PREPERATION OF QD-RGO HYBRID NANOMATERIALS; SIMPLE AND EFFECTIVE ROUTE TO AVOID INTENSE CHARGE CARRIER RECOMBINATION TO BOOST OPTO-ELECTRICAL PROPERTIES

S.P. RAJU[A*], K. HAREESH[B], H.V. CHETHAN[A], GANESH SANJEEV[C] AND S.D. DHOLE[D]

[A]*Department of Physics, Malnad College of Engineering, Hassan*
[B] *Department of Physics, Manipal Institute of Technology Bengaluru, Manipal Academy of Higher Education, Manipal 576104, India*
[C] *Microtron Centre, department of Physics, Mangalore University*
[D] *Department of Physics, Savithribai Phule Pune University*

**Corresponding author email id: puttaspraju@gmail.com*

Abstract **- The present scientific work reports on the preparation of nano-hybrid materials to transport electrons across a device to combat intense charge carrier recombination for opto-electronic applications. The present work would give simple and efficient ways to prepare such nanohybrid advanced materials. CdTe quantum dots (QD) were successfully decorated over reduced Graphene oxide (rGO) nano-sheets using in-situ one-pot hydrothermal method. As prepared nano-hybrid materials were characterised to confirm the formation of QD-rGO structures and analysis their properties to confirm the process of intense electron transferring from such 0D to 2D materials. XRD, TEM, UVS, and PLS spectroscopic techniques were used to confirm the formation of the above QD-rGO nano-hybrid material. Complete quenching of PL emission for QD-rGO hybrid system confirms the successful transmission of electrons to the highly conducting rGO nano-sheets.**

Keywords: QD-rGO hybrids, 2-D material, PL quenching, carrier transfer.

I. INTRODUCTION

Carbon based nanomaterials have gained enormous scientific interest since couple of decades due to their versatility exhibited in laboratory, medical diagnosis and manufacturing sectors [1][2][3]. These carbon-based nanomaterials are promising with variety of supreme properties like higher electrical and thermal conductivities, higher tensile strength, specific heat capacity, specific light absorption, and emission capacity, hydrophobicity, quantum confinement possibilities, surface to volume ratio, etc[4][5][6][7]. Due to its gifted chemical properties, it can acquire many different shapes which is another important advantage of building advanced technologies around it. Moreover, Carbon is the 15th most abundant material available on the earth. Such important nanomaterials, with such possibilities, are Graphene, Graphene oxide, carbon nanotube, carbon nano cones, fullerenes, carbon quantum dots, Graphene nano ribbons, carbon nano horns, carbon anions, carbon nano diamonds, etc. These individual nanomaterials exhibit prominent properties which is impossible by any known bulk materials. These are also superior among all other nanomaterials categories. Therefore, such carbon-based nanomaterials have found applications in important fields like optoelectronic devices, sensors, biomedical applications, technical textiles[8][9][10] etc,. These materials are the hopes for the future dream technological projects like space elevators, lightweight batteries for electrical aeronautical or space vehicles, versatile catalysts, etc. Therefore, investigations on such nanocarbon materials have been sprouted in different directions. one such important field of interest with respect to carbon nanomaterials is optoelectronic devices.

Among all the above corban-based nanomaterials, Graphene oxide (GO) is a cheap, biofriendly and easy to produce in bulk using modern hummer's method. After its reduction process these GO exhibit Superior conductivity properties which can be comparable with Graphene materials produced in other expensive methods. Charge transportation is highly promising in such reduced graphene oxide (rGO) materials.

Quantum dots (QDs) are quantum materials [11] which have been proven exhalent due to their superior optical characteristics like light absorption and band gap tunability properties. Because of these reasons it has been used in solar cells and light emitting device applications [12]. However, intense charge carrier recombination is a stumbling block in these QDs during its function in a QDs based solar cell in order to further improvise its efficiency.

