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Structural and Optical Study of TiO_2-Graphene Composite Films

Ankita Dubey[1], Ranveer Kumar[1], Anupama Chanda[1*]

[1]Department of Physics, School of Mathematical and Physical Sciences
Dr. Hari Singh Gour Vishwavidyalaya (A Central University),
Sagar - 470003, Madhya Pradesh, India,
Email ID: msankitad27@gmail.com, ranveerssi@yahoo.com, achanda@dhsgsu.edu.in*

Abstract: **TiO_2 and TiO_2-graphene composite films were prepared by a simple drop casting method using titanium di-isopropoxide and graphene precursor. The structural analysis of the films was done by X-ray diffraction which indicate presence of anatase phase of TiO_2 along with the appearance of graphene peak in TiO_2-graphene composite film. The morphology of the films was studied by scanning electron microscopy from which graphene sheets incorporated in TiO_2 nanoparticles can be seen. Absorbance study by UV-Visible spectroscopy indicate an increase in absorbance of TiO_2-graphene films in visible region. Spectroscopic ellipsometry study shows an increase in refractive index of TiO_2-graphene films in comparison to TiO_2 films which may be due to increase in crystallinity of TiO_2-graphene films. Optical absorbance study done on TiO_2 and graphene solution with different concentration of graphene shows an increase in extinction coefficient with increase in graphene content in TiO_2 measured at 632 nm. This indicates an increase in absorption of TiO_2 with increase in Graphene content which can be useful for visible light absorption applications.**

Index Terms: **TiO_2; Graphene; Optical absorption; Extinction coefficient, Refractive index**

I. Introduction

Titanium dioxide (TiO_2) a wide band gap semiconductor have attracted considerable attention due to its interesting properties like low cost, non- toxicity, stability, favorable band gap. Its modified electronic and optical properties finds large applications in various fields like photo-catalysis, energy storage, solar cells, spintronics, waste water management etc [Apno, 2003; Song, 2004; Qiu, 2011; Choudhury, 2011; Wang, 2006; Matsumoto, 2001]. It has also been widely used as anti reflection coatings. Due to its wide bandgap (3.0 – 3.2 eV), it is useful for limited region of solar radiation. Research is being focused to tune the bandgap and use it in several applications. Graphene is a one-atom-thick, two-dimensional substance composed of sp2 hybridised carbon atoms covalently linked in a hexagonal honeycomb lattice structure [Novoselov, 2004]. Because of its two-dimensional structure, graphene exhibits a linear dispersion relation known as the Dirac cone, implying that the charge carriers in graphene have no rest mass. This feature of graphene results in a number of exceptional properties, including a huge specific surface area, high carrier mobility, high Young's modulus, exceptional optical characteristics (97% transmittance), and good electrical and thermal conductivity [Neto, 2009; Bolotin, 2008;]. Graphene is a zero-band gap material in which the conduction and valence bands contact at a place known as the Dirac point, making it a semimetal. Graphene has piqued the curiosity of numerous research teams across the world because of its exceptional electrical, physical, and chemical capabilities. Superior electrical, mechanical, thermal, and catalytic qualities make this material appropriate for application in sensors, Li-ion batteries, nanofluids, nanocomposites, and biotechnology. It has a high potential for usage in a variety of technical domains, including electronics, supercapacitors, batteries, fuel cells, and solar cells [Kostarelos, 2014; Zhang, 2014; Sadeghinezhad, 2016; Goenka, 2014; Arnold, 2016; Lin, 2016]. It is reported that Graphene (G), Graphene oxide (GO) and reduced graphene oxide (RGO) form mixed composites with polymers [Nasir, 2020] and semiconductors [Nasir, 2022] which can be used in several applications like energy storage devices, water remediation, photocatalysis [Razaq, 2022] etc. They possess various functional groups which can be bonded with TiO_2 forming composites with synergistic features [Usharani, 2022]. Graphene-TiO_2 nanocomposite film development for solar applications has been the subject of several papers focused on various issues. Various deposition methods like Sol-gel methods [Ghamsari, 2008; Wang, 2002], chemical vapor deposition [Sun, 2008] electron-beam evaporation [Habibi, 2007], ion-beam assisted deposition [Yang, 2008], DC reactive magnetron sputtering [Tavares, 2007], RF reactive magnetron sputtering [Sung, 2007; Amor, 1998], and plasma enhanced chemical vapor deposition [Yang, 2006] have been used for deposition of TiO_2 thin films. In this paper, we have investigated the production of TiO_2 and TiO_2-graphene composite films by a simple cost effective drop casting method and studied their structural and optical properties. Very few studies have prepared the composite films by direct mixing of graphene in TiO_2 and used drop casting method.

