

## Synthesis and characterization of Nano-particulate TiO<sub>2</sub>-Graphene composite

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### ABSTRACT

Multifunctional hybrid materials are more capable than those based on pure nano-particulates. The present study focused on an efficient way to synthesis nano-particulate TiO<sub>2</sub>-Graphene composite (Gn-TiO<sub>2</sub>) to be used as an electrode material for Na ion rechargeable battery application. Graphite Oxide (GO) Synthesized from Kahatagaha vein graphite ore, in Sri Lanka was used for the study.

The composite was characterized using X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectrophotometry. The XRD pattern of GO, peak at  $2\theta = 9.6^\circ$  is disappeared confirming successful reduction of GO to Graphene (Gn) and the low intense broader peak appeared at  $2\theta = 26.54^\circ$  reveals successful formation of Gn. The peaks at  $2\theta$ ,  $25.3^\circ$ ,  $37.9^\circ$ ,  $48.0^\circ$ ,  $54.0^\circ$ ,  $62.6^\circ$ ,  $69.4^\circ$ ,  $75.0^\circ$ ,  $94.6^\circ$ ,  $114.3^\circ$  and  $118.7^\circ$  were assigned to the diffractions of the (1 0 1), (1 0 3), (2 0 0), (1 0 5), (2 1 3), (1 1 6), (2 1 5), (3 0 5), (3 0 7) and (2 1 9) crystal planes of the anatase phase of TiO<sub>2</sub> respectively. The average particle size of the Gn-TiO<sub>2</sub> nano-composite was 9.456 nm, according to the XRD it shows successful formation of the nano Gn-TiO<sub>2</sub> composite. The SEM analysis confirms the formation of graphene membranes. In addition, the bands around  $1552\text{ cm}^{-1}$  of FTIR are well exhibited the formation of graphene and also the bands appeared at the  $1416\text{ cm}^{-1}$  refers to Ti-O-Ti bond vibrations. According to the UV-visible absorbance spectrum of the Gn/TiO<sub>2</sub> nano-composite, the Band gap energy of the material is 3.229 eV. The Gn-TiO<sub>2</sub> composite produced here would be suitable for many applications including energy storage devices and sensors.

### 1. INTRODUCTION

Graphene is a single layer of sp<sup>2</sup> carbon lattice which has remarkable properties, such as large specific surface areas ( $2600\text{ m}^2\text{g}^{-1}$ ), high mobility of the charge carriers ( $2 \times 10^5\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ), high chemical stability and high elasticity [1, 4]. Due to these special properties, vast variety of research work has been focus on graphene. There are numerous graphene-based applications, such as sensors, transistors, nano electronics, super capacitors and energy storage systems [4].

TiO<sub>2</sub> is one of the most widely available and commercially viable photocatalyst [1]. Recently, it has been widely investigated as in electrode materials, photo catalysis, electronic devices and conversion devices due to its significant properties, such as low

cost, lack of reactivity with environment, strong oxidizing power, long-term stability against photo and chemical corrosion, better safety and environmental friendliness [2]. TiO<sub>2</sub> exists in two major phases known as anatase and rutile and the anatase phase exhibits the higher photo catalytic activity [4].

Due to all the remarkable properties of graphene and TiO<sub>2</sub>, recently it has been discovered that graphene/TiO<sub>2</sub> nano-composite has significantly higher photo catalytic activity, which is closely related to absorptivity, conductivity, controllability, etc [5]. So, the wide range of research work has been carried out using graphene/TiO<sub>2</sub> nano-composite in the fields of energy storage system, photo sensors, etc [1, 4]. In the present study, a novel method for synthesis of graphene/TiO<sub>2</sub> nano-composite is discussed due to its potential application as an anode in Na ion rechargeable battery. Further, since graphene is synthesized using Kahatagaha graphite, it would be a value addition to Sri Lankan graphite.

## **2. EXPERIMENTAL**

### **2.1 Synthesis of Graphene-TiO<sub>2</sub> (Gn-TiO<sub>2</sub>) Nano-Composite**

Graphite Oxide (GO) was prepared by the improved method using Kahatagaha graphite flakes ( $\leq 38\mu m$ ) as described elsewhere [6]. Graphene (Gn) was synthesized by a thermal process using prepared GO. The TiO<sub>2</sub> graphene composite was prepared as follows. 87.5ml of ethanol and 10ml of acetic acid were mixed together and 2.5ml Titanium (IV) isopropoxide (97%) was added. Clear aqueous was obtained. 400mg of pre-prepared Gn was added to the mixture and stirred for 10 minutes. Black suspension obtained was sonicated for 1 hour. While stirring the mixture 100ml of distilled water was added drop wise in 2 hours times. Excess 40ml of distilled water was added. The black suspension was kept in an oven at 100°C for 24 hours. Black colour Graphene-TiO<sub>2</sub> (Gn-TiO<sub>2</sub>) nano-composite was obtained.

