Hybridization and Characterization of Carboxylate-Rich Graphene Quantum Dots (GQDs)/TiO₂ Nanotubes for UV Detectors

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Abstract

Hybrid ultraviolet (UV) detectors were fabricated based on two-dimensional TiO_2 nanotubes coated with carboxylate-rich graphene quantum dots (CGQDs). TiO_2 nanotubes (TNTs) were synthesized by simple electrochemical process. CGQDs were synthesized by the liquid-phase extraction technique. CGQDs were characterized by TEM to image lattice arrangement and UV-vis to ensure their predominant properties. The structure and morphology of TNTs coated with CGQDs were characterized by SEM for surface morphology. To fabricate hybrid UV detectors, CGQDs were coated on TNTs surfaces by repeating the numbers of coatings. The two electronic probes were employed to measure electronic properties under the radiation of 365 nm UV light. The photocurrent density peaks are increased when the numbers of coatings are increased. The external quantum efficiency and spectral responsivity (R_s) were calculated from the illuminated time-dependent photocurrent density peaks. The spectral responsivity value (R_s) of CGQDs/TNTs which were coated with 15 times showed the highest of 95.50 mA W⁻¹ corresponding to the external quantum efficiency (EQE) of 0.32.

Keywords: Hybrid ultraviolet (UV) detectors; TiO_2 nanotubes; Carboxylate-rich; Graphene quantum dots

Introduction

Titanium dioxide (TiO_2) is a wide band gap semiconductor with an energy band gap of ~3.20 eV. In general, TiO_2 exhibits intrinsically an n-type semiconductor which plays an important role for many applications such as gas sensors, dye sensitized solar cells (DSSCs), photocatalysts, solar hydrogen production and so on [1 – 7]. According to wide band gap energy of TiO_2, Titanium dioxide can absorb light energy in specific range. Ultraviolet (UV) is a particular range of light with a wavelength of 10 – 400 nm therefore its energy is sufficient to excite electrons from a valence band to a conduction band resulting in useful optoelectronic applications, i.e., ultraviolet (UV) detectors [8]. Many researchers have focused to study on TiO_2 as UV detectors by using various processes. UV detectors based on TiO_2 nanowire arrays (TNAs)

were synthesized on transparent conductive indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) with different morphologies [9]. The device based on the vertically oriented TNAs on FTO showed more photoresponse properties than that of based on agglomerated TNAs on ITO. The hybridization of TNAs on SnO:F – coated glass with a spin-coated thin layer of poly (9,9-dihexylfluorene) was fabricated [10]. It allowed the dark current of 1.90 nA and a photoresponse peak of 568 mA W^{-1}. A photodetector based on TNAs was also invented by an inkjet printing method [11]. The printed photodetector exhibits highly transparent with a visible transmittance of 85% and a low dark current of 10 − 12 A with a high on/off ratio of 2000. Time-dependent photocurrent response measured under a bias voltage of 2 V showed a fast rise time of 0.40 s with a recovery time of 0.10 s. The fabricated UV detectors based on TiO$_2$ nanofibers [12] were synthesized by an electro-spun method and then transferred to pre-patterned electrodes revealed a predominant UV photoresponse of ~90 A W^{-1} and a response time ~5 s.

Recently, TNTs were studied as UV detector by the anodization method under a constant voltage of 50 V for 2 h and followed by Au nanoparticles uniformly deposited on TNTs by the anodization method in an aqueous solution of HAuCl$_4$·3H$_2$O (0.10 M in DI water) at voltage of 70 V. The UV detector device presented a high photocurrent and good responsivity [13]. However, the UV detectors based on wide band gap TiO$_2$ nanostructures still exhibit low sensitivity, and low photoresponse speed and large dark current due to their low charge separation and the fast recombination of electron-hole pairs [14]. Therefore, it is necessary to find extraordinary techniques to effectively improve the charge separation and slow down the recombination of photogenerated carriers. According to basic working principles, metal-semiconductor-metal (MSM) UV detectors based on wide band gap semiconductors [15] show a high and fast responsivity, are little affected by bias voltage, and have simple manufacturing processes, low cost and easy monolithic integration. Unfortunately, many previous studies have rarely investigated on metal-semiconductor-metal (MSM) and the metallization for the electrodes shadows the active light collecting region resulting in low gain and low spectral response. The interesting way to improve performance of UV detectors based on TiO$_2$ semiconductor is integration with other low-dimensional materials such as quantum dots, nanowires, nanotubes, and nanosheets.

