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Investigations of the optical and electrical properties of carbon quantum dots doped conducting polymers for organic solar cell applications

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Polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh) have much more attention in energy applications owing to their optical and electrical properties. To overcome the problems associated with these polymers, the Up-Conversion Carbon Quantum Dot (UC-CQD) based materials are employed. That has more desirable features, like hydrophilicity, low toxicity, and high water solubility. The UC-CQD in the electrochemical field is creating great attention to photoluminescent behaviors and low specific capacitance. When UC-CQD is combined with the conducting polymers, the optical properties are enhanced with the help of energy transfer processes. By the advantage of electropolymerization technique, the solubility problems are tackled, because the monomer has coated on the substrate. Herein, the preparation and characterization of the UC-CQD doped, PPy, and PTh films have been reported and their optical and electrical properties are investigated. The band gap of PPy and PPy-CQD is analysed from Tauc plot and calculated to be 2.54 and 1.69 eV respectively. The 50% and 60% mass loss were observed in thermogravimetric analysis for PPy and PPy-CQD respectively. These materials can be used for organic solar cell applications in near future.

Keywords: Conducting polymers, Electropolymerization, Organic solar cell, Upconversion

Conducting polymers based on polyaniline (PANI)[1], polypyrrole (PPy)[2], and polythiophene (PTh)[3] is currently receiving increased interest. The energy storage and conversion applications and their exceptional electrical and optical qualities are good. These particular polymers make organic solar cells (OSCs), also known as polymer solar cells, which serve as light-harvesting components for converting solar energy into electrical energy (OSCs). Functionalized polymers, such as carboxylate substituted PTh[4], are extensively used as light-harvesting materials[5]. However, to their low band gap and less electron recombination, the functionalized polymers have some drawbacks, high cost, poor solubility, and difficulty with synthetic procedures[6-8]. The usual polymers PANI, PPy, and PTh overcome the above-said problems. But they are unsuitable for making them OSCs light harvesting process because which having a large band gap and correspond solely to the visible region. The earth gets 52–55% (low energy) infrared light (IR) region[9]. These polymers cannot absorb this range due to band gap mismatch. Therefore, a photosensitizer or light converter is required to improve the light-harvesting properties of these materials. The conversion from low energy to high energy (upconversion) or high energy to low (down conversion) is called a light conversion. Upconversion (UC) material is capable of improving the light-harvesting properties of polymers because it converts infrared rays (low energy) to visible light (high) and the suitable for exciting the polymer. To minimize the mismatch band-gap issue; Here in the inorganic (lanthanide-based materials)[10,11], organic (perylene, naphtha-p-quinodimethane)[12], and carbon quantum dot (CQD) which have UC properties that have already been reported in various light harvesting application[13]. Among them, CQD is an inexpensive, highly soluble, and less toxic material[14]. So, which is used in sensor[15], bio-imaging[16], and catalyst applications[17-19],one research article reported that UC-CQD made from ascorbic acid and doped with TiO_2 is the best photocatalyst for dye degradation[20]. These results suggest that the CQD is an efficient material for the conversion of IR to visible light. Therefore, we plan to prepare the CQD doped polymer films for OSCs applications.

Chemical and electrochemical polymerization[21,22] are the processes used to prepare polymers from monomers. Electropolymerization[23] is the best way to produce polymer films for OSCs application, as the polymer grows directly on a fluorine tin oxide (FTO) plate. This method alleviates the problem of polymer solubility. In addition, polymer growth on FTO is that controlled by optimized scanning parameters. We have previously prepared and reported photoactive UC-CQD doped PANI films[24]. The electropolymerization method to study their optical and electrical properties. In this paper, we prepare CQD doped PPy and PTh photoactive films and investigate the optical and electrical properties of the OSCs applications.

Experimental Section

Preparation of carbon quantum dot

Carbon Quantum Dot (CQD)preparation followed the steps in the previous literature from ascorbic acid[20].

Preparation for PPy-CQD film

The PPy-CQDs film is prepared by a constant potential electrochemical method using three electrodes, FTO - working electrode (WE), silver/silver chloride - reference electrode (RE), and graphite - counter electrode (CE). 0.05 M PPy, 0.4249g of $NaNO_3$ and 1mL CQD in an aqueous solution acts as an electrolyte for electropolymerization. The window setting is 0 to +1.2 V, and the scan rate is 50 mV/s with 10 scans. We followed the same steps to prepare PPy film without adding CQD.

