiO<sub>2</sub> nanostructures using green synthetic method for photocatalytic activity applications in waste water treatment. The prepared nanostructures were proved the reduced excitons combination rate, improved surface area and superior crystallinity [5]. Manjula et al. (2018) investigated the structural, morphological and sensing properties of Jet Nebulizer spray pyrolysis effect on TiO<sub>2</sub>-SnO<sub>2</sub> thin films for removing heavy metal ions from the water [6]. Ravi et al. (2019) hydrothermally fabricated (grown) TiO<sub>2</sub> nanorods on F-doped tin-oxide (FTO) for CdS sensitized solar cell applications. This semiconductor sensitized solar cell (FTO/TiO<sub>2</sub>/CdS-8/ZnS-2) performance was studied and achieved 0.78% cell efficiency [7]. Arunkumar et al. (2020) investigated an uni-directional nanorods which was composed the microspheres and branched rutile phase-TiO<sub>2</sub> nanorods for solar cell applications. The well-controlled and various morphological images were achieved by hydrothermal method. These unidirectional TiO<sub>2</sub> nanorods were reached maximum solar cell efficiency of 1.76% due to its highest electron transport performance during the fabrication work [8].

In this research work, we report the preparation of TiO<sub>2</sub>/Ag doped-SiO<sub>2</sub>/TiO<sub>2</sub> thin film on glass substrate using a simple sol-gel spin-coating process and studied their optical properties. The preparation method and materials are discussed in section 2. The measurement results are analyzed in section 3 and summarized the work in section 4.

## 2. Experimental approach

### 2.1. Chemicals

Ethanol (C<sub>2</sub>H<sub>5</sub>OH), silver nitrate (AgNO<sub>3</sub>), sodium borohydride (NaBH<sub>4</sub>), deionized (DI, H<sub>2</sub>O) water, tetraethyl orthosilicate (TEOS, SiC<sub>8</sub>H<sub>20</sub>O<sub>4</sub>), titanium isopropoxide (TTIP, C<sub>12</sub>H<sub>28</sub>O<sub>4</sub>Ti), acetic acid (AcOH, CH<sub>3</sub>COOH), hydrochloric acid (HCl) and nitric acid (HNO<sub>3</sub>) were used as raw materials.

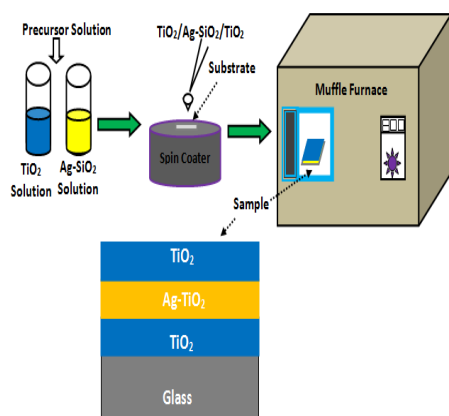


Fig. 1. The schematic diagram of the fabrication of TiO<sub>2</sub>/Ag-SiO<sub>2</sub>/TiO<sub>2</sub> thin films (color online)

Here, ethanol and DI water were used as solvents. Next, then nitric acid and hydrochloric acid were used as the hydrolysis catalysis.

### 2.2. Synthesis process of Ag-SiO<sub>2</sub> and TiO<sub>2</sub> solution

Ag-doped SiO<sub>2</sub> solution was prepared using the sol-gel technique and the procedural steps are discussed below. First, H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH are mixed with volume of 2:1 ratio and stirred for 5 minutes at room temperature (28°C). Under the stirring condition, 1.5 ml of TEOS and 6 ml of Ag colloidal solutions were added drop-wise and stirred for 10 minutes. The preparation of silver colloidal solutions was discussed in previous work [9]. Next, few drops of acetic acid added for the slower gelification process. This final solution was stirred for 90 minutes and kept for aging 24 hours at room temperature. Similarly, TiO<sub>2</sub> solutions were prepared by sol-gel method. Initially, H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH were mixed with 2:1 ratio and stirred for 5 minutes. Further, 1 ml of TTIP solution added by dropwise. Here, TTIP precursor based nanostructure is more stable and maintains the higher crystallinity as compare to the others precursors [10-11]. Next, 0.5 ml of HCl and one drop of HNO<sub>3</sub> added gradually and stirred for 15 minutes at room temperature.

### 2.3. TiO<sub>2</sub>/Ag-SiO<sub>2</sub>/TiO<sub>2</sub> thin film preparation

The alternating layers of sol-gel prepared TiO<sub>2</sub> solution coated on glass substrates using spin-coater with 3000 rpm for 30s. The TiO<sub>2</sub> coated substrate was calcined at 500°C for 20 minutes. Among the TiO<sub>2</sub> layers, Ag-doped SiO<sub>2</sub> thin film prepared and calcined. Fig. 1 shows the schematic diagram of preparation of TiO<sub>2</sub>/Ag-SiO<sub>2</sub>/TiO<sub>2</sub> thin film samples. After the sample preparation, the optical and physical properties of the thin film were characterized by UV-Vis Spectroscopy (Shimadzu, Japan), Fourier transform infrared spectroscopy (Perkin Elmer Spectrum-2, USA), X-ray diffractometer (X-Pert Pro, USA) and Micro-Raman spectroscopy (USA).

