



# Photosensitivity of Graphene Quantum Dots Dispersed Polyvinyl Butyral Nanocomposites

D Arthisree<sup>a</sup>, Girish M Joshi<sup>b</sup> & W Madhuri<sup>a\*</sup>

<sup>a</sup>Ceramic Composite Laboratory, Centre for Crystal Growth, SAS, VIT, Vellore-632014, Tamilnadu, India

<sup>b</sup>Department of Engineering, Physics and Engineering Materials, Institute of Chemical Technology, Mumbai off Campus Jalna - Marathwada Region, Aurangabad Road, Jalna- 431 203, Maharashtra, India

Received 5 April 2019; accepted 31 August 2021

The development of optically active polymer composites continues to be the research interest in the field of applied science. A polymer composite composed of polyvinyl butyral (PVB)/ Graphene Quantum Dots (GQD) that demonstrated significant photosensitivity has been studied in this work. A systematic influence of GQD on the photosensitivity to bandgap variation is observed. The surface morphology of loaded nano entities in the composites and their surface roughness was examined by TEM and AFM analysis.

**Keywords:** Graphene quantum dot, PVB, Photosensitivity, stopping potential, TEM, AFM.

## 1 Introduction

Designing of tunable optoelectrical composite materials with various polymers, thin-films, semiconductors and metals have been the key research interest over the past few years. Organic optoelectrical devices are more advantageous in fabricating and configuring that is challenging to be obtained from inorganic materials. In literature, nano entity dispersed polymer composites demonstrated the high conductivity, dielectric, mechanical, optical bandgap properties of quantum dots<sup>1,2</sup>. Several reports on inorganic quantum dots compositions like InAs/InGaAs and InAs/GaAs exhibited photoelectric and photoconductive antenna wafer properties<sup>3,4</sup>. Multilayer, inorganic CdS quantum dots dispersed in TiO<sub>2</sub>/PbS hybrid composite addressed photocurrent and electrochemical impedance response<sup>5</sup>. Due to challenges in casting the film and high toxicity of inorganic quantum dots, cost-effective carbon allotrope quantum dots have recently emerged as promising candidates with tunable optical and electrical properties, better surface grafting, and good dispensability<sup>6</sup>. GQD is considered as a novel material for various energy and environment-related applications due to their remarkable properties like low toxicity, sustainable photoluminescence and exceptional chemical stability<sup>7</sup>. Meanwhile, Polyvinyl

butyral (PVB) is a colourless and excellent flexible polymer with good optical properties and impact strength, often used as shatterproof glass, binders in paints, inks and adhesives<sup>8</sup>. Various optical properties with changes in the bandgap of semiconducting quantum dots and polymer nanocomposites have been reported previously<sup>9-11</sup>. On the other hand, there is no literature regarding the effect of polymer composites with nano-entities for their photosensitivity (stopping potential). Hence, we decided to prepare photoactive polymer nanocomposites using polyvinyl butyral (PVB)/graphene quantum dots (GQDs) and tested their photoelectric effect.

## 2 Experimental procedure

### 2.1 Chemicals and reagents

PVB powder was supplied by Kuraray India Pvt Ltd, New Delhi. The precursor for the GQD was chosen as rice flour that is an easily available common food source. An average particle size of 50nm GQDs was synthesized according to the literature report<sup>12</sup>.

### 2.2 Preparation of GQD

To prepare GQD, initially, 3g of rice flour was soaked in 40ml of double-distilled water. Then, the soaked rice flour solution was sealed into a 50-mL Teflon lined stainless autoclave and heated up to 150 °C in an oven for 6 hrs. Finally, the solution was filtered using a (0.22 mm size) membrane filter followed by

\*Corresponding author (E-mail: madhuriw12@gmail.com)

centrifuging at 5000 rpm for 1 hr. The final product was stored in an airtight glassware container.

### 2.3 Synthesis of PVB/GQD composites

To prepare the composite film, initially, 2g of PVB powder was dispersed in 100 mL of ethanol solvent and magnetically stirred at 420 rpm for 24 hrs. Meanwhile, in a clean test tube, 2 mL of prepared GQD solution was dissolved in 5 mL of ethanol and sonication for 20 min. Furthermore, three different loading compositions of PVB/GQD (9.5: 0.5, 9:1, 8.5:1.5) was prepared and magnetically stirred for 12 hrs at room temperature. The prepared composites were spread into a clean Petri dish for film formation and dried for 24 hrs.

