Structural and optical studies of $\text{TiO}_2\text{:Ag}_2\text{O}$ nanocomposite by sol-gel method

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As TiO_2 is suitable for electronic and electrical applications, in the present work the authors have successfully modified TiO_2 by adding silver (Ag) to form titanium oxide-silver oxide ($\text{TiO}_2\text{:Ag}_2\text{O}$) nanocomposite samples by using sol-gel technique. Characterizations of these composites have been performed using X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and UV-Vis spectroscopy. XRD study revealed that the crystal structure of the samples consisted of tetragonal and cubic phases. This study further showed an increment in the average crystallite size from 8 nm to 38 nm with an increase in Ag concentration. The increase in crystallite size has been confirmed additionally by SEM and AFM. The increment in the average particle size of the samples may be attributed to an increase in silver molarity in the TiO_2 matrix. Significant red shift in the absorption edge has been observed, causing reduction in the energy bandgap of the composites from 3.89 eV to 3.46 eV with an increase in particle size which is evident from UV-Vis spectroscopic studies. This wide-band gap properties of the $\text{TiO}_2\text{:Ag}_2\text{O}$ nanocomposite make it suitable for memory-storage devices and dielectric applications.

Keywords: *sol-gel; $\text{TiO}_2\text{:Ag}_2\text{O}$ nanocomposite; strain; Tauc plot*

1. Introduction

Due to its super-hydrophilic properties, TiO_2 has been widely used as an effective photocatalyst for environment purification [1, 2], and in antibacterial applications [3, 4]. However, the TiO_2 semiconductors have a wide band gap, which can only be activated by near-UV radiation [5]. Modification of TiO_2 surface by noble metals, such as Ag [6] removes electrons away from the TiO_2 surface, preventing the recombination of electrons with holes [7]. Chemical routes, such as sol-gel techniques, possess the advantage of low cost with respect to physical synthesis methods [8]. In order to explore electronic and electrical applications of TiO_2 , its modification was performed by addition of polymers [9–12], doping with noble metals [13], and other metal oxide-based semiconductors [13–19]. Various composites formed by TiO_2 and other inorganic oxides such as ZnO, SnO_2 , SiO_2 , In_2O_3 , Cu_2O , MgO,

WO_3 , MoO_3 , etc. have also been reported [13]. Various synthesis methods were used to synthesize metal oxide nanocomposites, such as wet-impregnation method, sol-gel method, hydrothermal method and microwave-assisted method [14]. In the present work, nanocomposite $\text{TiO}_2\text{:Ag}_2\text{O}$ was prepared at different molar concentrations through sol-gel method. The as-prepared nanocomposites were characterized by X-ray diffraction (XRD) technique for structural study. The morphological investigations were carried out by using atomic force microscopy (AFM) and scanning electron microscopy (SEM). To understand the optical properties of the samples, UV-Vis spectroscopy investigations have been performed.

2. Experimental

Titanium tetraisopropoxide (TTIP) ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$) and silver nitrate dihydrate ($\text{AgNO}_3 \cdot 2\text{H}_2\text{O}$) of 99.95 % purity were purchased from Sigma-Aldrich. Ethyl alcohol (ethanol) was used as a solvent in the reaction and was purchased

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Table 1. List of obtained $\text{TiO}_2\text{:Ag}_2\text{O}$ nanocomposite samples prepared using sol-gel method.

S. No.	Sample name	Molar concentration [mM]	
		TTIP	$\text{AgNO}_3 \cdot 2\text{H}_2\text{O}$
1	D1	1.0	0.0
2	D2	0.95	0.05
3	D3	0.9	0.1
4	D4	0.85	0.15
5	D5	0.8	0.2

