FABRICATION AND CHARACTERISTICS OF NANOCOMPOSITE TiO_2/GQDs THIN FILMS

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Abstract: *This work carries out the study and fabrication of TiO_2/Graphene Quantum Dots (GQDs) nanocomposite thin films to be applicated as an electronic collection material layer in nanostructured solar cells. The different concentrations of added GQDs by the spreading method were loaded on TiO_2/GQDs nanocomposite films. The fabricated films were investigated for their structural and morphological characteristics by X-ray diffraction spectroscopy; Ramam spectra and Scanning Electron Microscopy (SEM) imaging. The optical properties were investigated through absorption and fluorescence spectroscopy. The photoelectrical properties of the film were investigated on measuring I-V characteristics in the dark and when illuminated by the solar simulator AM 1.5G. The obtained results show that adding GDQs has significantly improved the photoelectronic properties of the materials.*

Keywords*: TiO_2, GQDs, nanostructure solar cells.*

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1. INTRODUCTION

TiO_2 is one of the promising materials for applications ranging from water spliting, solar cells, energy storage devices, optoelectronic devices, photocatalysis. Nanostructured TiO_2 films are used as the electron-collecting material layer and plays an important role to the parameters of the devices. However, TiO_2 is a wide band gap semiconductor material so it absorbs light in the ultraviolet region, in addition, the conductivity of TiO_2 is also very low, which limits a lot to improving the performance of solar cells as well as being less efficient when used as a photocatalyst under sunlight. On the other hand, the high recombination rate of the carrier is also a reason for the efficiency of solar cell devices as well as the low efficiency of photocatalysis. To overcome those disadvantages, the adding of semiconductor quantum dots

(QDs), such as CdS, CdSe, PbS, especially GQDs onto the TiO_2 material films has been proposed to expanding the working spectrum to the visible light region, increasing the ability to separate charge carrier pairs as well as increasing the ability to conduct electrons to the electrodes [1, 2, 3]. Among the quantum dots that are attracting researchers' attention, GQDs is a new type of material that has been researched and fabricated recently and it has many special physical and chemical properties such as high electrical conductivity, strong luminescence, luminescence wavelength changes with the excitation light wavelength [4, 5], capable of forming bonds with TiO_2 crystals [1, 6]. In addition, GQDs have more advantages than conventional semiconductor QDs that are easy to fabricate and very environmentally friendly. Therefore, the combination of GQDs with TiO_2 nanocrystals is considered to be able to give the material system with better optical absorption, reducing the recombination process due to the charge transfer between the nanocrystals TiO_2 and GQDs, increasing the conductive property of the material system. This promises to provide a material system with suitable properties for making 3rd generation solar cell devices as well as increasing their photocatalytic ability. In this work, we fabricated TiO_2/GQDs nanocomposite thin film used as an electronic collection layer in nanostructured solar cell devices. The different concentrations of added GQDs by the spreading method were loaded on TiO_2/GQDs nanocomposite films. The fabricated films were investigated for their structural and morphological characteristics by X-ray diffraction spectroscopy; Ramam spectra and SEM imaging. The optical properties were investigated through absorption and fluorescence spectroscopy. The photoelectric properties of the film were investigated on measuring I-V characteristics in the dark and when illuminated by the solar simulator AM 1.5G. The obtained results show that adding GDQs has significantly improved the photoelectronic properties of the material that can be applied to improve the performance of nanostructured solar cell devices.

2. CONTENT

2.1. Experimental setup

The chemicals used in this work are included: ethanol C_2H_5OH (99.7%,), aceton CH_3CHO (99.5%), zinc powder Zn (90%), hydrochloric acid HCl (1M), decon 90 (Fisher), deionized water, titanium dioxide (TiO_2-P25), graphene quantum dots (GQDs). GQDs were chemically prepared by initial carbon precursors trinitropyrene, sodium hydroxide with an average size of about 2-5 nm, have absorption spectra in the range of 300 -500 nm and luminescence with emission wavelengths from ultraviolet to 600 nm. The detail of the procedure was published in [7, 8]. Titanium dioxide TiO_2 P25 were added to ethanol, distilled water and GQDs, stirring for 15 minutes, then the mixture was ultrasonically vibrated for 30 minutes, as shown in Figure 1.