### 2.4 Characterization techniques

Photosensitivity was tested by using Plank's constant measuring setup, PC-101, with an accuracy of:  $\pm 0.2\%$ ,  $\pm 15$  V output, with a current multiplier of  $\times 0.01$  pA at  $30^\circ$  C. Surface morphology of the composite films has been analyzed using atomic force microscopy (AFM) (nano-surf easy scan) technique at 5  $\mu$ m magnification scale and transmission electron microscopy (TEM) (Techni G2-20 instrument).

## 3 Results and Discussion

AFM analyses were performed to examine the effect of GQD incorporation on the surface topography of the prepared film. Typical 2-D surface and 3-D topographic images are presented in Figure 1(a-d). Observation of a neat morphology (Figure 1(a)) depicting a plain surface (2-D) with a reduced height and depth profile in 3-D topography. The surface roughness ( $R_a$ ) was observed to be around 3.376 nm for the pure polymer film.

Wherein, for pure GQD (Figure 1(b)) the surface was found to have more agglomerated bright and dark regions with  $R_a$  value around 5.237 nm and an increase in the height and depth profile topography. However, loading a small amount of 0.5 wt% GQD in PVB matrix (Figure 1(c)) the  $R_a$  value was found to be 2.528 nm, which is comparatively lesser than the  $R_a$  value observed for neat polymer membrane. This reduction of  $R_a$  value for very small loading of filler in the composite film may be due to the aggregation of GQD in the PVB matrix<sup>13</sup>. Interestingly, for the higher loading of GQD (1.5 wt%) in the composite system, the  $R_a$  value increases approximately to 9.03 nm. The reason for the observation of high  $R_a$  value is due to the surface property of graphene<sup>14</sup> and

surface/interfacial interaction between polymer and GQD leading to the good mechanical stability of the prepared composite system<sup>15</sup>. Furthermore, to support the above information, the PVB/GQD (1 wt%) composite was subjected to TEM analysis and the image is depicted in Figure 2. The bright region represents PVB polymer and the aggregated dark cluster corresponds to the GQD's entrapment in the polymer matrix.

Figure 3. Shows the experimental setup of photosensitivity. Initially, the composite was placed on the window of the phototube (vacuum tube containing) with the light source at a distance, and the apparatus was calibrated to zero current.

When light is (halogen tungsten lamp, intensity= 12V/ 35W) incident on the nanocomposite with maximum intensity (increase the current flow), more electrons are ejected from the cathode metal plate and its corresponding voltage (stopping potential) was measured. The minimum negative potential given to the anode, at which the photo-current becomes zero, is called the stopping potential ( $V_r$ )<sup>16</sup>. They also indicate the minimum required potential for

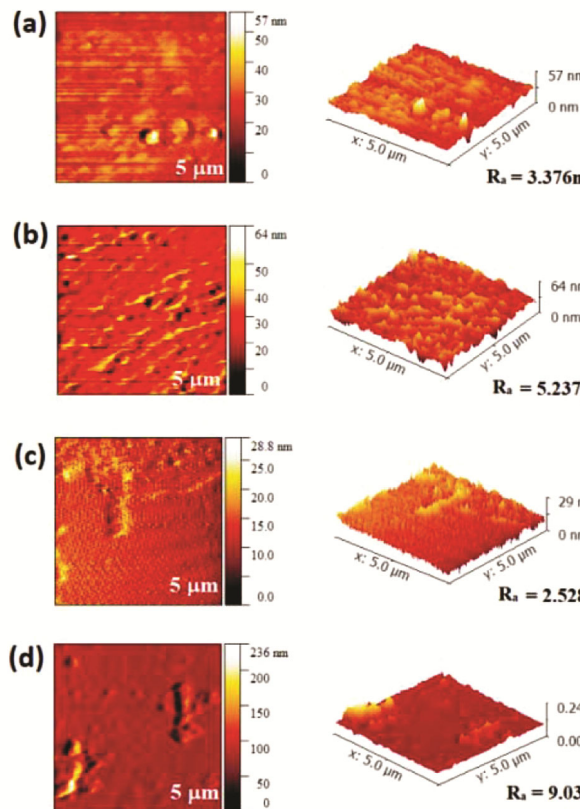


Fig.1 – AFM 2-D (left) and 3-D (right) images of a) Neat PVB, b) pure GQD, c) 0.5 wt%, d) 1 wt% nanocomposites.