Graphene is a material of choice in improving photocatalytic activity of TNTs due to a two dimension of hexagonal structured sp^2-hybridized carbon atoms network [16]. However, graphene has some limitations because it has no band gap. Unlike dimensionless GQDs, they are low-dimensional semiconductors with a band gap engineered by altering the size and edge chemistry [17 − 18]. As a result, GQDs are capable of extending the application of graphene from electronic to photoelectronic and photoelectrochemical devices. According to their useful properties, GQDs are desirable for efficient light harvesting. Moreover, their electronic levels and interfacing with other materials for charge transfer processes can could be useful for charge collection in solar cells [19 − 22]. In this work, GQDs in the type of carboxylate-rich (CGQDs) were employed that it is recently synthesized by the easy method from Graphene oxide (GO) dispersion by selective extraction processes [23]. As a consequence, it is possible to reduce cost and enhance photoresponsivity of UV detector successfully.

This paper is mainly focused on improving the photoresponsibility of photodetector based on low-dimensional hybridization of CGQDs on TNTs. TNTs were synthesized by an anodization method. Subsequently, TNTs were coated by GQDs in various the numbers of coatings. The

surface morphologies and the photocurrent abilities were successfully investigated. Here, the physical mechanism of enhancing photocurrent density can be interpreted by energy band diagram.

Materials and Methods

Synthesis of TNTs

Ti foils were used as substrates to form TNTs in the anodization process. 1.50×2.50 cm^2 pieces of Ti foils were cleaned in acetone, ethanol and deionized water, respective, for 15 min by sonicate in ultrasonic bath. The N_2 gas was used to dry a Ti piece. The apparatus for the anodization process was set up with two electrodes: Ti foil as anode and graphite sheet as cathode. A chemical bridge solution between two electrodes was mixed by 0.30 wt% NH_4F, 12% deionized water in ethylene glycol solvent. An applied voltage of 50 V at room temperature was employed as a condition for 6 h to form the ordered layer oxide TNTs. TNTs were cleaned again in ultrasonic bath to remove residue on their surfaces. Finally, to rearrange the amorphous to crystalline structure, as-anodized TNTs were annealed at 450 ºC for 2 h with applied temperature constant step at 3.75 °C min^{-1}

CGQDs Coated on TNTs

CGQDs prepared by selective liquid-phase technique [23] and supported by Korea Research Institute Chemical Technology (KRICT) were used in this work. To fabricate CGQDs films on TNTs, CGQDs on TNTs layer-by-layer were prepared by a spin-coating method. A concentrated CGQDs solution in ethanol (~10 mg mL^{-1}) was dropped on TNTs surface. CGQD films were homogeneously covered on TNTs at spin speeds of 1000 rpm for 20 s and 2000 rpm for 5 s. After that, CGQDs coated on TNTs were annealed at 100 ºC for 10 min to remove contaminations this temperature sufficient to remove water, organic and inorganic excess substance from CGQDs/ TNTs surface [24]. Process of this spin-coating CGQDs was repeated 5 times (CGQDs/TNTs 5 times), 10 times (CGQDs/TNTs 10 times) and 15 times (CGQDs/TNTs 15 times) to obtain various film thicknesses.

Fabrication of Metal-Semiconductor-Metal Photodetector Devices Based on CGQDs/TNTs

The key to fabricate of metal-semiconductor-metal photodetector type is to form Schottky contact between a metal and semiconductor. Thermal evaporator was utilized to deposit uniformly Cr/Au layer on TNTs and CGQDs/TNTs. In this study, Au layer was employed as metal electrode with the thickness of 90 nm. Cr was used as an adhesion layer between TNTs surface and Au. From these processes, Schottky contact was taken place at the site of the Au electrode-TNTs interfaces to create sensitive photodetectivity.

Results and Discussion

The top views and cross section SEM images of TNTs after annealed with 450 ºC are shown in Fig. 1 (a) − (b). They reveal that the highly ordered tubular structure is obtained with a diameter of 125 nm, wall thickness of 20 nm and tube length of about 2 mm. TEM images of CGQDs separated from GO dispersion by selective extraction processes are shown in Fig. 1 (c) − (d).