Titanium-dioxide (TiO_2) nanoparticles suspension concentration in ethanol by volume was 5% then the GQDs solution were added to TiO_2 solution with volume concentration at 0%, 5%, 10%, 20%, and 30%.

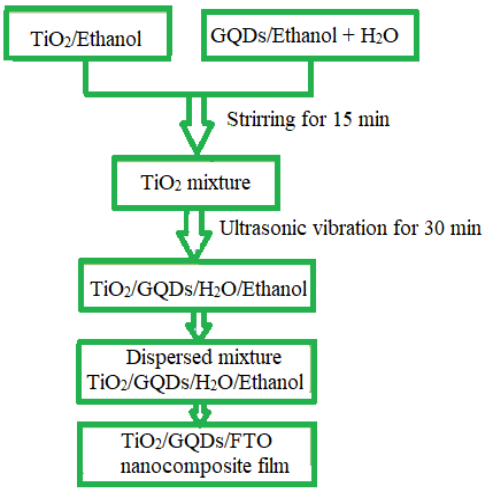

***Fig.1**. The procedure of fabrication of TiO_2/GQDs nanocomposite films*

The samples fabricated for the study include: Sample 0%: TiO_2 powder / ethanol and samples of nanocomposite TiO_2, GQDs/2ml ethanol in the ratios: 0.05%, 0.1%, 0.2%, 0.3% of GQDs in terms of mass. The solution mixtures were stirred for 15 minutes and then ultrasonically vibrated for 30 minutes so that TiO_2 was uniformly distributed with GQDs in water- ethanol medium. To investigate the photocurrent, the FTO/TiO_2/GQDs samples were fabricated as follows: Fluorine-doped Tin Oxide (FTO)/glass substrates were prepared using HCl solutions 1M and zinc powder. Firstly, cover the FTO substrates to be retained with vacuum tape. Secondly, a thin layer of zinc powder is evenly coated on the surface to be etched, after 15 minutes, the FTO layer completely corroded. The FTO substrates were cut into small pieces of the dimensions 4.5 cm x 1.5 cm and then etched as shown in Figure 2 then use vacuum tape to cover the parts without TiO_2/GQDs loaded on. The coated film is 1.5 cm x 0.5 cm in size. Drop 20 µl of TiO_2/GQDs solution on the prepared substrate, then it was placed on a ultrasonic vibrator to spread the membrane evenly. The sample was annealed at temperature of 80°C to evaporate the solvent. Finally, the sample was annealed at 450°C for 30 minutes.

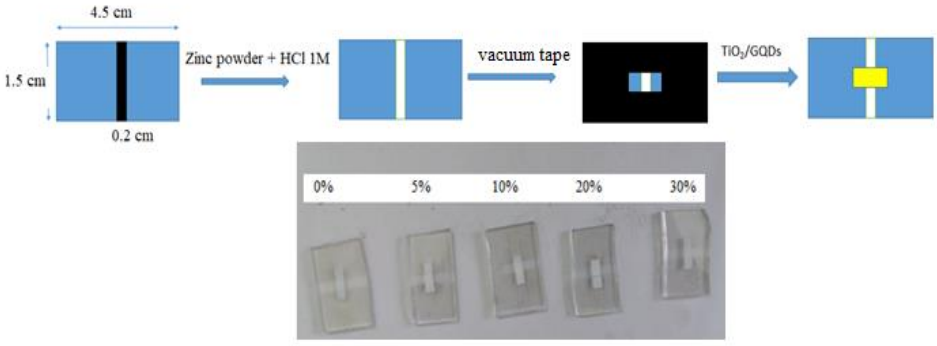

Fig. 2. Schematics of TiO_2/GQDs composite films synthesis by spreading method and the photogragh of TiO_2/GQDs composite films with volume concentration of GQDs at 0%, 5%, 10%, 20%, and 30%.