from Merck-Millipore (99.5 % purity). Titanium precursor (TTIP) (at different molarities: 1 mM, 0.95 mM, 0.9 mM, 0.85 mM and 0.8 mM) was measured and added to the corresponding beaker containing ethanol, and stirred for 2 h at room temperature. Silver nitrate ($\text{AgNO}_3 \cdot 2\text{H}_2\text{O}$) (0.0 mM, 0.05 mM, 0.1 mM, 0.15 mM and 0.2 mM) was then added to the corresponding TTIP solution as shown in Table 1. The solution mixture was then stirred at 600 rpm at 70 °C for 2 h. Later, 0.15 mL distilled water was added for hydrolysis and again stirred for 30 min. Finally, 1.0 mL HCL (35 wt.%) was added to the mixture and stirred till homogeneous sol was obtained. The sols were then kept at room temperature in vacuum-desiccators for 2 days to 3 days for gelation. The gel was dried at 120 °C. The dried powder was ground by agate mortar and pestle and sintered at 300 °C for 8 h to get the desired nanocomposite samples D1, D2, D3, D4 and D5 (Table 1). The samples were characterized using Rigaku MiniFlex II, Japan (1.54 Å $\text{CuK}\alpha$ radiation) X-ray diffractometer for confirmation of the crystal structure and purity of the as-prepared nanocomposites. Morphology of the samples was studied by atomic force microscope (model Solver-NEXT, Make-NT-MDT, Russia) and JEOL-JAPAN (JSM 6390A) scanning electron microscope. Optical absorption study was done by using Shimadzu UV-1700 spectrophotometer (Europe).

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

Fig. 1 presents the XRD pattern of as-prepared $\text{TiO}_2\text{:Ag}_2\text{O}$ nanocomposites. All the peaks are in

agreement with JCPDS Card No. 71-1169 (standard TiO_2) and JCPDS Card No. 41-1104 (standard Ag_2O) which can be indexed corresponding to the tetragonal reflections of TiO_2 and cubic reflections of Ag_2O . X-ray diffraction analysis was done in the range of 20° to 80° (2 θ) at a scan rate of 3° (2 θ) per minute.

Fig. 1. XRD patterns of as-prepared $\text{TiO}_2\text{:Ag}_2\text{O}$ nanocomposites prepared via sol-gel method (* – TiO_2 peaks, + – Ag_2O peaks).

Cell parameters (a and c) were calculated from the diffraction patterns and the values obtained are $a = 3.171$ Å and $c = 4.757$ Å for pure TiO_2 sample (D1) and, $a = 3.188$ Å and $c = 4.767$ Å for nanocomposite samples (D2-D5). These smaller values of lattice parameters indicate the presence of strain in the crystal lattice of the samples. Small variation in the intensity and broadening of the peaks suggests rearrangement of the crystal planes according to the molar ratio [20]. The presence of extra peaks near 57° and 76° may be due to

some unreacted precursors remaining in the obtained powders. The strong and clear peaks confirm crystallinity of the samples with no characteristic peaks of impurity phases. All the diffraction peaks are broadened which suggests small crystallite size in the material [20]. From the X-ray diffraction patterns, an increment in (1 1 1) plane of Ag₂O and reduction of (1 0 1) plane of TiO₂ constituents is clearly observed with respect to the increase in Ag molar concentration which could be related to the increment in the overall crystallite size of these nanocomposites [21].

Fig. 2 shows variation in the peak width (FWHM) for both TiO₂ ($2\theta = 25.12^\circ$) and Ag₂O ($2\theta = 32.09^\circ$) constituents in the as-prepared nanocomposite samples. Variation in the width of the peaks is inversely proportional to the crystallite size of the material [21].

From the FWHM plot (Fig. 2), it may be inferred that the crystallite size of the TiO₂ component increases with the increase in the Ag concentration up to sample D3. But it reduces for samples D4 and D5 with further increase of Ag concentration. However, the crystallite size of Ag₂O component shows an increment in the crystallite size with respect to an increase in Ag concentration for all the samples. The shift towards lower Bragg angle represents the presence of uniform strain in the crystallites of the as-prepared samples [22, 23]. Table 2 shows the values of average crystallite size and strain for TiO₂:Ag₂O nanocomposite which have been calculated from the values of lattice parameters obtained from the diffraction patterns.