The high-resolution TEM image in Fig. 1 (d) presents those CGQDs with lattice spacing of 0.23 ± 0.02 nm corresponding to the hexagonal pattern of graphene with the (1100) lattice fringes with an arranged in a hexagonal honeycomb carbon network [25 – 26]. These TEM results reveal that CGQDs used in this work is in graphene shape with diameter of 0.23 ± 0.02 nm. However, the difference of diameter size between CGQDs and SEM is unable to observe CGQDs on TNTs surfaces due to the limitation of our SEM and TEM.
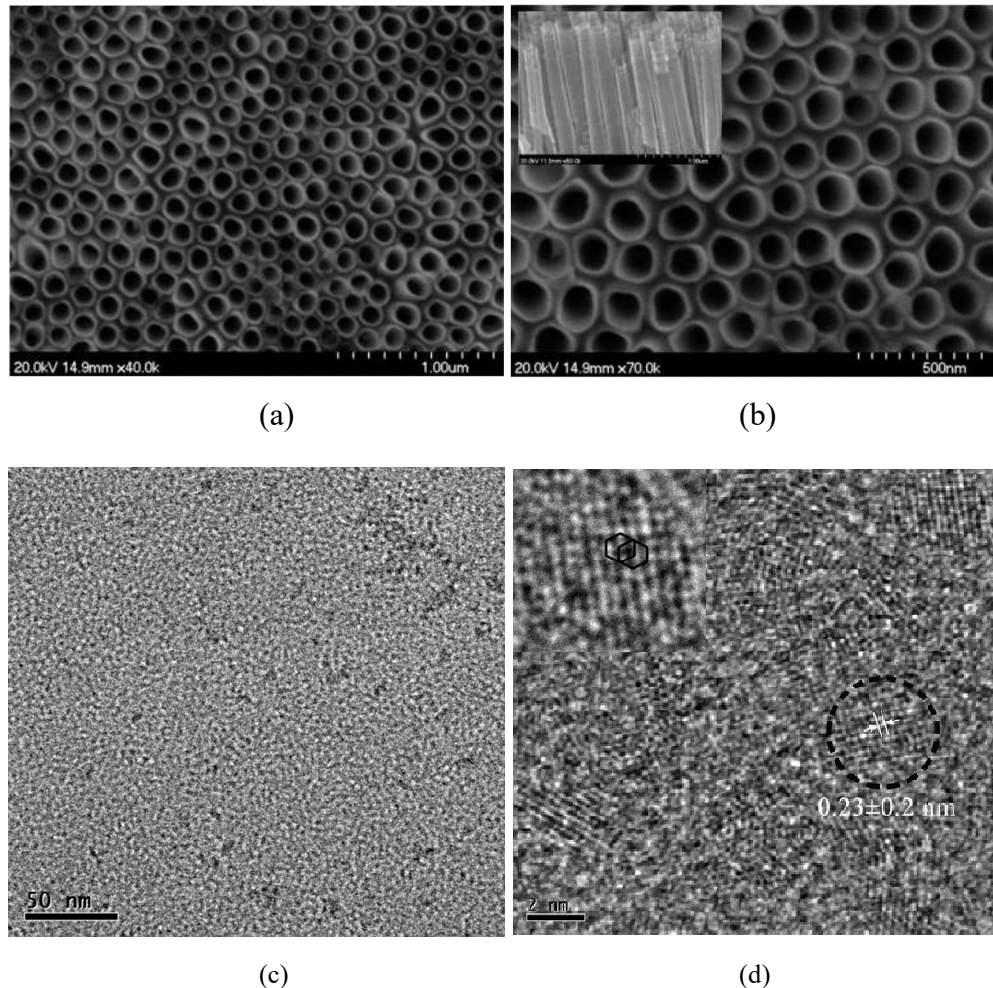

(a)   (b)

(c)   (d)

Fig. 1 Top-view FE-SEM images of bare-TNTs under magnifications of (a) 40 k, (b) 70 k (inset image shows the cross section), (c) TEM images of CGQDs and (d) High-resolution TEM showing the lattice spacing distance.