QD sensitized solar cells (QSSC) utilize number of benefits from QDs to boost its light conversion efficiency such as higher extinction co-efficient, larger natural length of Bohr exciton, multi charge carrier generation, etc. These QDs are comparatively better materials to traditionally used dyes in DSSC as they are more resistant to photobleaching. However, QDSSC consisting of QDs alone would suffer from intense charge carrier recombination. Because charge carriers must hop from one QD to other QD to reach their respective electrodes in such solar cell. Moreover, such charge carrier recombination is further increased when organic capping molecules are placed around each QDs. These organic molecules also participate in charge carrier trapping and reduce their hopping fluency in the QDs layer. All these reasons lead to the reduction of overall efficiency of QDSSCs. However, the above problem can be effectively fixed by introducing some conducting sheets inside QDs layer as shown in Figure 1. In this situation, photo excited QDs would give away their electron directly to such conducting sheets without going for the hopping. Then, charge carriers would travel in those conducting sheets making their journey ease to reach their respective electrodes. This would ultimately reduce recombination of photo-generated charge carriers in QDSSC [13] [14]. Graphene is highly suitable material in this context to be used as such conducting sheets. However, the production of pure and monolayer Graphene sheets is not so easy (expensive as well) to produce in larger amount with higher purity.

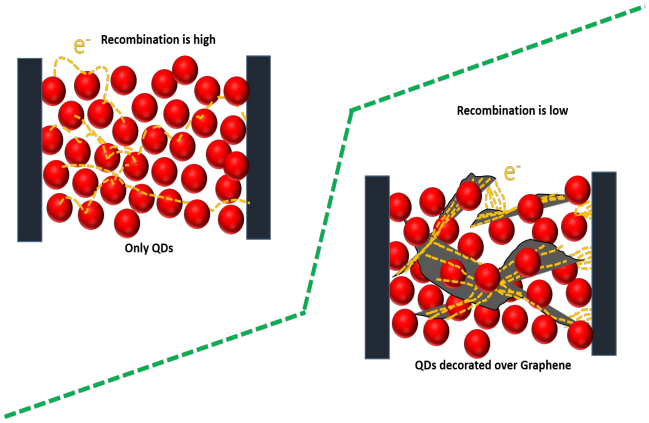

Figure 1. QDs in QDSSC with and without introducing Graphene Oxide sheets.

Moreover, higher purity could be achieved only through bottom approaches like CVD [15-16]. On the other hand, graphene oxide (GO) can be easily synthesized in larger amount using top down exfoliation approach from bulk graphite material. On the other hand, synthesis of GO is not complicated or expensive when compared with production of pure Graphene sheets using CVD methods. Especially, GO synthesis in bulk production also can be achieved in this way. Reduction of GO sheets further enhance their properties which is almost resembling to pure graphene sheets prepared by expensive bottom-up approaches. In account of all the above, this present chapter deals with the preparation of QD-rGO hybrid materials. GO were synthesized using modern Hummer's method. They were reduced to rGO sheets. Finally, as reduced GO were decorated with QDs using hydrothermal method to prepare hybrid QD-rGO materials.

In order to get the synergetic effects, it is possible to prepare nanohybrid materials with itself or other nanomaterials. This in turn makes such hybrid nanomaterials as more functionally possible for the above applications. One such superlative combination is graphene oxide with quantum dots. These two materials are phenomenal materials to themselves. Quantum dots are special kind of nanomaterials which are made from semiconducting nano single crystals whose exciton bohr radius is lesser than the physical dimension of the nanomaterials itself. Because of the charge particles de-Broglie wavelength is comparable to the physical size of the nanomaterial QDs are made to exhibit quantum confinement effect. Therefore, these QDs can produce electron hole pairs in larger number. If these QDs are embedded on rGO sheets, due to its sp3 hybridisation of rGO, it can contribute to intense electron transportation process. This in turn enhances the optoelectronic device efficiency. However, there are very less awareness and literature available on these hybrid nano materials.

Moreover, studies which should demonstrate on efficient embedding of QDs on rGO 2D materials have to be carried more in number with economically viable methods. Therefore, this study presents a simple and efficient method to produce QD-rGO hybrid nanomaterials using simple one pot synthesis hydrothermal method.

II. EXPERIMENTAL DETAILS

A. Materials: chemicals of analytical grade were purchased from suitable companies. FLUKA and ALDRICH chemicals such as Cadmium chloride (99%) and Sodium tellurite (99% pure) respectively were purchased. Sodium borohydrate, 3-Mercaptopropionic acid (MPA), Tri-Sodium citrate dehydrate were purchased from MERCK chemicals. All experiments were carried out in this study using double distilled water.