From Table 2, it is observed that the crystallite size of the as-prepared pure TiO₂ sample (D1) is smaller than that of its bulk counterpart, which is well supported by the increase in the values of strain in the samples. Other researchers [24, 25] have reported that the strain in the samples is inversely proportional to the crystallite size, and this is clearly observed in the present samples. The change in the strain may be due to the change in the bond-length and in the values of lattice constants (a and c) and also due to rearrangement of crystal planes, resulting in overall reduction of the crystallite size [26, 27]. Fig. 3 shows the variation

Fig. 2. Variation of peak-width (FWHM) of as-prepared samples: (a) TiO₂ composition, (b) Ag₂O composition (Inset shows variation of crystallite size of respective components).

in the crystallite size obtained by the Scherrer analysis [20, 21] of TiO₂:Ag₂O nanocomposites.

From Fig. 3, systematic increment is observed in the crystallite size with an increase in Ag concentration in the samples. This increment in the crystallite size is supposed to be due to rearrangement of crystal planes which increases the strain. This may be due to the increase in the number of intrinsic and/or extrinsic defects developed by Ag incorporation in the lattice sites as well as interstitials of the TiO₂ matrix, resulting in the increased strain in the system [28]. This can be observed from

Table 2. Calculated values of average crystallite size and strain for the as-prepared TiO₂:Ag₂O nanocomposites.

S. No.	Sample code	Average crystallite size (d)		Strain (ϵ)
		[nm]		
1.	D1	8.4		21.1×10^{-3}
2.	D2	24.4		14×10^{-3}
3.	D3	26.5		13.4×10^{-3}
4.	D4	32.8		11.9×10^{-3}
5.	D5	38.6		10.8×10^{-3}

Fig. 3. Variation of crystallite size of as-prepared TiO₂:Ag₂O nanocomposites with respect to Ag molarity.

Fig. 4. AFM images of the as-prepared samples: (a) D1, (b) D2, (c) D3, (d) D4, and (e) D5 (A represents 2D images and B represents 3D images of corresponding samples).

the strain values given in Table 2. The same phenomenon is well-reflected in the AFM and SEM images of the TiO₂:Ag₂O nanocomposites.

3.2. Atomic force microscope (AFM) analysis

For further morphological investigation, all the samples were characterized using AFM on $2 \mu\text{m} \times 2 \mu\text{m}$ area for better visualization. Fig. 4 represents the AFM images of the composites.

AFM images (Fig. 4A) show the presence of well-dispersed particles having well-defined grain boundaries. It shows that the pure TiO₂ sample (D1) has smaller dimensions, while elongated and larger particle size was observed for the TiO₂:Ag₂O nanocomposite samples (D2 to D5). These observations are in accordance with the result obtained from the XRD analysis of the sam-

ples. The 3D analysis of the corresponding AFM images of the samples was performed to calculate the average height of the particles. In the 3D images (Fig. 4B) similar trend was observed, in which the average height of the particles increased from 9 nm (for sample D1) to 60 nm (for sample D5). From the AFM analysis, it may be inferred that the sample D1 has uniform distribution of small particles having average size of 10 nm, while the composite samples D2 to D5 show well dispersed particles varying from 8 nm to 24 nm for sample D2 to 10 nm to 45 nm for sample D5. Table 3 shows the average particle size of the as-prepared samples obtained from the AFM images.

3.3. Scanning electron microscope (SEM)

Fig. 5 represents the scanning electron microscopy (SEM) images of the samples. All the

Table 3. Average particle size of as-prepared $\text{TiO}_2\text{:Ag}_2\text{O}$ nanocomposite samples obtained via AFM images.

S. No.	Sample code	Average particle size [nm]
1.	D1	10
2.	D2	19
3.	D3	23
4.	D4	26
5.	D5	31

samples were analyzed at 10 kV accelerating voltage. The SEM images show the presence of homogenous, well-dispersed particles having well-defined grain boundaries.

Fig. 5. SEM analysis of the samples: (a) D1, (b) D2, (c) D3, (d) D4, and (e) D5.