I-V curve measurements from applied voltage -5 – 5 V of bare-TNTs compared with CGQDs/TNTs devices are shown in Fig. 2 (a) and (b). The two electronic probes method under ambient air condition and room temperature was employed to obtain I-V data. At an applied voltage from -5 – 5 V, the dark current density changed from -8.05 – 13.12 $\mu A\ cm^{-2}$ while the photocurrent density changed from -15.46 – 26.28 $\mu A\ cm^{-2}$ for bare-TNTs under the radiation of 365 nm UV light. At an applied voltage from -5 – 5 V, the dark current density changed from -652.04 – 6507 $\mu A\ cm^{-2}$ while the photocurrent changed from -1000.40 – 7960 $\mu A\ cm^{-2}$ for CGQD/TNTs 15 times under the radiation of 365 nm UV light. It is found that at an applied voltage 5 V, the dark current density changed from 13.12 (bare-TNTs) – 6507 $\mu A\ cm^{-2}$

(CGQD/TNTs 15 times) and under the radiation of 365 nm UV light, the photocurrent density changed from 26.28 (bare-TNTs) – 7960 µA cm^{-2} (CGQD/TNTs 15 times).

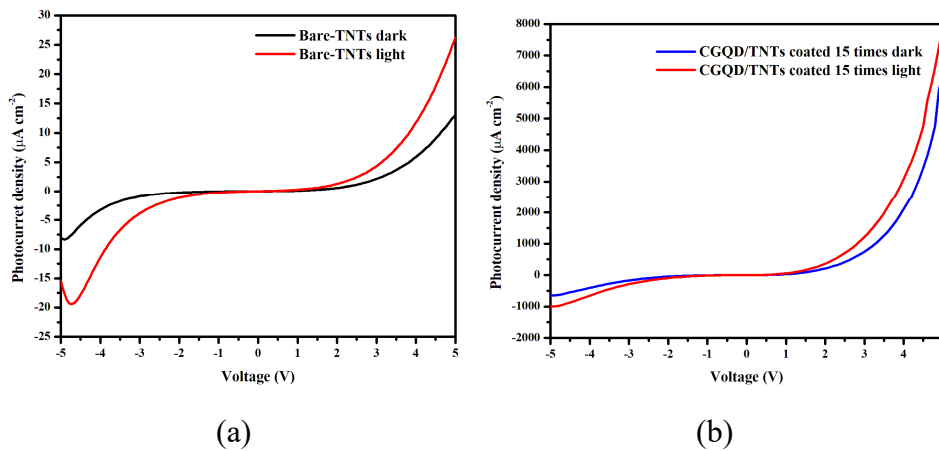(a)   (b)

Fig. 2 Photocurrent versus voltage curves of (a) bare-TNTs and (b) CGQDs/TNTs 15 times.

These changes may be resulted from the increased density of surface states of TNTs surface by CGQD coatings. As we known, CGQDs normally exhibit high surface and carrier charge transfer properties. Therefore, CGQDs/TNTs photodetector has more surfaces to interact with UV light than bare-TNTs also resulting in higher carrier charge transfer. The enhancement of photocurrent and faster responsible with UV light when CGQDs coated on TNTs surfaces can be explained by the mechanism of the simplified Au electrode to CGQD/TNTs interface energy diagram in Fig. 3. First, the Schottky contacts were formed by Au electrode deposited on TNTs surface. The carrier charge transport methods can be explained as follows. When light hits the detector, the desired signal is generated by the transport of photogenerated electrons from the CGQDs/TNTs to the Au electrode over the potential barrier by the quantum-tunneling properties of electrons. The dark current is contributed by the hole injection from the Au electrode to the CGQDs/TNT. This mechanism can be confirmed that CGQDs/TNTs device produces more photogenerated electrons than bare-TNTs device.
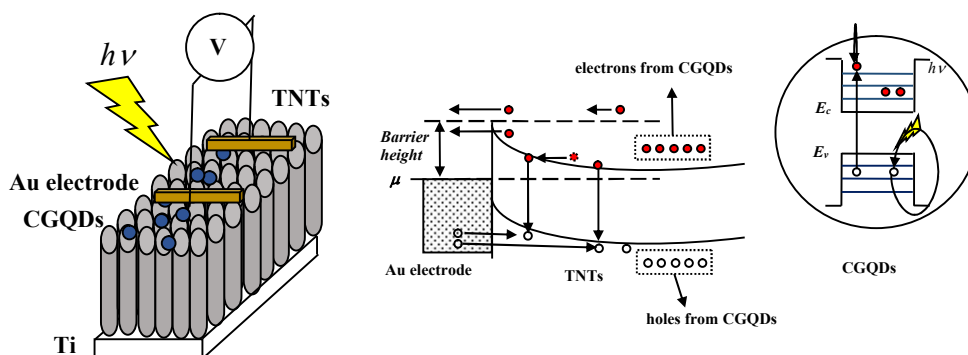

