Synthesis of GQD-MOF Composite for Optoelectronics Applications

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***Abstract*—**Metal Organic Framework are relatively new class of advanced materials built from metal ions with well-defined coordination geometry and organic ligands. Various properties of MOFs such as luminescence, Porosity, conductance, tunable, portability can be used for photovoltaic applications fluorescence/ electrochemical signal-based bio and chemo detections. MOF's have very low conductivity to increase their conductivity they are generally doped with metal nanoparticles or quantum dots. In the proposed work aim is to assemble graphene quantum dot (GQD) - Metal organic framework (MOF) composite. Its characterization was carried out by using I-V probe station, FTIR, UV/Vis, PL studies. And it showed significant increase in conductivity of the system. GQD-MOF composite is used for the photovoltaic applications.

Keywords*—*GQD; MOF; Photovoltaic

I. INTRODUCTION

Graphene - Graphene is a allotrope of carbon with 2-dimensional properties [1]. Graphene-is define as one atom thick layer of graphite. In Graphene charge carriers can travel thousands interatomic distances without scattering, the carbon-carbon bond length in Graphene is approximately 1.42 Å .Single layer Graphene prepared by CVD starts to show defects at ~500 °C. Graphene has high thermal stability and possibility of ballistic conductance , the electronic mobility of Graphene is very high and due to the strength of its 0.142 nm-long carbon bonds, Graphene is the strongest material ever discovered, with an ultimate tensile strength of 130,000,000,000 Pascal's (or 130 gigapascals), compared to 400,000,000 for A36 structural steel, or 375,700,000 for Aramid (Kevlar) Graphene is the strongest and thinnest material made up of single layer of carbon atoms, has the property of flexibility and transparency. Heat and electricity makes graphene a good conductor. The graphene has been used for designing high speed electronic devices in the era where technology changes very rapidly. These sensors also help in finding explosives. To separate gases, nanoscale membranes with pores in it have been used. The display devices like mobile screen, OLED has replaced the conventional screens. The batteries used in mobile phone lithium-ion charges at faster rate and they use graphene on anode surface. [2-4]

Quantum dot is known for material so small that it is limited to a particular point (zero-dimensional), which leads to electrons and holes trapped inside the material with well-defined energy levels in accordance with quantum theory. Quantum dots are crystals of few nanometers range, generally containing few dozen atoms. They're synthesized via semiconductor materials. They are also called as artificial atoms because they behave like individual atom but they're crystals. QDs exhibit unique optical properties due to material band gap energy and quantum well phenomena. Because of their small size the dots behave as quantum wells. [5]

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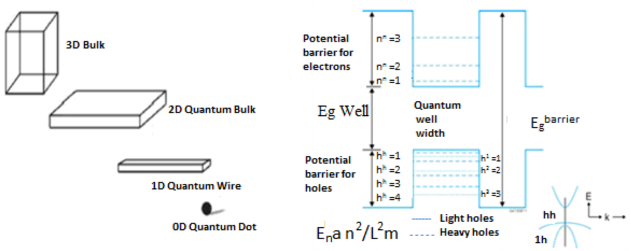

Figure 1.1 Quantum Confinement and quantum well created due to small-bandgap

Researchers observed quantum dots in mice lymph nodes for 4 months QDs may be deployed for in seeing tumor mass. This ability to mapone-cell is important to several research areas. Quantum dots in nanobio acts as donator fluorophores in FRET, here huge extinction coefficient stands them up to other fluorophores. Also the broader absorbance of Quantum Dots helps in particular excitation of donor and a least excitation of a dye acceptor in FRET-based studies.

Graphene quantum dots (GQDs) are defined, as a type of zero-dimensional material with distinctiveness derived from both carbon dots (CDs) and Graphene, considered as unbelievably a small piece of graphene. The 2D graphene sheets can be converted into zero dimensional GQDs, this GQDs show a new phenomenon due to edge effects and quantum confinement, which are like CDs. GQDs provides better-quality in comparison with organic dyes and semiconducting quantum dots (QDs), [6] GQDs provides excellent properties, like high photo stability against photo bleaching and blinking, low toxicity and biocompatibility. Unlike their cousins, CDs, GQDs clearly acquire a graphene structure inside the dots, in spite of the dot size, which endow them with some of the extraordinary properties of graphene. For these reasons, GQDs have engrossed major attention from researchers.