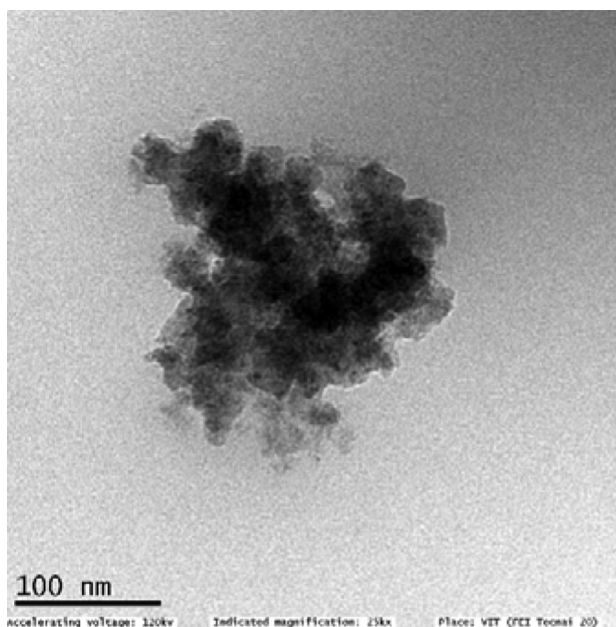


Fig. 2 — TEM image of PVB/GQD 1 wt% nanocomposite.

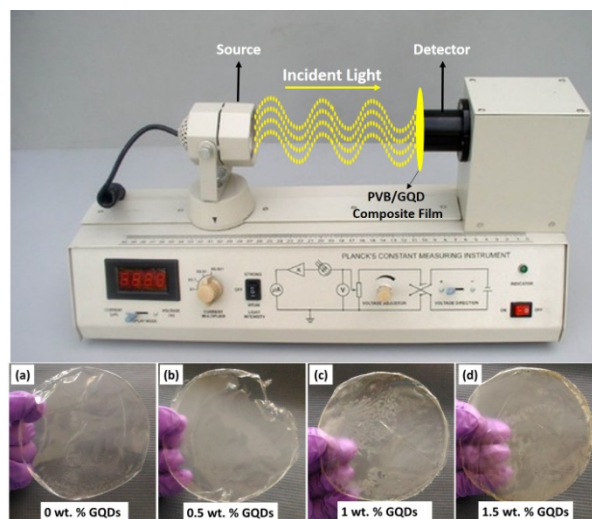


Fig. 3 – Photosensitivity apparatus and casted film images of a) pure PVB, b) 0.5 wt%, c) 1 wt%, d) 1.5 wt% loaded GQD nanocomposites.

photosensitivity. Generally,  $V_r$  is measured for various coloured filters (red, orange, yellow, green and blue) in the range of -0.31 to -1.06 V depending on the frequency and wavelength of the filters. Figure 4 Represents the plot of stopping potential and direct bandgap as a function of loading wt% of GQD in the composite system.

The bandgap results are reproduced from our previous observation<sup>17</sup>. In our present study, when the pristine PVB (without any GQD loading, 0wt %) film was exposed to the source light, the  $V_r$  is found to

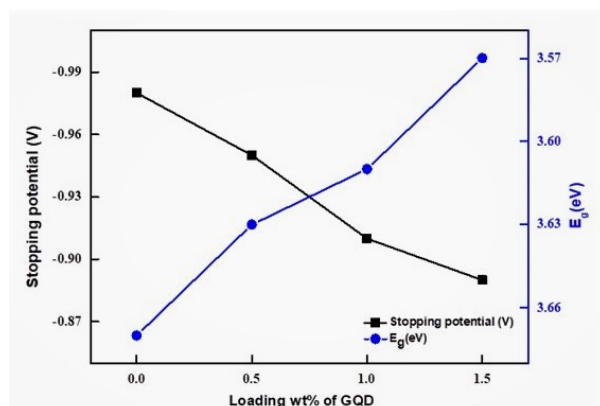


Fig. 4 — Plot of stopping potential and direct bandgap as a function of loading wt% of GQD in PVB composite system.

be -0.98 V (in Figure 4) and their corresponding maximum bandgap 3.67 eV.