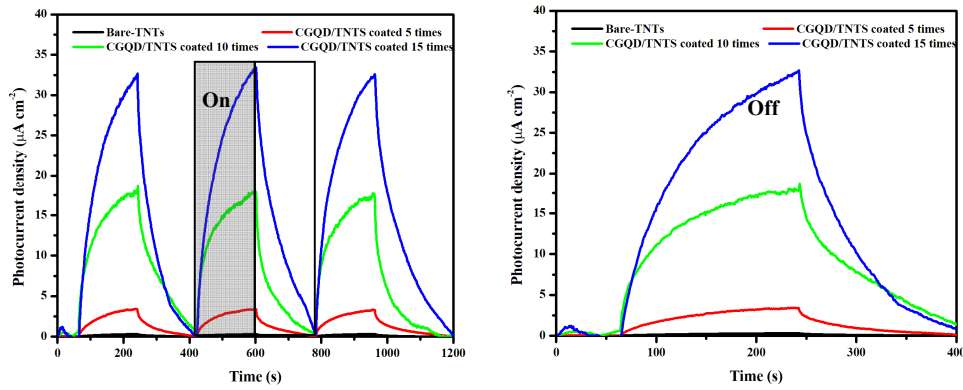**Fig. 3** The energy diagram carrier transport mechanisms of Au electrode and CGQDs/TNTS interface.

Fig. 4 Time-dependent photocurrent responsible spectra of CGQDs/TiO$_2$ devices.

The irradiation light source (VL-4 LC 4 W) with power density of 350 µW cm^{-2} at wavelength of 365 nm was used. The performance of photosensitive device was determined by two parameters: spectral responsivity (R_s) and external quantum efficiency (EQE) that can be expressed by [27]:

$$R_s = \frac{I_{ph}}{P_0 \cdot S},$$ (1)

where I_{ph} is the difference between illuminated current and dark current $I_{ph} = I_{illuminated} - I_{dark}$, P_0 is the light power density irradiated on devices, and S is the area of devices. $I_{illuminated}$ and I_{dark} are from values of the electronic probe measurements. The area of Au electrode was taken into account as S.

$$EQE = \frac{R_s \cdot hc}{e\lambda},$$ (2)

where h represents the Planck's constant, c stands for the velocity of light, e is the electronic charge and λ is the wavelength of the irradiation light.

Table 1 The illuminated photocurrent density, spectral responsivity (R_s) and external quantum efficiency (EQE) of all devices.

Materials	$I_{illuminated}$ (µA cm^{-2})	R_s (A W^{-1})	EQE
Bare-TNTs	3.29×10^{-1}	9.40×10^{-4}	3.20×10^{-3}
CGQDs/TNTs 5 times	3.43	9.82×10^{-3}	3.34×10^{-2}
CGQDs/TNTs 10 times	18.76	5.36×10^{-2}	1.82×10^{-1}
CGQDs/TNTs 15 times	33.43	9.55×10^{-2}	3.25×10^{-1}

The illuminated photocurrent density, spectral responsivity (R_s) and external quantum efficiency (EQE) values of all devices are shown in table 1. It is found that the time-dependent photocurrent can be increased by increasing CGQDs coatings. The highest spectral responsivity (R_s) value of CGQDs/TNTs 15 times is 95.50 mA W^{-1}. This corresponds to EQE of 0.32.

Conclusion

CGQDs coated on TNTs were developed to fabricate UV detectors. It is shown that the amount of CGQDs increases when the numbers of coating increases. The two electronic probes were used

to measure the photocurrent density of all devices. Under applied voltage from -5 − 5 V, the dark current density increases greatly when CGQDs were used when compared with bare-TNTs. Under irradiation of 365 nm UV light, photocurrent density is changed from 25 μA cm^{-2} for bare-TNTs to 7960 μA cm^{-2} for CGQDs/TNTs 15 times. The highest spectral responsivity (R_s) value of CGQDs/TNTs 15 times is 95.50 mA W^{-1} corresponding to EQE of 0.32. These show that photodetectors based on CGQD/TNTs can be used to develop as sensitive UV detectors.

Acknowledgement

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