Crystalline metal-organic frameworks (MOFs) are produced by reticular synthesis, by creating strong bonds between organic and inorganic units. Cautious choice of MOF constituents can yield crystals of high thermal and chemical stability and ultra-high porosity. These characteristics let the interior of MOFs to change chemically which is used in gas storage, gas separation, and catalysis, with other applications. The precision usually uses in their chemical alteration and the capability to enlarge their metrics without changing the fundamental topology which cannot be attain with other solids. MOFs having shape of building units and chemical composition can be varied inside a particular structure that already exist and may direct to materials that propose a synergistic combination of properties. [7] Metal−organic frameworks, or MOFs, have appear as a wide class of crystalline materials with ultrahigh porosity and massive internal surface areas, enlarge beyond 6 000 m2 /g. The above-mentioned properties, together with astonishing degree of variability for both the components that is organic and inorganic and their structures make MOFs used for potential applications in clean energy, mainly considered as storage media for gases like hydrogen and methane, and due to high-capacity adsorbents to meet a variety of separation needs. Additional applications in thin film devices, membranes and biomedical imaging are quickly attaining importance. Since 1990s, highest growth was experienced in this field of chemistry, as confirmation is not only by the large number of research papers published but also by the expanded scope of research. Also, the number of monographs and review articles increase in the last five years, the matic issue of Chemical Reviews, contain the most updated contributions from leading MOF researchers throughout the world, is essential to mark the growth made thus far in a complete manner. The scope of the volume varies from topology analysis and molecular simulations to synthesis, and from gas storage, separations, and catalysis to applications in biomedicine from adsorptive and optical to ferroelectric properties. Also, they belief that this will provide a helpful resource for new and current researchers in this field. [8] One of the trademark of MOFs is their topologically diverse and aesthetically pleasing structures, several of which are resulting from minerals in nature. Developing a target structure with definite properties and functions signify an eternal aspiration for materials scientists. [9] To reverse-engineer the beautiful formation from nature, the first step is to understand the primary geometric principle

II. MATERIALS AND METHODS

A. Preparation of Graphene Oxide:

Hummers method are used for the preparation of graphene oxide. As already published work by author in previous article [10]. Then Graphite (1.0g) was mixed with H2SO4 (60mL, 98%) in slow addition of 5.8 g KMnO4 with continuous stirring for 0.5 h in an ice bath. The prepared solution was heated for 2 h at 30°C, thereafter slow addition of 40mL deionized water is mixed. Again, the reaction was heated for 30 min at 90°C, and then deionizer water (80mL) was added. In the next step H2O2 (10mL, 30%) was added to the reaction as the temperature decreased to 60°C providing an orange yellow solution. Two hundred milliliters of 5% HCl solution was added, the supernatant was decanted and centrifuged with deionizer water to pH 4 to 6, and the mixture solution was further dialyzed in a dialysis bag for 2 days. In the end low density graphene oxide was obtained by lyophilizing at −48°C, 21 Pa, and GO was obtained as gray-yellow powder.

B. Preparation of Graphene Quantum Dots:

Graphene quantum dot is prepared by using graphene oxide [10]. In the first step Graphene Oxide is suspended in concentrated sulfuric acid (H2SO4) for 6 hrs. and then treated them with 60wt. % KMnO4. The H2SO4 conditions aid in exfoliating the graphite oxide and the subsequent graphene structures. Further, the reaction mixture was stirred at room temperature for 1 h and then heated at 55-70°C for additional 1h. When all of the KMnO4 had been consumed by pouring over ice containing a small amount of H2O2 in the reaction mixture, the solution was filtered over polytetrafluoroethylene (0.22 μm) membrane, and we obtain Blue GQDs.

C. Synthesis of Iron Based MOF

Synthesis of amine functionalized MOF was pursued in following steps, firstly mix 0.08968g of Fecl3 (ferric chloride) and 0.09875 g of H2N- BDC linker in 15ml of DMF. Sonicator was used here for dissolving the metal precursor. Then the solution was poured into tightly sealed capped vial. Heat the solution for 24 hours at 1450c and let the solution cool to room temperature. Filtration and collection of residue is pursued in this step. After that, residue is washed with 15 ml of methanol and stores it for further use.

D. Surface Modification of GQD:

Nanocomposite of GQD and MOF is made by direct heating of MOF at 145^0c and after reaching the required temperature blue GQDs are slowly added. Then the reaction mixture was further kept at 145^0 c and then cooled for 15 min. After which the Incubation is done for 1 hour at room temperature. It results in the formation of composite of GQD and MOF, which results in surface modification of GQDs.

III. RESULTS AND DISCUSSION

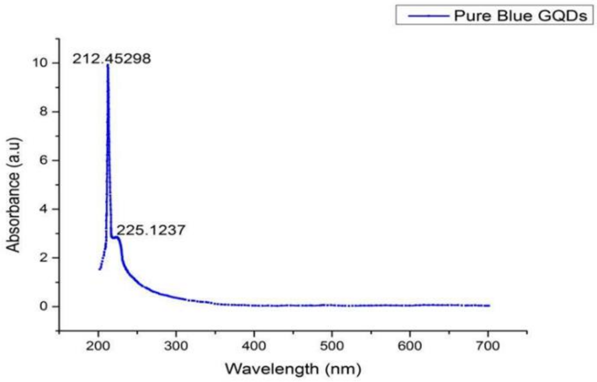

Fig 1.2 The above figure shows the absorbance curve of blue Graphene quantum dots excited at 212nm to 225nm.