Preparation for PTh-CQD film

The same electrochemical setup has been used to prepare the PTh-film but 0.2 mL of distilled thiophene0.1 g of BT_4NF_6, and 1mL CQD in acetonitrile solution is used as an electrode, and the window setup is -1 to +1.8 V and the scan rate is 50 mV/s with 10 scans. We followed the same steps to prepare PTh film without adding CQD.

Results and Discussion

Electropolymerization of PPy and PThfilms

Fig. 1a shows the electropolymerization of PPy on the FTO plate. In the first step, radial cations formed in the oxidized state where electrons here are lost. The two primary radicals then combine to form a positively charged dimer. The next pyrrole molecule follows the same process (oxidation, coupling, and randomization)[25]. This process, if repeated and pyrrole converted to polypyrrole called chain propagation. Since the electron spin density is high at the *o*-position, a chain reaction occurs at the ortho-position. Layered PPy is confirming through in Fig. 1a graph. Electropolymerization of PTh has the principle mechanism of the conversion of thiophene to PTh have shown in Fig. 1b.

CV and impedance study of PPy

In Fig. 2 (a & b), the electrical properties of the PPy films[26] were investigated using 0.5M H_2SO_4 in an aqueous electrolyte solution. PPy current range is 3.5mA. When the PPy is doping with CQD, the current range improves to 5.8mA. This result confirms that the CQD improves the electrical properties of PPy, and the current density is also enhanced. This result concludes that PPy-CQD has better electrical conductivity than PPy. It has confirmed the impedance study. The resistance range of the PPy-CQD is lower than PPy.

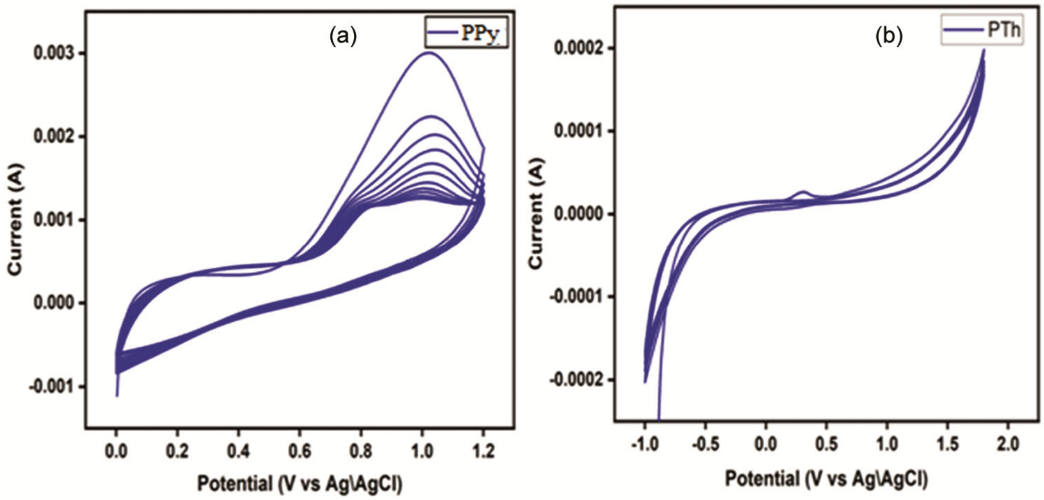

Fig. 1 ─Electropolymerization of PPy and PTh films.

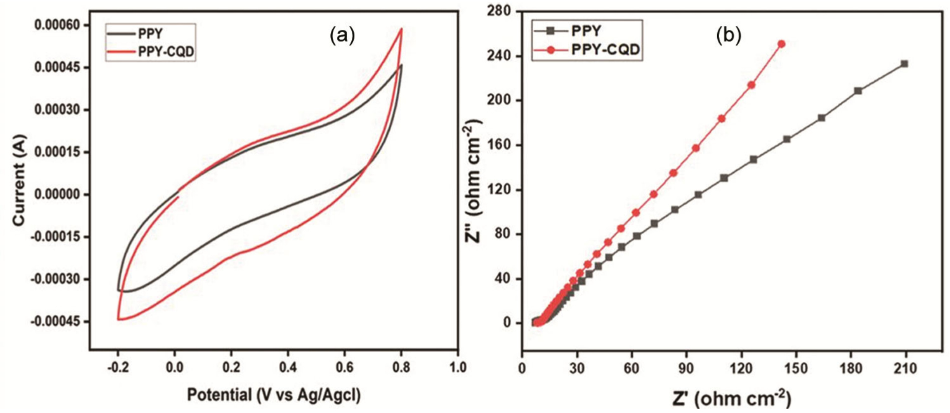

Fig. 2 — Current (a) and impedance (b) study of polypyrrole films.