### **2.2 Characterization**

Materials were characterized using X-ray diffraction (XRD) analysis. Regaku ultima VI, X-ray Diffractometer with Cu K<sub>α</sub> ( $\lambda = 1542 \text{ \AA}$ ) radiation was used to analyze the structure of the sample. Crystallographic information was obtained with the aid of the ICSD data base.

Scanning electron microscopic analysis (LEO 1420 vp) was used to investigate the morphology of the materials with maximum enabled instrument resolution.

The Fourier Transformed Infrared spectroscopy (FTIR) (Bruker Tensor 27) was carried out to determine the type of the atomic bonding in composites. UV-visible absorption spectroscopy (Shimadzu 120) was used to find the energy band gap of the developed composite.

### 3. RESULTS AND DISCUSSION

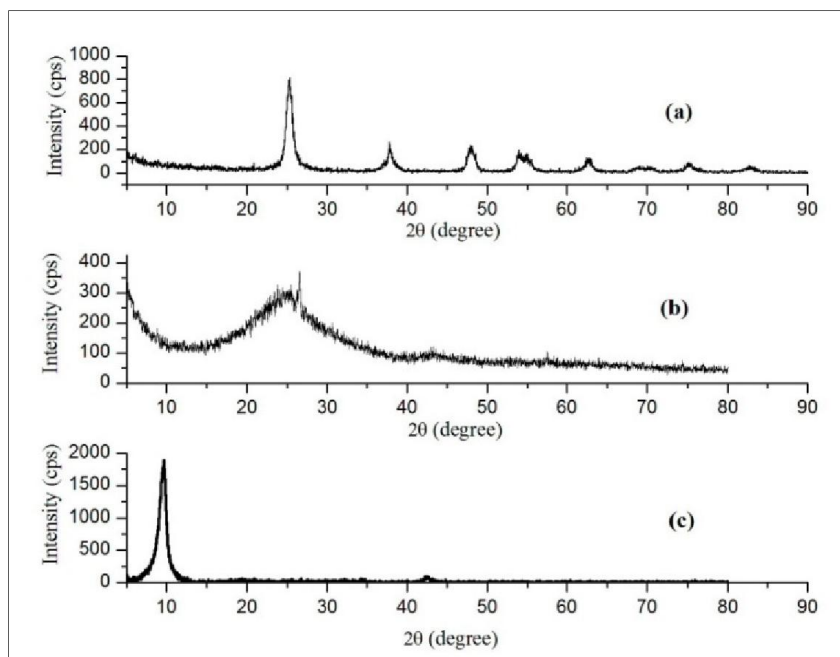


Fig. 1: XRD patterns of (a) Gn-TiO<sub>2</sub> nano-composite, (b) graphene, (c) Graphite Oxide

The Fig. 1 shows the XRD spectra of Gn-TiO<sub>2</sub> nano-composite, GO and Gn. The GO had an intense peak at  $2\theta = 9.6^\circ$ , corresponding to the (0 0 1) plane as shown in the Fig. 1(c). When the GO was reduced to Gn, the diffraction peak at  $2\theta = 9.6^\circ$  was disappeared and a new broader peak appeared at  $2\theta = 26.54^\circ$  as shown in the Fig. 1(b) corresponding to the Gn (0 0 2) plane. Fig. 1(a) shows XRD spectra of Gn/TiO<sub>2</sub> nano-composite. The peaks respectively at  $2\theta$ ,  $25.3^\circ$ ,  $37.9^\circ$ ,  $48.0^\circ$ ,  $54.0^\circ$ ,  $62.6^\circ$ ,  $69.4^\circ$ ,  $75.0^\circ$ ,  $94.6^\circ$ ,  $114.3^\circ$  and  $118.7^\circ$  were assigned to the diffractions of the (1 0 1), (1 0 3), (2 0 0), (1 0 5), (2 1 3), (1 1 6), (2 1 5), (3 0 5), (3 0 7) and (2 1 9) crystal planes of the anatase phase of TiO<sub>2</sub>. The diffraction peak of Gn was not distinguishable in the XRD patterns of the nano-composite presumably due to high intensity of TiO<sub>2</sub> peak. All the peaks in the X-ray diffraction pattern could be identified as anatase phase of TiO<sub>2</sub> according to the ICSD Collection Code: 154604. The average particle size of the Gn-TiO<sub>2</sub> nano-composite was 9.456 nm, according to the maximum diffraction peak at  $2\theta = 25.3^\circ$  calculated using Scherrer's equation.