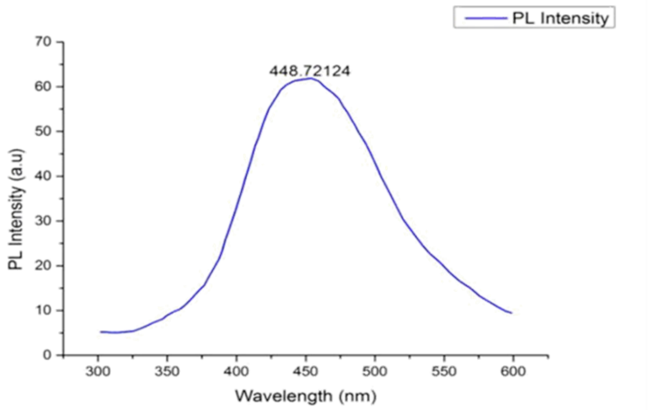

Fig 1.3 GQDs exhibit unique optoelectronics properties owing to the quantum confinement effect, the PL spectra of Graphene Quantum dots is shown in figure with emission peak of 448nm and excited at 212.45 nm wavelength

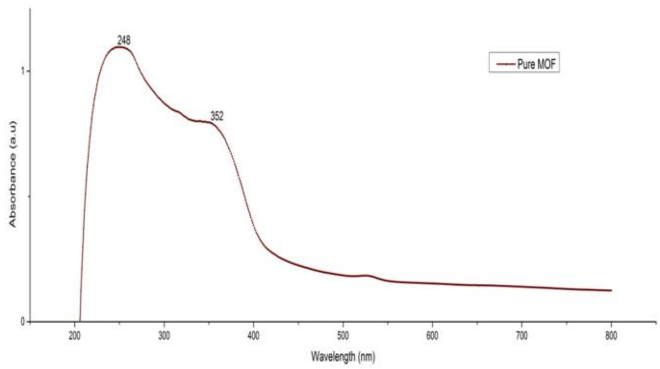

Fig 1.4 UV graph shows the absorbance curve of Iron based MOF defining the excitation range 248nm- 352nm.

The Figure above shows the photoluminescence spectra of MOF with emission peak of 435nm and excited wavelength is 248nm power in DMF. Broad absorption and emission spectra of MOF suggests that the transition responsible for the photoluminescence takes place between deeply trapped charges (localized donor and acceptor levels).

The latest research has been going on the use of grapheme quantum dots and metal organic frameworks to be used in photovoltaic technologies. The current density of GQD-MOF nano-composite has been simulated to verify the change in current density with the bias voltage across the sample.

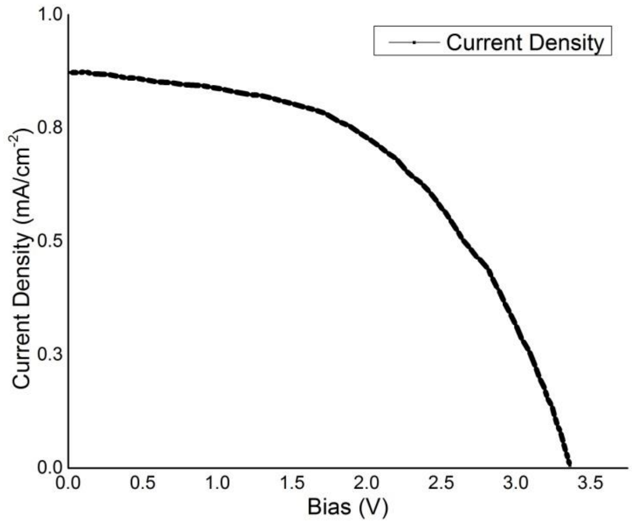

Fig 1.5: Current density of GQD-MOF nanocomposite

As shown in the figure, the resistance of the GQD-MOF nano-composite decreases with the increase in bias voltage as the grapheme quantum dots facilitates the flow of more charge with the increase electric field across the nanocomposite sample due to the bias generated.

III. CONCLUSION

The iron-based metal organic framework provides a base for the quantum dots to absorb wide range of spectrum from which the photons are used to generate electron-hole pair (excitons) which is transmitted through the MOF layer (low conductivity) making a significant change in the efficiency.

Higher recombination rate and low conductivity of the metal organic framework reduces the efficiency but it can be compensated with the use of materials with higher conductivity to provide a path for the diffusion and drifting of charge carriers such as grapheme nano-rods/nanotubes, etc. The use of Metal organic framework helps in providing the sufficient elasticity and flexibility with the capability to withstand higher current densities.

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