2.2. Results and discussion

Figure 3 shows the SEM image of TiO_2/GQDs samples spreaded on silicon substrate with different concentrations of GQDs, annealed at 450°C for 30 minutes. As shown in Figure 3, the fabricated TiO_2/GQDs films are quite porous with 18-25 nm TiO_2 particles. The images of the GQDs can not be observed because they are so small that the SEM method can not recognize them.

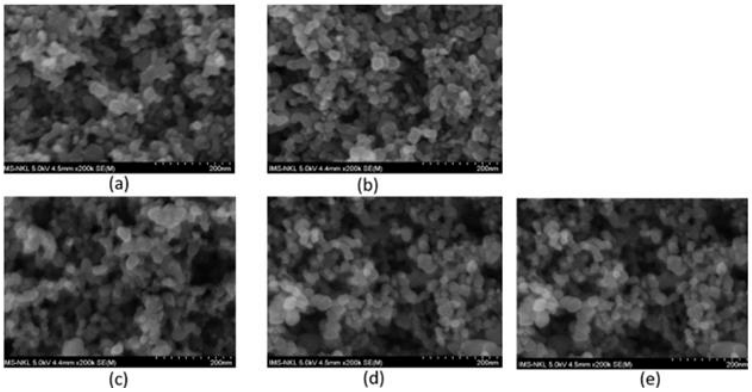

Fig.3. SEM images of TiO_2/GQDs with GQDs concentrations a) 0%, b) 5%, c) 10%, d) 20%, e) 30%

Figure 4 shows the XRD spectrum of the TiO_2/GQDs films after annealing. As can be seen on the Figure, the peaks on the XRD spectrum corresponded with anatase phase TiO_2 and no strange peaks appeared. This proves that after being annealed at 450°C for 30 minutes, TiO_2 films are completely become anatase phase. When adding GQDs to TiO_2 material, the diffraction peaks of TiO_2 remain unchanged and strange peaks did not appear, indicating that the addition of GQDs does not change the crystal structure of TiO_2.

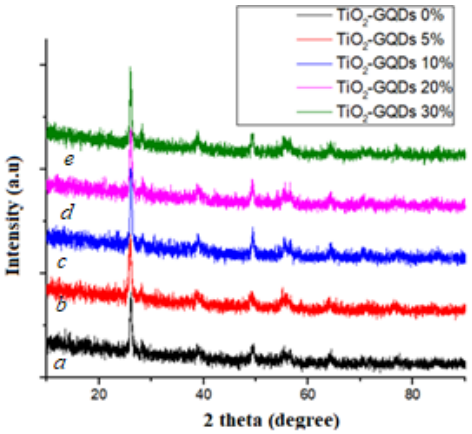

Fig.4. XRD diffraction patterns of TiO_2/GQDs with GQDs concentrations a) 0%, b) 5%, c) 10%, d) 20%, e) 30%

In addition, it can be seen that the thin film included only pure TiO_2, the TiO_2 particles are lacking in high porosity. After being mixed with GQDs (Figure 3 b, c, d, e), it seems that the presence of GQDs enhances the binding between TiO_2 and TiO_2 particles, so the film has an attachment cohesive and less porous.