The surface morphology and the microstructure of the Gn-TiO<sub>2</sub> nano-composite were investigated as shown in the Fig. 2 by scanning electron microscopy (SEM). It is clearly observed the curled and wavy structure of graphene in SEM images in Fig. 2. We believed that the few layer graphene have been successfully synthesized. TiO<sub>2</sub> nano particles in the nano-composite were not observed in the SEM images clearly due to the extreme fineness of nano TiO<sub>2</sub> particles. Nevertheless the presence of nano size TiO<sub>2</sub> particles in the composite was detected by XRD as shown in Fig. 1. Therefore both XRD and SEM are used to verify the Gn and TiO<sub>2</sub> in the composite.

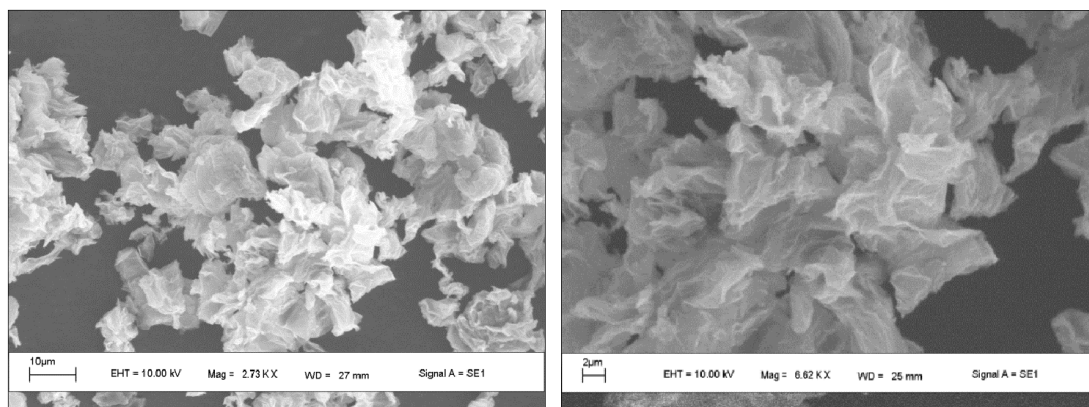


Fig. 2: SEM of Gn-TiO<sub>2</sub> nano-composite at different magnifications

Fig. 3 shows the FTIR spectra of TiO<sub>2</sub>/Gn composite (a), GO (b) and Gn(c). It is found that different types of oxygen functionalities are present in GO confirming various oxygen configurations as shown in Fig. 3(b). Epoxides (C–O–C) and structural hydroxyls (C–OH) attributed bands can be seen at 996 cm<sup>-1</sup> and 1224cm<sup>-1</sup>, and carboxyl (COOH), ketonic species (C=O) and C–O attributed bands can be seen at 1621 cm<sup>-1</sup> and 1735cm<sup>-1</sup>. Band around 3183 cm<sup>-1</sup> is attributed to free hydroxyl (C–OH) from water vapour. In this process, Thermal reduction process is used to reduce GO to Gn and it is found that *sp*<sup>2</sup>-hybridized C=C peak of reduced graphene at the band 1552 cm<sup>-1</sup>. Band at 947 cm<sup>-1</sup> is attributed to remaining epoxide (C–O–C) attached to the graphene basal plane in Fig. 3(c). The bands appeared at the 1416 cm<sup>-1</sup> in Fig. 3(a) refers to Ti-O-Ti bond vibrations.