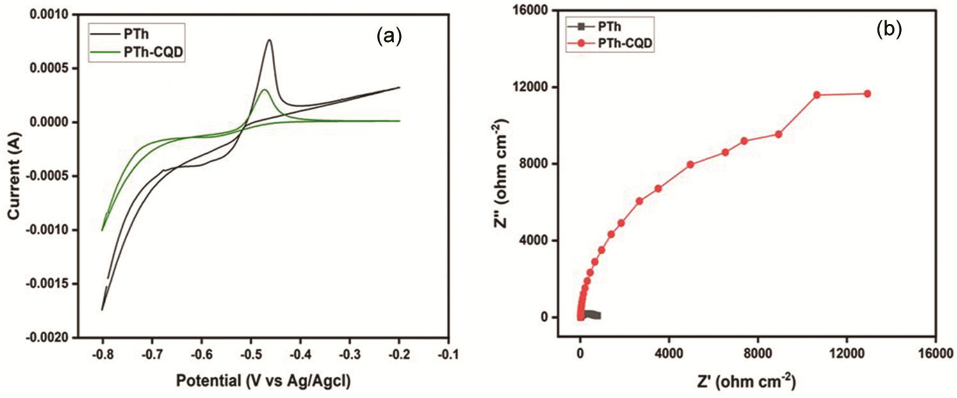

Fig. 3 —(a) Current and (b) impedance study of PTh films.

CV and Impedance study of PTh

The current study of PTh and PTh-CQD investigated with the help of 0.1M $LiClO_4$-acetronitrile electrolyte. The PTh has a higher current range which is 9mA (Fig. 3a). When the polymer is doping with CQD the current is reduced. The reason is that the coated pyrrole and CQD are homogeneous mixtures (water medium). So, that polymerization growth is improved, and the current range increased. But, the thiophene and CQD are heterogeneous media (water-acetronitrile). The polymer growth was minimized in the CQD added to the thiophene electrolyte. Therefore, the current range decreased. The resistance range of PTh was also low, as shown in Fig. 3b. Moreover, the resistance is also very high in CQD doped thiophene. The results show that the CQD-doped PTh is not used, for electrical applications. Here, only focus on PPy doped CQD films involves further studies for OSCs application.

UV and FT-IR study of PPy films

Figure 4a shows the absorption spectra of PPy films recorded by UV-Vis spectroscopy. PPI has an absorption peak presented at 408 nm[27]. It is assigned to the π-π* transition of the C=N bond PPy binds to CQD, the absorption peaks slightly the position changes due to the interaction polymer chain with the CQD carbonyl group. PPy-CQD was observed at ~414 nm, which is a redshift from the PPy absorption peak. This result confirms that the CQD improves the optical properties of the PPy chain. Figure 4b exhibits the FT-IR spectra of PPy films. PPy N-H stretching frequency presented at 3434 cm^{-1} while PPy-CQD peak is 3230 cm^{-1}. This result also suggests the binding of the CQD carbonyl to the polymer chain. C-H stretching, C=C, C-N, and C-H bending peaks of PPy appeared at 2924,1743,1461, and 904 cm^{-1}. The peaks slightly shifted their position in PPy-CQD shifting confirms the binding interaction of polymer and CQD[27,28] (Table 1).

Band gap study of PPy films

The band gap is calculated by the following formula:

$$\alpha (h\upsilon) = A^* (h\upsilon - Eg)^{n/2}$$

where, α - absorption coefficient, h - Planck's constant, υ - light frequency, A - constant's value,