II. EXPERIMENTAL

A. Preparation of TiO_2 and TiO_2-Graphene Composite Thin Films

Titanium di-isopropoxide was used as the precursor for TiO_2 film. In the first step titanium di-isopropoxide was added in 10 ml of methanol. After that, the solution was continuously stirred with a magnetic stirrer while being held at 60 ^oC for 1 hour for complete dissolution. A little amount (25µl) of the solution was obtained in a pipette and drop casted onto glass substrates. Using the same procedure a weighted amount of graphene was added to the above prepared solution and kept stirring for 1 hour. The graphene used here is microwave exfoliated graphene. Similar way using drop casting, TiO_2-Graphene film was deposited on glass substrates. After the films were deposited both films were annealed in air at 400 ^oC for 1h.

B. Characterization

X-ray powder diffraction (XRD) (Bruker-D8 Advance) using Cu Kα source of wavelength 1.54056 A was used to study the phase and crystal structure of the films. Scanning electron microscopy (SEM) Hitachi-S520 (Oxford link ISISSEM model), Japan was used to study the morphology of the films. The absorbance spectra of the films were studied in the wavelength range 250–800 nm (Perkin-Elmer UV/VIS Spectrometer, model Lambda 950). The optical constants like refractive index and extinction coefficient of the films were studied by a Spectroscopic ellipsometer (M 2000 series of J A Woollam). Extinction coefficient is also found out in a separate absorbance set up by using He-Ne laser of 632 nm wavelength.

III. RESULTS AND DISCUSSION

X-ray diffraction pattern taken on TiO_2 and TiO_2 – Graphene films is shown in figure 1. The diffraction peak around 25.5^0 on both films is ascribed due to (101) plane which is the highest intense plane of anatase TiO_2. The peak around 26.7^0 on TiO_2-graphene film is due to graphene which may have arisen due to graphene forming secondary phase. From the figure it can be noted that peaks of TiO_2-graphene films are sharper than that of TiO_2 films which may be due to an increase in crystallinity of the TiO_2-graphene films. This may be due to addition of graphene, the crystallinity is enhanced which is not clear at present. This needs more investigation.

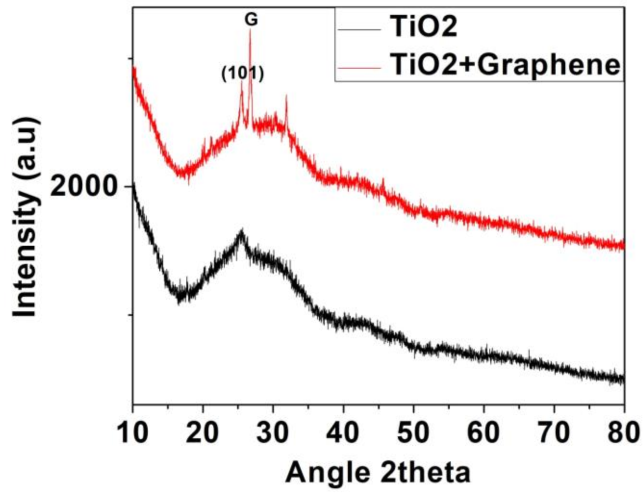

Figure 1: XRD pattern of TiO2 and TiO2-Graphene films

Figures 2a shows the SEM image taken on TiO_2 thin film from which smooth structure of the films with few nanoparticles can be seen. Figure 2b shows the SEM image taken on Graphene-TiO_2 thin film from which graphene sheets incorporated in TiO_2 nanoparticles can be seen.