A. Synthesis of QDs

One pot hydrothermal synthesis method was utilised for the aqueous growth of MPA stabilised CdTe QDs. Core QDs were Synthesised with fixed molar ratio of Cd:Te:MPA::1:0.25:8. Tri-Sodium citrate dehydrates (100mg) and Sodium Borohydrate (50mg) was dissolved in 40ml of double distilled water with Cd, Te and MPA precursor. So-prepared reaction mixture was poured into autoclave of Teflon housing with stainless steel. This setup was kept in hot air oven with fixed temperature 180ºC. The reaction was carried out for 11 minutes for the growth of QDs with desired size for bio-applications.

B. Synthesis of GO

Modern hummer's method [17] (with minor modification) was used to synthesis GO samples. The Figure 1 clearly shows the synthesis of GO samples. Initially, 0.5 mg Graphite powder and 0.5 mg sodium nitrate were mixed with sulphuric acid of 23 ml in a conical flask placed in an ice bath. The reaction mixture was continuously stirred. Potassium permanganate of 3 g was dissolved bit by bit to avoid explosion of the reaction mixture which is below 20°C. Later the temperature was raised to 35°C by replacing ice bath to water bath. After getting a dark colored paste the whole reaction mixture was diluted to increase the overall volume using 100 ml of water (@ 90°C, stirring).

C. Preparation of hybrid QD-rGO

Using hydrothermal method QDs were grown over GO sheets. As prepared rGO were suspended in growth medium of QDs. The procedure to grow the QDs have been already published in somewhere by the same authors (Journal of Luminescence 192 (2017) 17–24)

D. Preparation of QD-rGO hybrid materials

1. Preparation of GO samples

Modern hummer's method [17] (with minor modification) was used to synthesis GO samples. The Figure 2 clearly shows the synthesis of GO samples. Initially, 0.5 mg Graphite powder and 0.5 mg sodium nitrate were mixed with sulphuric acid of 23 ml in a conical flask placed in an ice bath. The reaction mixture was continuously stirred. Potassium permanganate of 3 g was dissolved bit by bit to avoid explosion of the reaction mixture which is below 20°C. Later the temperature was raised to 35°C by replacing ice bath to water bath. After getting a dark colored paste the whole reaction mixture was diluted to increase the overall volume using 100 ml of water (@ 90°C, stirring).

After an hour of stirring the reaction mixture was further diluted with 500 ml of water. Sodium hydroxide (30% v/v) of 3 ml was poured into the reaction mixture at last. Then, the color of the solution in the flask was slowly turned to dark brown to yellow. This is an indication of successful exfoliation of GO sheets from bulk graphite powder by top down approach. As prepared GO sheets in water were washed with hot water to remove any remaining unreacted acid contents.

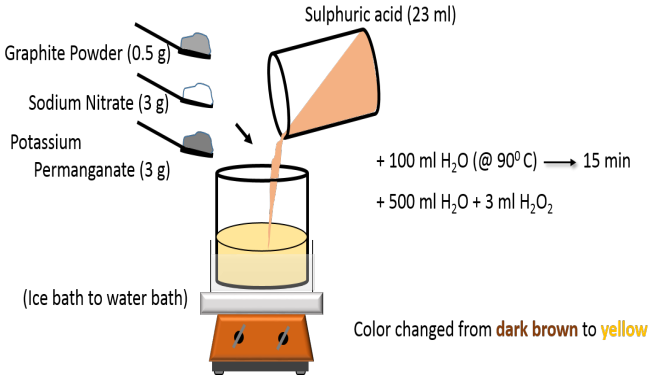

Figure 2. Scheme of preparation of GO materials

2. Preparation of QD-rGO samples

Introducing above prepared GO in the growth media (water) of QDs is the first step in preparing QD-rGO hybrid material. Initially, borohydride (50 mg) was dissolved in water with the presence of GO samples for the process of reduction of GO samples. Then, samples were washed and introduced in the growth media of QDs. These rGO samples of 20 ml (1 mg/ml) were used instead of using just double distilled water in the growth of QDs. Rest of the procedure is as same for synthesis of QDs.

III. RESULTS AND DISCUSSION

Different structures of QDs have been well established in the area of opto-electronic research as explained in all the above chapters. QDs are very special materials since they absorb and emit light within the sensitivity domain of human eyes. Such light of all possible wavelength can be achieved by tuning their physical size of a very short domain. Therefore, QDs are used in bio-tagging and bio-imaging applications. Especially, the tuning can be done on the size domain of QDs for the wavelength of light (highest intensity) reaching earth surface from the sun due to which QDs are used in solar cell applications.