From Fig. 5 it may be inferred that sample D1 shows cubical morphology. Since the particle is formed by the bonding of crystallites having the same phase and is an agglomerate of the crystallites [7], hence the particle size observed is larger than that of crystallite size obtained from XRD studies. Slight distortion in the shape of the particles for the nanocomposite samples (D2 to D5) is also observed which may be due to the incorporation of Ag ions in the TiO_2 . SEM analysis also shows the increment in the size of the particles with respect to Ag concentration. The enhancement in the size could be attributed to the effect of Ag_2O as the number of lattice defects increases with the increase in Ag_2O content, leading to distortion in the surface of the material. This provides suitable sites for the crystallites to agglomerate and grow which causes an increase in particle size. The obtained results are in accordance with those of the XRD and AFM analyses, which also confirms the

increase in size of the nanocomposite with respect to Ag concentration.

3.4. UV-Vis analysis

Optical absorption of the $\text{TiO}_2\text{:Ag}_2\text{O}$ nanocomposite was studied by UV-Vis spectroscopy. The samples were scanned in the range of 190 nm to 700 nm. For the UV-Vis absorbance analysis, the samples were ultrasonically dispersed in absolute methanol (CDH, Germany) before measurement and absolute methanol was used as a reference.

Fig. 6. Optical absorbance spectra of the as-prepared $\text{TiO}_2\text{:Ag}_2\text{O}$ nanocomposite samples obtained via UV-Vis spectroscopy.

From the absorption spectra (Fig. 6), it may be inferred that the samples show significant blue shift in the absorption edge as compared to that of bulk TiO_2 (3.2 eV) suggesting an increase in the band gap of the samples [29]. Also the presence of the single narrow peak in the spectra of the samples D1 and D2 suggests that the samples comprise well

dispersed homogeneous particles with narrow size distribution [24, 30]. The absorbance spectra show a red shift in the absorption edge of the samples D2 to D5 as compared to that of the D1. This refers to the decrease in bandgap as well as the increase in the particle size of the samples [29]. The reason can be attributed to the increase in Ag concentration in the nanocomposites. Also the spectra show the presence of an extra small and broad peak for the sample D3 to D5, whose intensity increases with increase in Ag concentration in the samples [31]. This extra peak suggests the presence of heterogeneously distributed particles as compared to the homogeneous particles in sample D1 [32]. This phenomenon is also observed in the AFM and SEM images of the samples showing the presence of large and dispersed particles in samples D3 to D5.

From the absorption spectra of the samples, the bandgap of the TiO₂:Ag₂O nanocomposite can be calculated using the energy-wavelength equation [32]:

$$E = \frac{hc}{\lambda} \quad (1)$$

where, h is the Planck's constant = 4.135667×10^{-15} eV, c is the speed of light = 3×10^8 m/s and λ is excited absorption edge (in nm). This method considers only the absorption edge of the spectra, hence the role of other particles in the bandgap is not taken into account. This is because at absorption edge, only the largest particles contribute to the absorbance. To determine the true optical bandgap of the samples, Absorption Spectra Fitting Procedure known as Tauc relation is utilized [33]. According to the Tauc relation, absorption coefficient (α) is calculated using Beer-Lambert law [33], given by:

$$\alpha = \frac{2.303A}{l} \quad (2)$$

where A is absorption obtained from the absorption spectra, l is the thickness of the sample holder (in the case of cuvette, $l = 10$ mm). According to Tauc equation [31, 36, 37]:

$$\alpha hv = B(hv - E_g)^n \quad (3)$$

where B is a constant, hv is the energy of incident photons and value of n depends upon the type of

transitions (1/2 for allowed direct, 2 for allowed indirect, 3/2 for forbidden direct and 3 for forbidden indirect transitions [33]) and E_g is the band gap. Fig. 7 shows the variation of $(\alpha hv)^2$ with respect to incident photon energy (hv). As suggested by various researchers [34–36], the direct bandgap of the samples has been determined by extrapolating the linear portion of the plot on hv -axis. The point of intersection of extrapolated straight line on the hv -axis gives the value of the bandgap (E_g) of the corresponding sample.