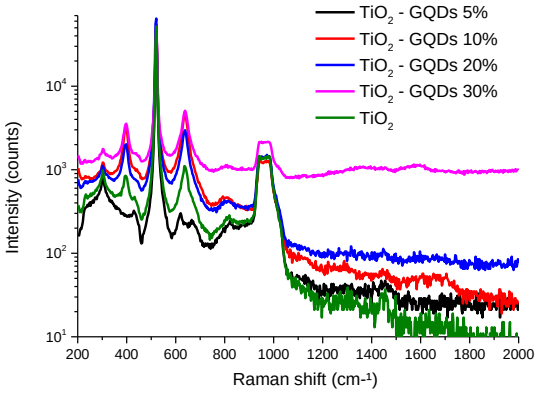

Fig. 5. Raman spectra of TiO_2/GQDs with different concentrations of GQDs

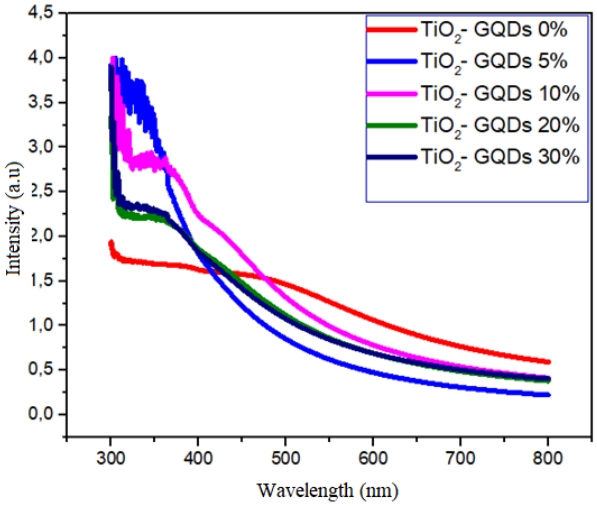

Fig. 6. Absorption spectra of TiO_2/GQDs with different concentrations of GQDs

Due to the reason that the existence of GQDs in the TiO_2/GQDs composite films were not observed by SEM images and X-ray diffraction patterns, Raman spectroscopy was conducted on the fabricated samples. The results are as shown in Figure 5.

From Figure 5, one can see that the TiO_2/GQDs composite films with different concentrations of GQDs all appear strong peaks corresponding to the number of waves at about 395 cm^{-1}, 521 cm^{-1}, 638 cm^{-1} which characterized the properties of anatase TiO_2 material. In addition, there are some peaks with much smaller intensity at the wave number position of about 1376 cm^{-1} and 1675 cm^{-1}, corresponding to the vibrational mode that responsible for the D and G bands of the quantum dot graphene material. With those results, the presence of GQDs in the TiO_2 films can be confirmed so TiO_2/GQDs nanocomposite films have been successfully fabricated.

The TiO_2/GQDs films on the glass substrate were heat treated for UV-VIS absorption spectroscopy. The results are shown in Figure 6. It can be seen that the pure TiO_2 film absorbs in the ultraviolet region, but the absorption tail extends to the region above 500 nm. This is

because the TiO_2 material has a high porosity, which causes light to be scattered strongly, so the transmittance of the film is reduced. With adding GQDs, the absorption intensity of TiO_2/GQD films at wavelength below 500 nm was significantly enhanced, especially in the ultraviolet range from 350 to 400 nm. TiO_2/GDQs samples with 5% and 10% GQDs concentration showed the strongest absorption. This is consistent with the fact that both TiO_2 and GQDs materials strongly absorb in the UV region. In addition, GQDs also partially absorb light in the 500 nm region. Above 500 nm of wavelength, the films containing GQDs have reduced absorption intensity compared to the TiO_2 sample. This is because the overlap of GQDs between TiO_2 nanoparticles increases the bonding ability between the materials. Therefore, the film is not too porous like pure TiO_2 film, thus reducing the scattering phenomenon in the film. This is consistent with the results of SEM image studied as presented in the previous section.

The optical properties of TiO_2/GQDs nanocomposites are also studied through fluorescence spectrometry. Figures 7a and 7b are the fluorescence spectra of TiO_2/GQDs film samples with different concentrations excited by lasers with wavelengths of 325 nm and 420 nm, respectively. In the case of excitation at 325 nm (Figure 7a), the emission peak is observed at about 400 nm with weak intensity in all samples. Those peaks are related to a direct transition (band - band). A strong spectral band at longer wavelengths from about 450 nm to 750 nm occurs both in pure TiO_2 and GQDs-doped films. The strong luminescence of TiO_2 films in the visible light is thought to be emission processes from surface states due to oxygen vacancies and defects on TiO_2. This result coincides with the results of Yu Chen *et al*. [9] and many other studies on TiO_2 nanomaterials. When adding GQDs to the TiO_2 film, the luminescence intensity of the samples corresponding to the band-band emissions and the emission due to the surface state increased significantly compared to the pure TiO_2 film and the spectral form was completely unchanged.