A. Structural properties of QD-rGO hybrids

The images appeared for QD-rGO samples showing the presence of some solid chunks of sizes around 3 nm to 4 nm confirms that some nanoparticles were grown over graphene sheets. The EDX spectrum shown in the inset of the same Figure 3 confirms the presence of Cadmium and Tellurium elements in the QD-rGO samples. This clearly proves that such solid chunks are CdTe QDs. All the above concludes that CdTe QDs were successfully decorated over rGO sheets. Structural properties of QD-rGO hybrids are analyzed using XRD studies. The Figure 4 is showing the XRD pattern for GO, QD and QD-rGO samples. The single and sharp peak for GO samples has been strongly lowered for QD-rGO sampwhich is a clear indication that GO sheets were reduced [18]. Moreover, at the same time QDs were decorated over them. The XRD pattern for pure QDs shown in the inset of Figure 4 was clearly appeared. However, the suppression of these peaks for QD-rGO hybrid is mainly due to the dominancy of signal from reduced Graphene sheets at 10° [19].

B. Optical properties of QD-rGO hybrids

Figure 5 shows the light absorption properties of as prepared hybrid materials. The curve of pure CdTe QDs has a shoulder peak appeared at around 530 nm along the X-axis. Besides, GO sheets have their peak position at 230 nm (π to π* transition of C=C bonding). The curve in the blue color corresponding to QD-rGO hybrid samples is having its geometry different from those curves for QD and GO samples. This is due to the firm interaction of QDs and GO sheets to become hybrid systems by altering the physical parameters of the materials responsible for optical exciton creation. However, variation in size distribution of QDs grown in the hydrothermal autoclave with slightly varied size distribution (related to FWHM) cannot be ruled out. Such variation of size distribution of QDs is due to local environment effect as QDs