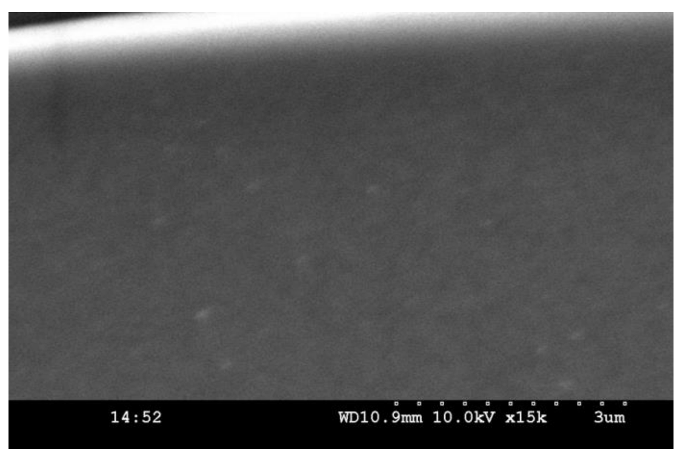

Figure 2a: SEM image of TiO_2 film

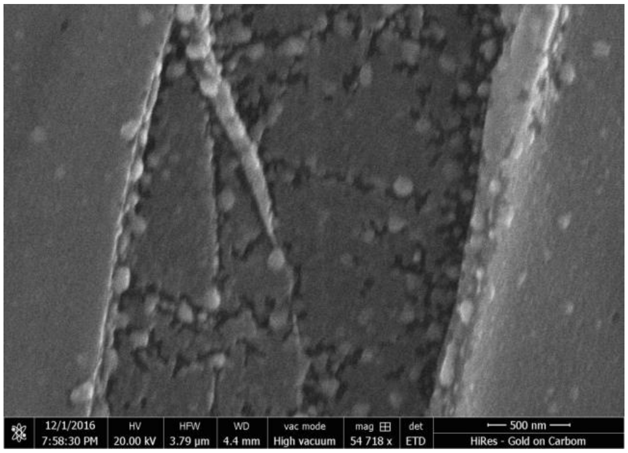

Figure 2b: SEM image of TiO_2-Graphene film

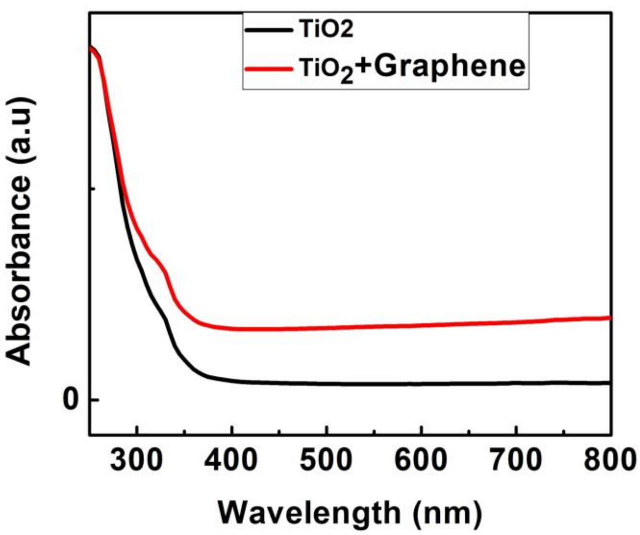

Figure 3: UV-Visible absorption spectra of TiO_2 and TiO_2+Graphene films

Figure 3 shows the UV-Visible spectra taken on TiO_2 and TiO_2-Graphene films deposited on glass substrates. From the figure it can be seen that the absorbance of TiO_2-Graphene films is increased in comparison to pure TiO_2 which can be beneficial for visible region optical application.

A spectroscopic ellipsometry study was conducted to determine the films' refractive index and extinction coefficient. The ellipsometry result obtained on the TiO_2 and TiO_2-graphene composite films are displayed in Fig. 4a and b. It demonstrates that TiO_2 has refractive index of approximately 1.6 and TiO_2-graphene thin film has refractive index of 2.06 around 520 nm region. Increase in refractive index of TiO_2-graphene films in comparison to TiO_2 films may be due to increase in crystallinity of TiO_2-graphene films which is in agreement with XRD data. Figure 4b shows the extinction coefficient of both films from which it can be seen that the extinction coefficient of TiO_2-Graphene films is more than that of TiO_2 films. Extinction coefficient more indicates absorption of TiO_2-graphene films is more in comparison to TiO_2 films which is also confirmed from UV-Visible study.