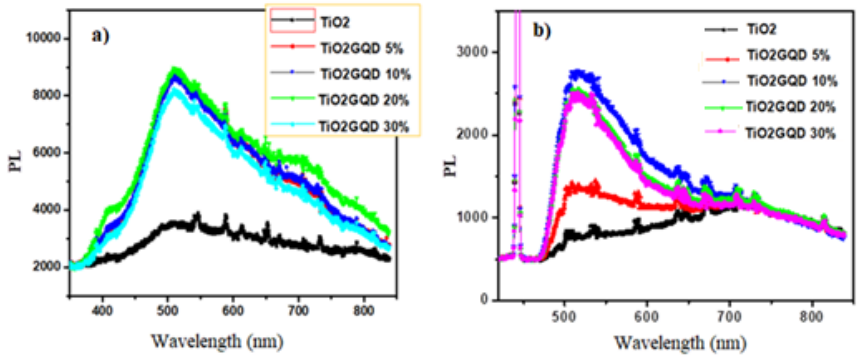

Fig.7. Photoluminenscence spectra of TiO_2/GQDs with different concentrations of GQDs: a) 325 nm and b) 420 nm excited wavelengths

This phenomenon can be explained as follows: The electrons of GQDs, after being excited to the conduction band, have shifted to the conduction band of TiO_2 due to the difference in energy levels of the two materials. The electron then recombines with the hole in the valence band of TiO_2 leading to emitting luminescence. From Figure 7, it can be seen that when the

GQDs concentration changes, the photoluminescence (PL) spectrum also changes but not much and the sample with 20% GDQs gives the highest intensity of PL spectral peaks.

With excitation wave at 420 nm which has a lower energy than the band gap of TiO_2 so there is a indirect transition band to band in the material system. Luminescence emitting due to surface states at wavelengths in the range 470 nm to 750 nm. When the concentration of GQDs increased, the intensity of the PL spectrum increased and reached the maximum in the sample with 10% GQDs, then began to decrease gradually. These results indicate that the nanopcomposite TiO_2/GQDs films have a charge transfer between GQD and TiO_2 and the transfer depends not too much on the content of GQDs particles.

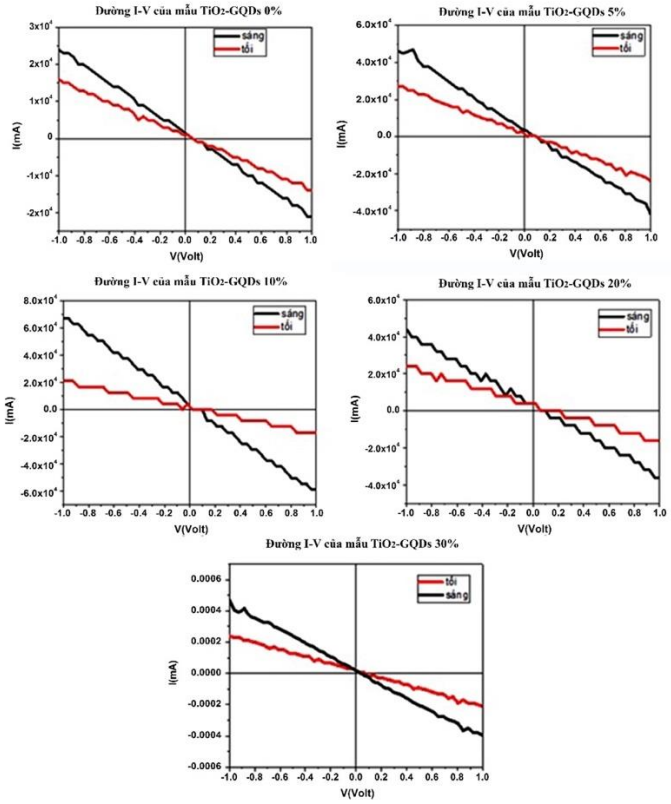

Fig. 8. I-V characteristic curve of TiO_2/GQDs in dark and under ullimination

To investigate the photoelectrical properties of the TiO_2/GQDs films, I-V measurement under illumination and in dark was conducted. The measured potential ranges linearly from -1V to 1V. The results are as shown in Figure 7 and Table 1. It can be seen that when illuminated, the photocurrent intensity of all TiO_2 films with GQDs increases and has a larger value than that of TiO_2 films without GQDs. This proves that the nanocomposite films exhibits better photoelectric properties than pure TiO_2 films. The highest current is 10% TiO_2/GQDs sample. This is completely consistent with the results of fluorescence spectroscopy studies of the materials. 10% samples with 10 % GQDs show better charge transfer and has maximum PL spectral intensity.