## 3. Results and discussion

The obtained TiO<sub>2</sub>/Ag-SiO<sub>2</sub>/TiO<sub>2</sub> thin films were characterized by UV-Vis spectrophotometer, FTIR spectroscopy, XRD technique and RAMAN spectroscopy. UV-vis spectrophotometer is a primary technique for the optical study of prepared nanostructures.

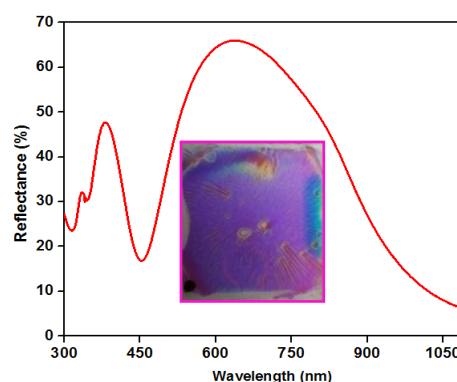


Fig. 2 The UV-Vis reflection spectrum of TiO<sub>2</sub>/Ag-SiO<sub>2</sub>/TiO<sub>2</sub> thin films (color online)

Fig. 2 shows the reflectance spectrum of  $\text{TiO}_2/\text{Ag-SiO}_2/\text{TiO}_2$  thin film investigated by UV-Visible spectrophotometer.

Table 1. FTIR transmittance spectrum of  $\text{TiO}_2/\text{Ag-SiO}_2/\text{TiO}_2$

Wavenumber ( $\text{cm}^{-1}$ )	Assignment	Ref.
798, 950, 1070	silica	[12]
950, 798, 450	Si-OH stretching, Si-O-Si symmetric stretching, $\text{SiO}_4$	[12] [13]
1390, 1450	$\text{NO}_3^-$ ions	[14]
1635	O-H	[18], [19], [20], [21]
3430	Si-OH, Si-O-Si	[15],[16],[17]

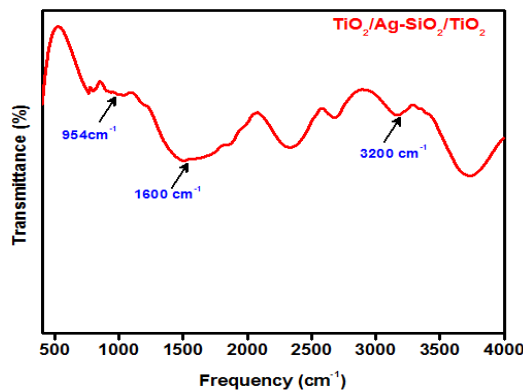


Fig. 3. FTIR transmittance spectrum of  $\text{TiO}_2/\text{Ag-SiO}_2/\text{TiO}_2$  thin films (color online)

The reflectivity was measured from the range of 300 to 1100 nm and achieved the maximum reflectance ~67% with glass substrate, which reveals the superior optical properties in this work. The higher reflectance was observed from 450 to 1000 nm wavelength region and center wavelength of 640 nm. The reflectance spectrum is mainly dependent on the various parameters such as thickness of the layer, concentration of the precursors, spin rate (RPM), calcinations temperature, substrates, surface structure of the thin films etc. FTIR spectrum shows the various functional groups present at various positions. Fig. 3 depicts the FTIR transmission spectrum of Ag doped- $\text{SiO}_2$  thin film sandwiched between  $\text{TiO}_2$  layers on the glass substrates. The presented peaks between 700-900  $\text{cm}^{-1}$  were attributed to the vibration modes of  $\text{TiO}_2$  and near 954  $\text{cm}^{-1}$  is association of Si-O-Ti [24-26]. The broadband around 1600  $\text{cm}^{-1}$  and 3200-4000  $\text{cm}^{-1}$  is characteristic of O-H stretching vibration mode of hydroxyl groups and water molecules [18-19]. Senthil et al. (2017) reported the two major functional groups of O-H and C=C moieties at 1635 and 3315  $\text{cm}^{-1}$  due to the presence of silver [22,14].