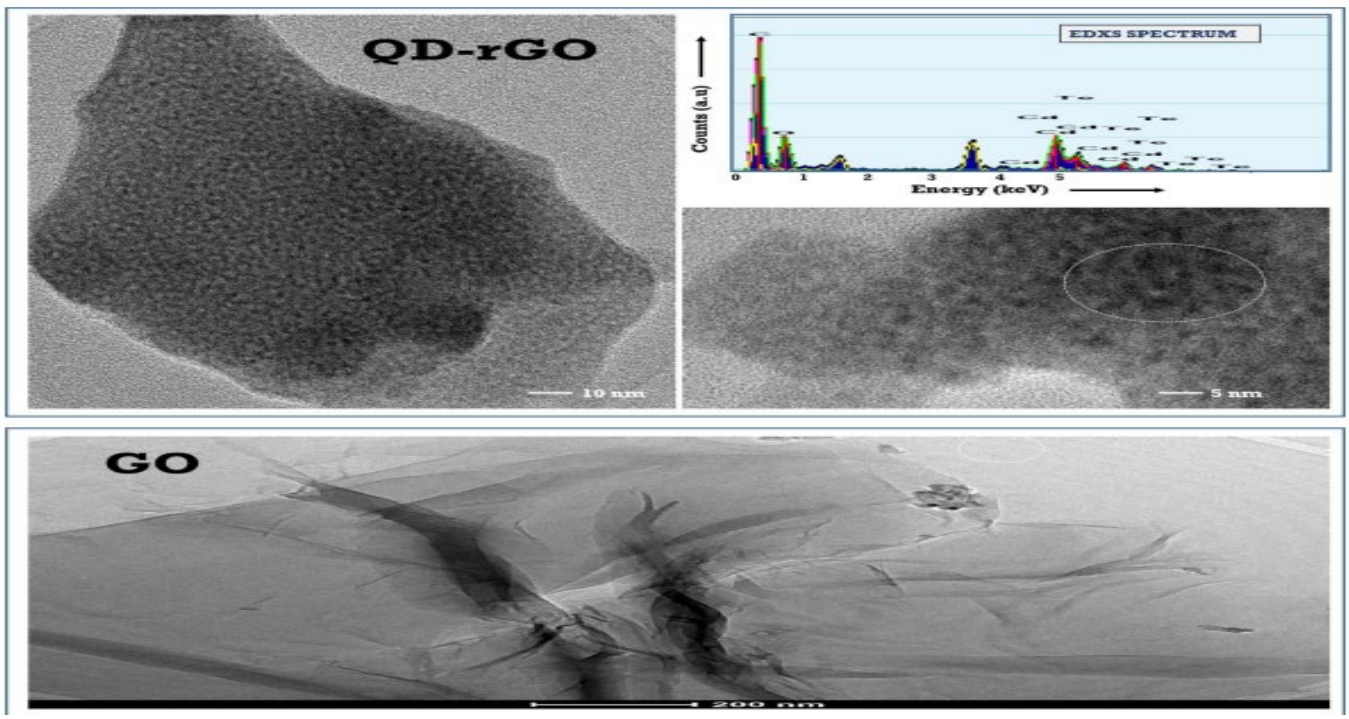

Figure 3. TEM images of rGO and QD-rGO (EDX spectra in the inset) hybrid nanoparticles

were directly grown over GO sheets. This depends also on the

sheets' geometry and local GO surface chemical situations. Moreover, interaction of QDs with GO sheets slightly increases the absorption of light from such hybrid systems comparing to QDs as can be seen in the Figure 5 Because, inhere, hybrid complex sheets also begin to take small participation in the same absorption process.

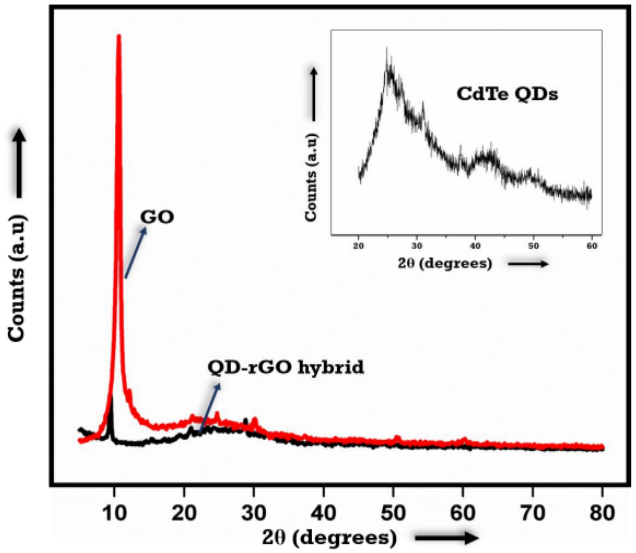

Figure 4. XRD spectra of GO, QD- rGO and QD (in the inset) samples.

Ultimately, optically excited electrons have to be transferred to such conducting nanosheets is the vital motive of the present investigation to enhance the opto-electronic properties of the prepared hybrid materials.

Such electron transferring can be clearly confirmed by analyzing their PL emission studies and their resulting curves. Figure 6 shows the light emission (Fluorescence) properties of QD-rGO hybrid systems. The PL emission curve for CdTe QDs was remarkably diminished after the growth of QDs over rGO nano-sheets. This is due to the electron transferring of QDs to GO sheets. Absorbed light from a material enables a number of processes in it depending on their fundamental properties and physico-chemical situations.

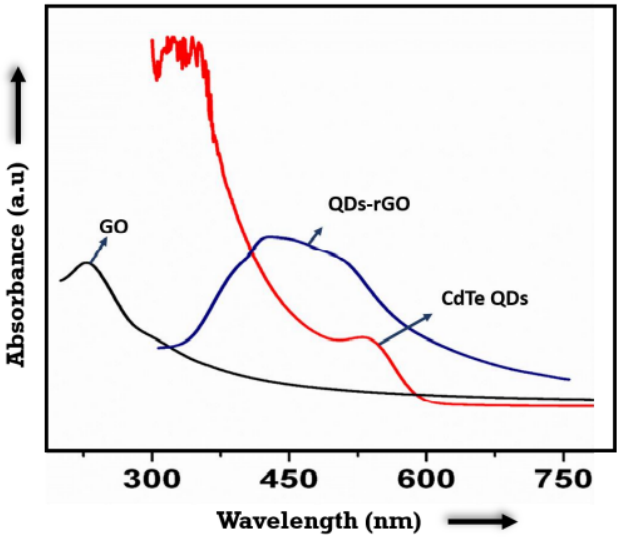

Figure 5. UVS spectra of QDs, GO and QD-r GO samples.