Fig. 7. Tauc plot of as-prepared nanocomposite samples.

Table 4 shows the values of the bandgap of each sample calculated using both the methods viz. energy-wavelength equation (equation 1) and absorption spectra fitting method (Tauc plot).

From Table 4, one may infer that with an increase in Ag concentration there is a significant decrease in the bandgap of the samples, from 3.89 eV for D1 to 3.46 eV for D5, but it is still significantly greater than that of bulk TiO₂ ($E_g = 3.2$ eV). The reason for the increase in bandgap as compared to the bulk counterpart can be explained with the help of quantum confinement theory (QCT) [37, 38]. According to QCT [37, 38], smaller crystallite size should have larger band gap and large crystallite size should have smaller band gap. The obtained band gap values validate the increase in the crystallite size. An increase in the number of Ag⁺ ions in the TiO₂ matrix may increase the number of energy

Table 4. Energy bandgap of the as-prepared samples calculated from energy-wavelength equation and Tauc plot.

Sample name	Absorption edge [λ]	E _g (by energy – wavelength equation) [eV]	E _g (by absorption spectra fitting method: Tauc plot) [eV]
D1	345nm	3.57	3.89
D2	355nm	3.49	3.71
D3	364nm	3.40	3.60
D4	371nm	3.34	3.52
D5	377nm	3.29	3.46

levels in the nanocomposite [32], thus resulting in narrowing of the bandgap of the samples. These results are in accordance with the results obtained from XRD, AFM and SEM.

4. Conclusion

Sol-gel technique was used to prepare TiO₂:Ag₂O nanocomposites of varying sizes. This study reveals that by increasing Ag concentration, the particle size is increased which is confirmed by the X-ray diffraction, AFM, SEM and optical absorption studies. Absorption spectrum shows red shift in the absorption edge with an increase in the Ag concentration. Blue shift of the absorption edge is observed in the samples D1 to D5 as compared to that of bulk TiO₂. The wide-band gap property of TiO₂:Ag₂O nanocomposite makes it a suitable material for memory-storage and dielectric applications.