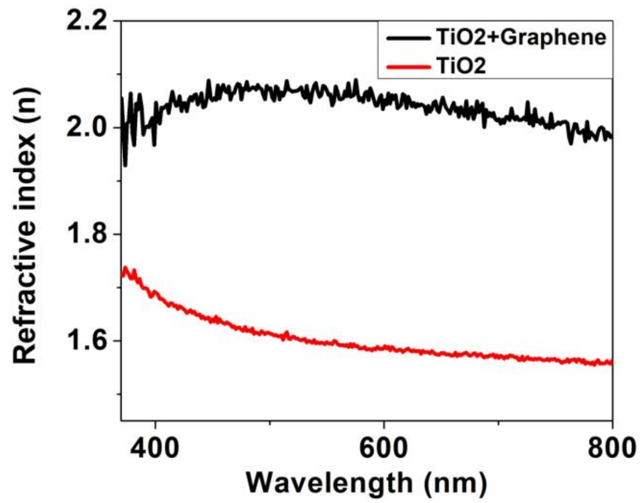

Figure 4a: Refractive index of TiO_2 and TiO_2-Graphene films

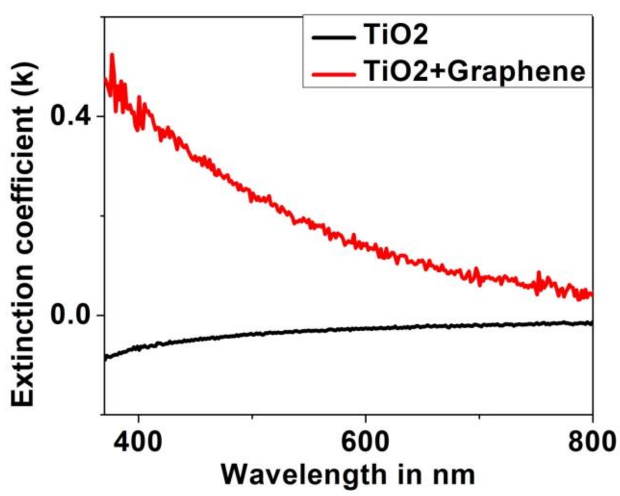

Figure 4b: Extinction coefficient of TiO_2 and TiO_2-Graphene films

In another optical set up absorbance study was done using He-Ne laser at 632 nm. Figure 5 shows the extinction coefficient taken on TiO_2 and graphene solution with different concentration of graphene from which it can be noted that there is an increase in extinction coefficient with increase in graphene content in

TiO_2. This indicates an increase in absorption of TiO_2 with increase in Graphene which can be useful for visible light absorption applications. This study is in agreement with UV-Visible spectra and ellpsometry data.

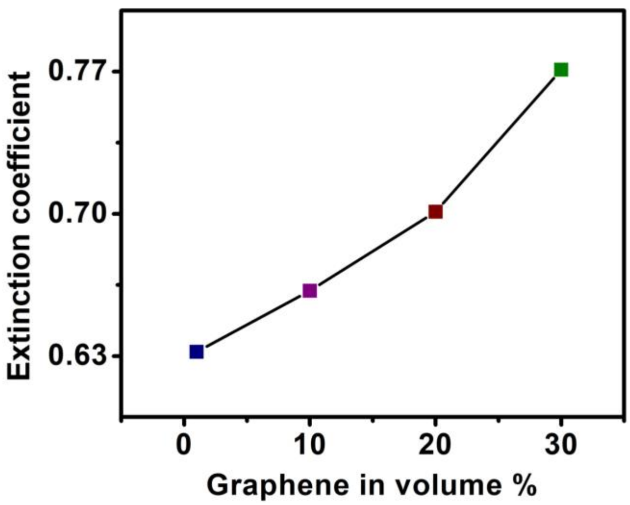

Figure 5. Optical analysis of TiO_2 and graphene solution at 632nm

CONCLUSION

A drop casting technique was used to effectively deposit TiO_2 and TiO_2-graphene composite films. Anatase phase of TiO_2 along with graphene peak ensures formation of TiO_2 and TiO_2-graphene composite films. Graphene sheets incorporated in TiO_2 nanoparticles are visible in the SEM picture of TiO_2-Graphene composite film. The UV-Visible spectra indicate an increase in absorption in visible region in TiO_2-Graphene composite films. An increase in refractive index indicating an increase in crystallinity and increase in extinction coefficient giving an increase in absorption in visible region in TiO_2-graphene films. The optical analysis shows an increase in extinction coefficient of TiO_2 with increase in graphene content indicating increase in absorption of TiO_2 with Graphene, which is beneficial for applications involving the absorption of visible light.

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