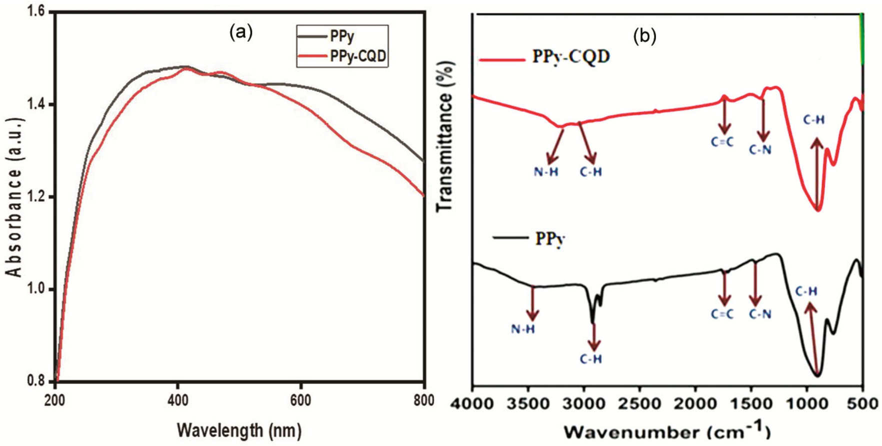

Fig.4 —(a) Absorption and (b) FT-IR study of PPy films.

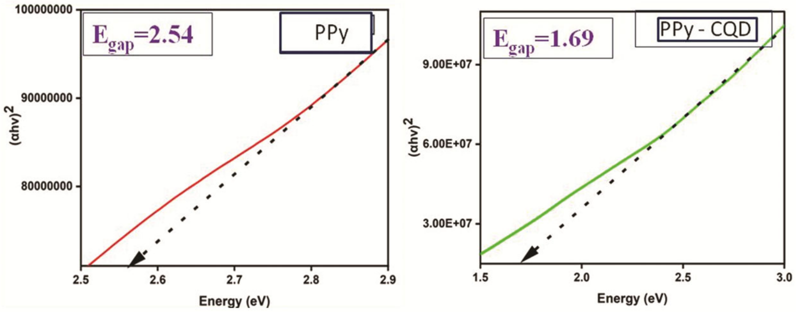

Fig. 5 — Bandgap study of (a) PPy and (b) PPy-CQD

Table 1—FT-IR spectra interpretation of PPy filmsassignment PPyPPy- CQD.

N-H (quinoid ring) Stretching	3434	3230
C-H Stretching	2924	2926
C=C	1743	1656
C-N	1461	1418
C-H Bending	904	899

Eg - bandgap energy, and n - number of transitions in the semiconductor. We calculate the band gap using the above formula. The PPy band gap is 2.54eV which was shown in Fig. 5. The band gap decreased when the CQD was added. PPy-CQD is 1.69eV. Low band gap materials are suitable for energy conversion applications, so PPy-CQD is a promising material for OSCs.

Fig. 6 exhibits the PPy two mass losses due to polymer chain degradation[29,30] occur around 190°C and 350°C, and 50% of the mass remains at 500°C. PPy-CQD shows the same decomposition, but the 60% remains at 500 °C, confirming that the thermal stability of the CQD doped PPy is improved. Thermal enhancement demonstrates the strong interaction between CQD and PPy polymer chains.

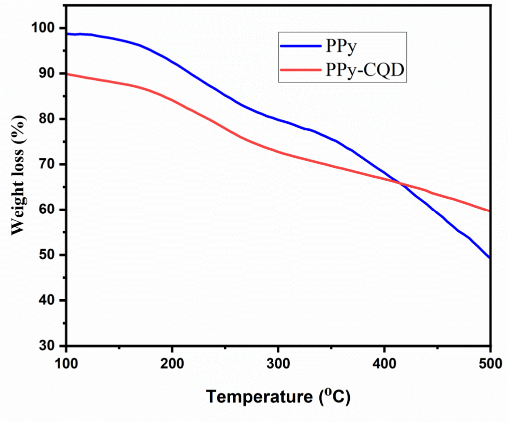

Fig. 6 — TGA thermograms of PPy and PPy-CQDs

Conclusion

PPy and PTh films have been prepared from the CQD using pyrrole and thiophene monomers using electrochemical polymerization. In this polymerization process, CQD binds strongly to the polymer chain. As a result, the electrical properties of PPy-CQD improved. This is studied by CV and impedance electrochemical techniques. Unfortunately, the electrical properties of PTh-CQD are lower than PTh due to the heterogeneous electrolyte (aqueous-acetonitrile solution) used to polymerize thiophene. Therefore, we only analyze the PPy films for OSCs application. Generally, OSC donor materials have unique properties such as high absorption, low bandgap, and superior thermal stability. Our PPy-CQD film has all these properties, suggesting that this film is a suitable material for OSC application.

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