The crystalline structural properties of  $\text{TiO}_2/\text{Ag}$  doped- $\text{SiO}_2/\text{TiO}_2$  thin film were characterized by X-ray diffractometer using Cu- $\text{K}\alpha$  radiation operated at 45 kV and 30 mA over  $2\theta$  in range of  $10^\circ$  to  $80^\circ$ . The X-ray diffraction pattern was recorded with the scanning rate of 5.71°/sec. Fig. 4 shows the XRD pattern of  $\text{TiO}_2/\text{Ag}$  doped- $\text{SiO}_2/\text{TiO}_2$

thin films. First, the wider diffraction peak is noticed at  $2\theta$  which is corresponding to the  $\text{TiO}_2$  on the glass substrate [2]. The diffraction pattern confirmed the formation of crystalline silver, anatase  $\text{TiO}_2$  and  $\text{SiO}_2$  phase in the material. As noticed in the pattern, three distinct peaks located at  $2\theta = 44.3^\circ$ ,  $51.6^\circ$  and  $64.4^\circ$  corresponding to the Ag orientation (200), (104) and (220) respectively [23]. These silver peaks are less intense and narrow. Further, silicon, titanium, oxide (Si-O-Ti) phases are indexed in the diffraction patterns with the accordance of standard JCPDS (ICSD 89-8099). Junlabhut et al. reported that the phase transformation of intermediate Si-O-Ti structure disappears with effect of temperature elevation from 350°C [3]. The obtained result indicates the silver (Ag), titanium (Ti) and silica (Si-O) are mixed at the atomic level. The crystallite size was calculated  $2\theta = 25.8^\circ$  from the main peak related to the Si-O-Ti in the diffraction pattern using Debye-Scherrer's formula, i.e.,

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

Here, k is the constant (0.89),  $\lambda$ - the incident wavelength (1.54060),  $\beta$ - the full-width half-maximum (FWHM) of the diffraction peak and  $\theta$ - the diffraction angle [4, 15]. The calculated result shows the crystallite size for Si-O-Ti was 8.3 nm.

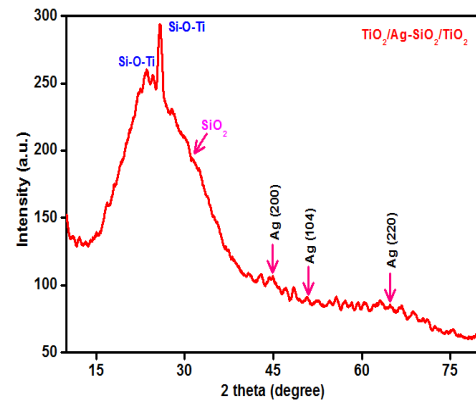


Fig. 4. XRD pattern of  $\text{TiO}_2/\text{Ag}$  doped- $\text{SiO}_2/\text{TiO}_2$  thin films (color online)

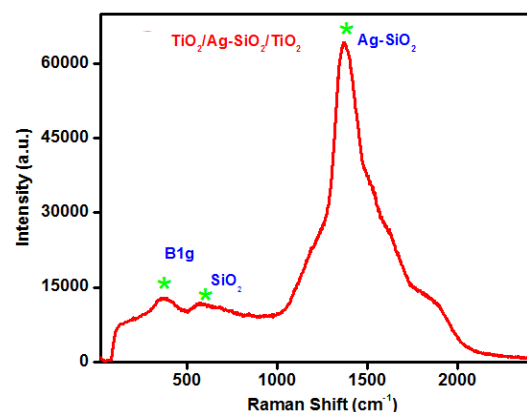


Fig. 5. Raman spectroscopy spectrum of  $\text{TiO}_2/\text{Ag-SiO}_2/\text{TiO}_2$  thin films (color online)

Fig. 5 shows the Raman spectrum of TiO<sub>2</sub>/Ag-SiO<sub>2</sub>/TiO<sub>2</sub> coatings on glass substrate using the excitation laser source (785 nm) at room temperature. The Raman bands are noticed at 374.27, 568.33 and 1363.3 cm<sup>-1</sup>. The TiO<sub>2</sub> anatase phase was confirmed at 374.27 cm<sup>-1</sup> (B1g) with less intense peak observed around 568.33 cm<sup>-1</sup> is SiO<sub>2</sub> broad peak. Finally, the maximum intensity peak appeared at 1363.3 cm<sup>-1</sup> due to the presence of Ag-doped silica [25-27].

#### 4. Conclusions

In summary, visible and near-IR light-reflective TiO<sub>2</sub>/Ag doped-SiO<sub>2</sub>/TiO<sub>2</sub> coatings were deposited on glass substrate by sol-gel spin coating method. The optical and crystalline properties of Ti, Si and Ag additives were investigated by UV-Vis, FTIR, XRD and RAMAN spectroscopy. UV-Vis spectrum showed 67% enhanced optical reflectance and noticed the broader band gaps at 650 nm. This occurrence implies the effect of surface plasmon resonance of Ag nanoparticles and the highest refractive index of titanium. Furthermore, XRD result was confirmed the presence of Ag, Ti and Si-O at atomic level. Furthermore, the FTIR and RAMAN spectra were explored the various vibrational modes of TiO<sub>2</sub>/Ag-SiO<sub>2</sub>/TiO<sub>2</sub> layers.

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