Upon increasing the loading weight fraction of GQD to 0.5 wt% on the PVB matrix, a decrement in  $V_r$  value up to -0.95 V was noticed with a bandgap at 3.63 eV. Furthermore, increase in the loading of GQD to 1 and 1.5 wt% the  $V_r$  value was observed to be -0.91, -0.89 V with reduced bandgap values 3.61 and 3.57 eV respectively. Overall, as the loading of GQD increases, the photo potential is found to decrease, and the minimum  $V_r$  value of the prepared composite was found to have the lowest bandgap. This enhances the sensitivity of PVB with GQD loading in the composite system. The significant increase in the carrier mobility that is generally observed in GQD may be the reason for such enhanced photosensitivity<sup>18</sup>, indeed researches have been focusing on the development of various sensors depending on fluorescent quenching activity of GQDs which induces the photoelectron transfer<sup>19</sup>. Thus further loading of GQD may lead to good quality photosensing composites. Presumably, the colour, optical property and chemical interaction of GQD on the PVB membrane play an important role for the present observation. Overall, the opacity of composite film decreases as a function of loading wt% of GQD which promotes the photoelectron transfer and hence the photosensitivity.

#### 4 Conclusion

Influence of the GQD loading on the photosensitivity for the prepared nano composite is studied. Changes in surface roughness and morphology were confirmed by AFM and TEM analysis. Significant reduction in stopping potential from -0.98V to -0.89V was observed as a function of loading weight fraction of GQD and

bandgap. Increase in carrier mobility of composite system may be the reason for lowering in the stopping potential value. The prepared nano composite may be suitable for the development of a new kind of optoelectronic and organic photo-cell/optical-wave guide applications.

### Acknowledgement

The authors are highly thankful to VIT University for TEM facility.

### References

- 1 Lakshmi N V, Tambe P & Sahu N K, *Compos Interface*, 25 (2018) 47.
- 2 Kou L, Li F, Chen W & Guo T, *Org Electron*, 14 (2013) 1447.
- 3 Golovynskyi S, Seravalli L, Datsenko O, Trevisi G, Frigeri P, Gombia E & Ohulchanskyy TY, *Nanoscale Res Lett*, 12 (2017) 335.
- 4 Gorodetsky A, Yadav A, Avrutin E, Fedorova K A & Rafailov E U, *IEEE J Sel Top Quantum Electron*, 24 (2018)1.
- 5 Shi X, Xu J, Shi S, Zhang X, Li S, Wang C & Li L, *J Phys Chem Solids*, 93 (2016) 33.
- 6 Wang R, Lu K Q, Tang Z R & Xu Y J, *J Mater Chem A*, 5 (2017) 3717.
- 7 Bacon M & Bradley S J & Nann T, *Part Part Syst Charact*, 31 (2014) 415.
- 8 Toriki A M, Živković I, Radmilović V R, Stojanović D B, Radojević V J, Uskoković P S & Aleksić R R, *Int J Mod Phys B*, 24 (2010) 805.
- 9 Sun D, Sue H J & Miyatake N, *J Phys Chem C*, 112 (2008) 16002.
- 10 Abdelsalam H, Atta M M, Osman W & Zhang Q, *J Colloid Interface Sci*, 603 (2021) 48-57.
- 11 Gao X, Zheng L, Zheng H, Cheng X & Zhang DW, *Mater Lett*, (2021) 130530.
- 12 Kalita H, Mohapatra J, Pradhan L, Mitra A, Bahadur D & Aslam M, *RSC Adv*, 6 (2016) 23518.
- 13 Qiu S, Wu L, Pan X, Zhang L, Chen H & Gao C, *J Membr Sci*, 342 (2009) 165.
- 14 Selvam M, Sakthipandi K, Suriyaprabha R, Saminathan K & Rajendran V, *Bull Mater Sci*, 36 (2013) 1315.
- 15 Song W, Gu A, Liang G & Yuan L, *Appl Surf Sci*, 257 (2011) 4069.
- 16 Sproull R L & Phillips W A, Courier Dover Publications, 3<sup>rd</sup> Edn, (2015) *John Wiley & Sons, Inc*, New York, 1980.
- 17 Arthisree D L, Sumathi R R & Joshi G, *Polym Adv Technol*, (2018) 1.
- 18 Cayuela A, Soriano M L, Carrillo-Carrión C & Valcarcel M, *Chem Commun*, 52 (2016) 1311.
- 19 Zhou X, Ma P, Wang A, Yu C, Qian T, Wu S & Shen, *J Shen Biosens Bioelectron*, 64 (2015) 404.