Table 1. Curent and resistance of the TiO_2/GQDs films at a potential of 1V

Sample	$I_{illuminated}$ (μA)	I_{dark} (μA)	$I_{illuminated/dark}$	$R_{illuminated}$ (MΩ)	R_{dark} (MΩ)	$R_{illuminated/dark}$
TiO_2/GQDs 0%	0.237	0.157	1.509	4.219	6.369	0.662
TiO_2/GQDs 5%	0.461	0.273	1.688	2.169	3.663	0.592
TiO_2/GQDs 10%	0.695	0.211	3.293	1.439	4.739	0.304
TiO_2/GDDs 20%	0.427	0.247	1.728	2.342	4.049	0.578
TiO_2/GQDs 30%	0.461	0.239	1.928	2.169	4.184	0.518

The resistance of the films without illumination is smaller than that of the TiO_2 films, indicating that GQDs reduce the resistance of the TiO_2 films and increase the photoelectric properties of the films. These results are shown in Table 1 in which one can see the 10% sample gives the largest change rate and reaches a value of 3.29 times. Moreover, the resistance of TiO_2/GQDs films is also significantly smaller than that of pure TiO_2 film. This result shows that TiO_2/GQDs can improve the performance of solar cells.

3. CONCLUSION

TiO_2/GQDs nanocomposite films have been successfully fabricated by spreading method with different GQDs concentrations from 0 to 30% by volume. TiO_2/GQDs films increase the light absorption capacity of materials in the ultraviolet region. The good charge transfer process between GQDs and TiO_2 contributes to increasing charge separation of the material system. The sample with 10% GQDs reaches a value of 3.29 times, the resistance of TiO_2/GQDs films is also significantly smaller than that of pure TiO_2 film. With properties such as strong light absorption (especially in the ultraviolet) and high electrical conductivity, GQDs can overcome the disadvantages of TiO_2 material. Nanocomposites TiO_2/GQDs layers can be used as electron collectors for nanostructured solar cells with high efficiency.

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CHẾ TẠO VÀ KHẢO SÁT CÁC TÍNH CHẤT ĐẶC TRƯNG CỦA MÀNG MỎNG NANOCOMPOZIT TiO_2/GQDs

***Tóm tắt**: Trong bài báo này chúng tôi nghiên cứu và chế tạo màng mỏng na nô compozit TiO_2/GQDs (Chấm lượng tử Graphene) ứng dụng làm lớp vật liệu thu điện tử trong pin mặt trời cấu trúc nano. Nồng độ khác nhau của GQDs được phủ bằng phương pháp trải trên màng mỏng na nô compozit TiO_2/GQDs. Đặc điểm cấu trúc và hình thái của các màng mỏng na nô compozit TiO_2/GQDs được khảo sát bằng phương pháp nhiễu xạ tia X, phổ Ramam và chụp ảnh SEM. Tính chất quang học được khảo sát bằng phương pháp đo phổ hấp thụ và phổ huỳnh quang. Tính chất quang điện của màng mỏng được nghiên cứu thông qua đo đặc trưng I-V trong bóng tối và khi được chiếu sáng bởi đèn mô phỏng ánh sáng Mặt trời AM 1.5G. Kết quả thu được cho thấy việc bổ sung GDQs đã cải thiện đáng kể các đặc tính quang điện tử của vật liệu.*

***Từ khóa**: Ôxít Titan (TiO_2), Chấm lượng tử Graphene (GQDs); Pin mặt trời cấu trúc nano.*