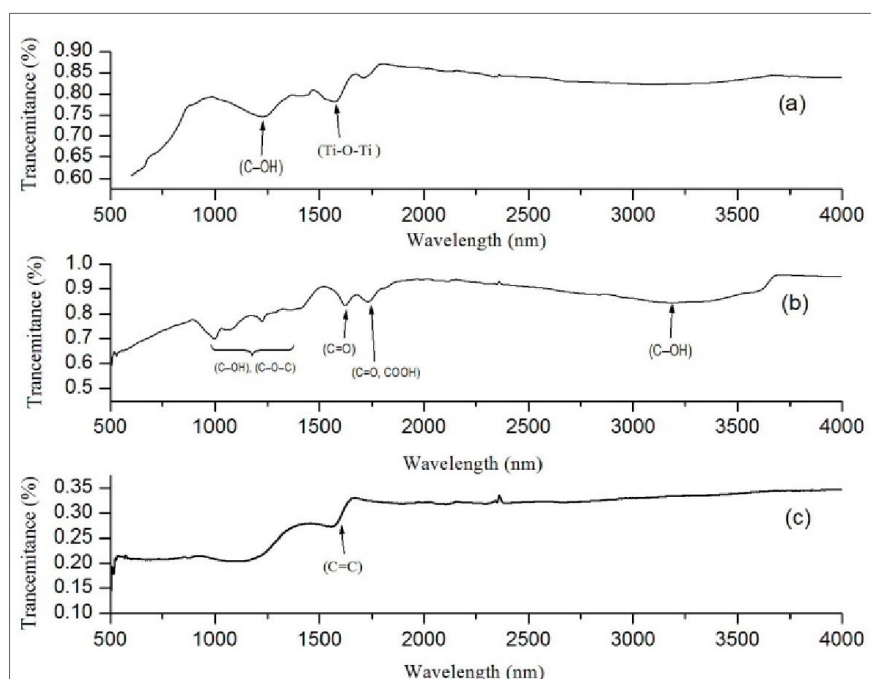


Fig. 3: FTIR spectra of (a) Gn-TiO<sub>2</sub> nano-composite, (b) Graphite Oxide, (c) Graphene

UV-visible absorbance spectrum of the Gn-TiO<sub>2</sub> nano-composite was shown in Fig. 4. It could be clearly seen that the shoulder peak at about 225 nm. Band gap energy of the material was calculated using the strong cut off wavelength at 384.79 nm where the absorbance value was minimum. Calculated band gap energy of the composite was 3.229 eV. The band gap of TiO<sub>2</sub> decreased from 3.239 to 3.173 eV when the particle size decreased from 29 nm to 17 nm and then increased from 3.173 eV to 3.289 eV as the particle size decreased from 17 nm to 3.9 nm (band gap) according to H. Lin and *et.al* [7], this reviles synthesized TiO<sub>2</sub> particle on Gn should be in the range of 17 nm to 3.9 nm which tallied with the calculated particle size (9.456 nm) using Scherrer's equation.

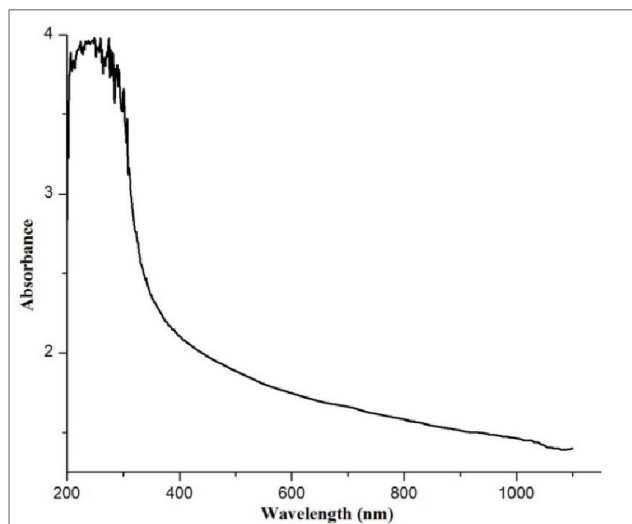


Fig. 4: UV-visible absorbance spectrum of Gn-TiO<sub>2</sub> nano-composite

#### 4. CONCLUSIONS

Characterization of nanocomposite TiO<sub>2</sub>-Gn revealed that the anatase crystalline structure of TiO<sub>2</sub> is remained in the composite and the transition status of material highlighted the specific band gap is being 3.229 eV. TiO<sub>2</sub> nano particles in the nanocomposite could not be seen in the SEM images due to the extreme fineness although it is detected through XRD. TEM would give better results for nano TiO<sub>2</sub>. Further research is underway to investigate novel anode material for Na ion rechargeable battery using TiO<sub>2</sub>-Gn nanocomposite.

#### ACKNOWLEDGEMENT

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