Luminescence phenomena are related to absorption and emission of light energy by a material system even though emitted light may not be of the same energy comparing to its absorbed light. This belongs to the process which follows radiative decay mechanisms. However, luminescence is not only the way the material behaves after absorption of light. In luminescence, electron has to come back to the ground state to emit absorbed light from the same material.

If sufficiently higher energy is provided, electrons may also lose the columbic interaction with atomic nucleus (or loose bonding with other atom, if it is a molecule) and may not return to its ground state. In the same way, some situation is created where optically excited electrons from a material are collected from other material when they are in different chemical potentials. This follows nonradioactive decay mechanism where no light is emitted out from the material system.

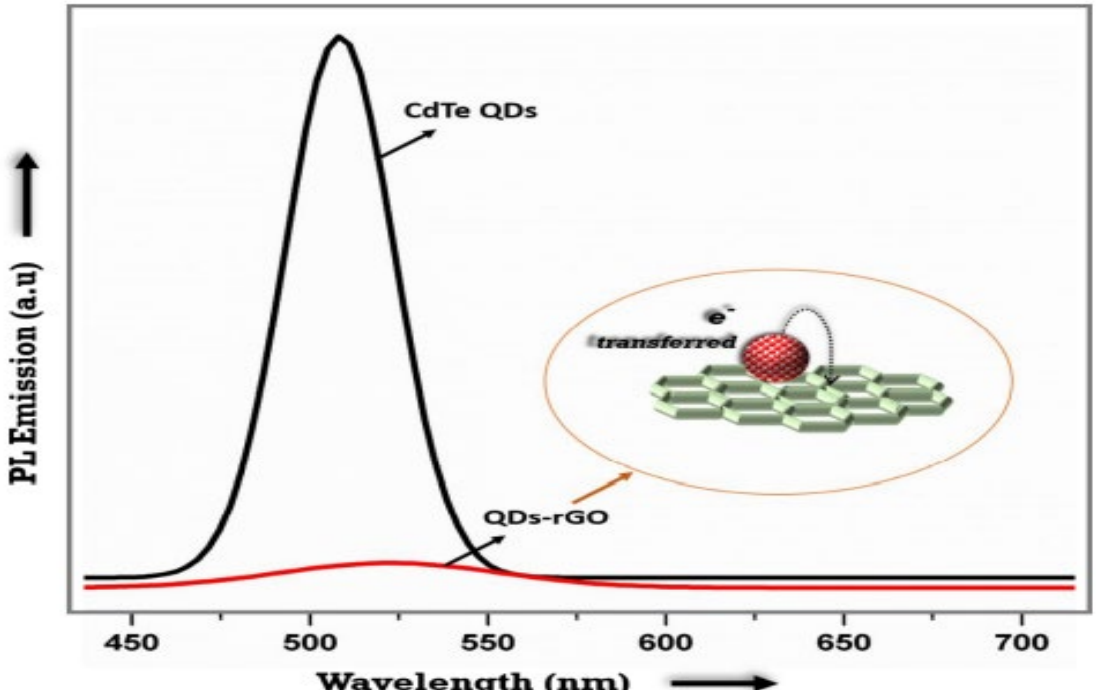

Figure 6. TEM images of rGO and QD-rGO (EDX spectra in the inset) hybrid nanoparticles

Graphene is a zero-band gap material which can easily collect excited electrons from other materials when are in firm contact. Therefore, when QDs are decorated over GO sheets, optically excited electrons from the QDs can easily be transferred to GO sheets. When such hot excited electrons are transferred to GO sheets without reaching their ground energy states, eventually the emission of light from QDs is obviously quenched. This is how the PL emission properties proves that the excited electrons are transferred to GO conducting sheets. This would effectively increase efficiency of solar cells when QD-rGO hybrids are used in it. Instead of hopping from one QD to another QD, electrons are transferred to highly conducting nano-sheets [20]. This would avoid intense charge carrier recombination in such light to electrical energy converter as it was explained above in the introduction section of the present chapter.

IV. CONCLUSION:

Graphene Oxide 2D materials were synthesized by using modern Hummer's method. The GO samples were successfully reduced and then QDs were decorated over rGO sheets to prepare QD-rGO hybrid materials using hydrothermal method.

V. ACKNOWLEDGEMENT

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