References

- [1] GRÄTZEL M., *Nature*, 414 (2001), 338.
- [2] FUJISHIMA A., HONDA K., *Nature*, 238 (1972), 37.
- [3] CHEN X., MAO S. S., *Chem. Rev.*, 107 (2007), 2891.
- [4] ASAHI R., MORIKAWA T., OHWAKI T., AOKI K., TAGA Y., *Science*, 293 (2001), 269.
- [5] BURDA C., LOU Y., CHEN X., SAMIA A. C. S., STOUT J., GOLE J. L., *Nano Lett.*, 3 (2003), 1049.
- [6] IJIMA S., *Nature*, 354 (1991), 56.
- [7] ZHONG Z., LIN M., NG V., NG G. X. B., FOO Y., GEDANKEN A., *Chem. Mater.*, 18 (2006), 6031.
- [8] CAO S., YEUNG K. L., YUE P. L., *Appl. Catal. B*, 76 (2007), 64.
- [9] KUMAR R.; REDA M. EL-SHISHTAWY, BARAKAT M. A., *Catalysts*, 6 (2016), 76.
- [10] WANG S., MINGTAI W., YONG L., LIDE Z., *J. Mater. Sci. Lett.*, 18 (1999), 2009.
- [11] ZHENG MAO-PING, YAN-PING J., GUO-LIANG J., MING-YUAN G., *J. Mater. Sci. Lett.*, 19 (2000), 433.
- [12] WAGHMODE BABASAHEB J., HUSAIN Z., JOSHI M., SATHAYE SHIVARAM D., PATIL KASHINATH R., MALKHEDE DIPALEE D., *J. Polym. Res.*, 23 (2016), 1.
- [13] HABIB M. D. AHSAN, SHAHADAT M. D. TUSAN, BAHADUR N. M., ISMAIL IQBAL MI, MAHMOOD ABU JAFAR, *Int. Nano Lett.*, 3 (2013), 1.
- [14] ASHOK C. H., RAO V. K., SHILPA C. CH., *J. Nanomater. Mol. Nanotechnol.*, 5 (2016), 12.
- [15] ASHOK C. H., VENKATESWARA R., SHILPA C. CH., *J. Nanomed. Nanotech.*, (2015).
- [16] GOVINDHAN P., PRAGATHISWARAN C., *J. Mater. Sci.: Mat. El.*, 27 (2016), 8778.
- [17] TAN X., XIANGLI L., TAO Y., YANG Z., *Trans. Tianjin Univ.*, 22 (2016), 211.
- [18] KHOJASTEH H., MASOUD SALAVATI-NIASARI, ALI A., FARSHID A., MORTEZA E., *J. Mater. Sci.: Mat. El.*, 27 (2016), 1261.
- [19] RUSU E., URSAKI V., GUTUL T., VLAZAN P., SIMINEL A., in: *3rd International Conference on Nanotechnologies and Biomedical Engineering*, Springer Singapore, (2016) 93.
- [20] KUMAR A., JOSE R., FUJIHARA K., WANG J., RAMAKRISHNA S., *Chem. Mater.*, 19 (2007), 6536.
- [21] CHEN D., FUZHI H., YI-BING C., RACHEL A. C., *Adv. Mater.*, 21 (2009), 2206.
- [22] WEIBEL A., RENAUD B., BOULC' F., KNAUTH P., *Chem. Mater.*, 17 (2005), 2378.
- [23] THIRUVENKATACHARI R., VIGNESWARAN S., MOON I. S., *Korean J. Chem. Eng.*, 25 (2008), 64.
- [24] YANG J., MEI S., FERREIRA J. M. F., *Materials Science Forum, Trans Tech Publications*, 455 (2004), 556.
- [25] NAVIN K., KURCHANIA R., *Appl. Phys. A-Mater.*, 121 (2015), 1155.
- [26] YANG J., MEI S., FERREIRA J. M. F., *J. Colloid Interf. Sci.*, 260 (2003), 82.
- [27] YANG J., MEI S., FERREIRA J. M. F., *J. Eur. Ceram. Soc.*, 24 (2004), 335.
- [28] BINDU P., THOMAS S., *J. Theoretic. Appl. Phys.*, 8 (2014), 123.
- [29] KOUTU V., SHASTRI L., MALIK M. M., *Mater. Res. Express*, 4 (2017), 034001.
- [30] LI XIAO-LIN, PENG Q., YI JIA-XIANG, WANG X., LI Y., *Chem. Eur. J.*, 12 (2006), 2383.

- [31] WANG X., ZHUANG J., PENG Q., LI Y., *Nature*, 437 (2005), 121.
- [32] WILLANDER M., NUR O., SADAF J. R., QADIR M. I., ZAMAN S., ZAINELABDIN A., BANO N., HUSSAIN I., *Materials*, 3 (2010), 2643.
- [33] SATOH N., NAKASHIMA T., KAMIKURA K., YAMAMOTO K., *Nature Nanotechnol.*, 3 (2008), 106.
- [34] WEN BAO-MEI, LIU CHUN-YAN, LIU Y., *New J. Chem.*, 29 (2005), 969.
- [35] WEN BAO-MEI, LIU CHUN-YAN, LIU Y., *J. Phys. Chem. B*, 109 (2005), 12372.
- [36] KIM CHUNG-SIK, MOON B. K., PARK JONG-HO, CHOI BYUNG-CHUN, SEO HYO-JIN, *J. Cryst. Growth*, 257 (2003), 309.
- [37] ASHRAFI A., *Quantum Confinement: An Ultimate Physics of Nanostructures* in: UMAR A. (Ed.), *Encyclopedia of Semiconductor Nanotechnology*, American Scientific Publishers, California, 2011, p. 1.
- [38] *Chapter 3. UV-Vis and PL Spectroscopy of ZnO Nanorods and Nanotubes*, in: CHALLA S.S., KUMAR R. (Eds.), *UV-Vis and Photoluminescence Spectroscopy for Nanomaterials Characterization*, p. 63.

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