Carbon Quantum Dot-Polypyrrole Nanocomposite for Supercapacitor Electrodes

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Abstract

A CQD-polypyrrole composite was developed as a supercapacitor electrode material. Carbon quantum dots (CQDs) were synthesized using citric acid as carbon precursor. The CQDs were incorporated in a polypyrrole matrix by dispersing them during the in-situ polymerization of pyrrole. The structure and morphology of the composite were characterized using FT-IR, XRD, TEM. Cyclic voltammetry and galvanostatic charge-discharge studies were performed using a three-electrode system to understand the electrochemical behaviour of the sample. The composite showed a 33% increase in the specific capacitance as compared to neat polypyrrole.

1. Introduction

Energy storage has become need of the hour and many devices have been developed over the years to store energy and overcome the problem of limited energy supply. Supercapacitors are a relatively new means of energy storage when compared to other storage devices, and are preferred due to their very high capacitance, high power density and high durability\cite{1}. Supercapacitors could be of three main types; electric double layer capacitors which can store charge electrostatically, pseudocapacitors, which can store charge electrochemically, and hybrid capacitors, which combine the properties of both EDLCs and pseudocapacitors. The materials used for supercapacitor electrodes plays an important role in determining the properties of the electrochemical behavior. A variety of materials like carbonaceous materials (activated carbon \cite{2}, carbon aerogels\cite{3}, graphene\cite{4}, CNTs\cite{4}, CQDs\cite{5}\cite{18}), metal oxides\cite{6} and conducting polymers\cite{4} can be used in electrodes, depending on the type of supercapacitor required and the properties desired. Quantum dots are semiconductor nanoparticles less than 10 nanometers in size which could be thought of as a new potential option for use as materials in supercapacitor electrodes\cite{7}. The benefits of using quantum dots, and specifically carbon quantum dots in energy storage devices should be determined experimentally and then these materials can be utilized accordingly\cite{5}. Due to their good solubility, robust chemical inertness, outstanding electronic properties as electron donors and acceptors and low toxicity, CQDs can be handled easily and safely\cite{7}. Electrode for supercapacitor applications should exhibit electrochemical properties like high conductivity, corrosion resistance, high surface area per unit volume and high surface area per unit mass\cite{8}. It should also be inert, should be environment friendly and affordable. The pore size of electrodes is another important factor in determining specific capacitance and specific energy. Reduction in pore size
generally leads to an increase in its capacitance and specific energy[9]. Nanocomposites have shown remarkable properties in electrochemical field due to their chemical stability and wide range of applications[10]. A lot of research is being done to make a material which can be used as an electrode for supercapacitor and works efficiently. Many nanocomposites such as reduced graphene oxide-polyaniline[4], graphene-polypyrrole[11], carbon quantum dots-polyaniline[4], graphene-polyamide etc. have been tried earlier.

The primary goal of this project is to synthesize carbon quantum dots-based nanocomposite using polypyrrole matrix and develop a material which can be used as electrode for supercapacitor. This paper reports the use of CQD-PPy composite as a supercapacitor active electrode material. The CQDs are decorated on polypyrrole matrix which enhances the specific capacitance of the material. PPy when reinforced with CQDs act as conducting matrix and lends pseudocapacitance to the material. This paper focuses on studying the behavior of CQD-PPy composite and future studies will be based on increasing the efficiency of the material.

2. Experiment section

2.1. Materials

Citric acid (99% LR) was procured from Thomas Baker, Ethanol (99.9% CS reagent), Pyrrole (Avra), HCl (37%) (Rankem), H2O2 (30%) (Rankem), were all laboratory grade reagents and were used as received.

2.2. Synthesis of CQD

Following the procedure of Paikaray et. al., a solvothermal bottom up procedure was adopted for the synthesis of carbon quantum dots (CQDs) [12]. 5 wt% (2.63g) of citric acid was added to a solution of 30 mL of H2O and 20 mL of ethanol. This solution was kept in 80 mL of Teflon-lined stainless-steel autoclave for 4-5 hours at 120 °C. The autoclave was allowed to cool naturally after the reaction was completed. The obtained solution was kept under UV (356 nm) and fluorescence was observed [12].

2.3. Synthesis of Polypyrrole (PPy)

An acidic solution of pyrrole was first prepared by dissolving 4 mM (268 μL) of pyrrole in 4 mL of 1N HCl. The acidic solution was further stirred for 30 minutes at room temperature. 200 μL of H2O2 (30%) was added to the acidic solution of pyrrole and it was stirred again for 12-14 hours at room temperature[13]. After complete polymerization, a dark (black) slurry was obtained and was centrifuged. It was washed with methanol and distilled water several times and then it was dried at 70 °C for 12 hours in vacuum oven.

2.4. Synthesis of CQD-PPy nanocomposite

Carbon quantum dots were prepared using citric acid as mentioned earlier in section 2.2. 4 mL of as-synthesized CQD were added to the acidic solution of pyrrole as under section 2.3. 200 μL of H2O2 (30%) was added to CQD-pyrrole solution and stirred again at room temperature for 12-14 hours. The colour of solution changed from light green to dark black as polymerization proceeded. The slurry obtained after 12-14 hours of stirring was centrifuged and was decanted. It was washed several times with water and methanol and vacuum dried at 70 °C for 12 hours before any further characterization. A black coloured powder was thus obtained[13].

3. Characterization

The Fourier transform infrared (FT-IR) spectra were measured for CQD, polypyrrole and CQD-PPy nanocomposite using Thermo Scientific Nicolet IS10 IR spectrometer with wavenumber ranging from
400 to 4000 cm$^{-1}$. X-ray diffraction pattern was obtained for PPy and CQD-PPy nanocomposite by Rigaku made Ultima IV X-ray diffractometer. The electrochemical studies were performed using cyclic voltammetry (CV) (Pine Research Instrumentation, WaveNow). Galvanostatic charge discharge measurements were taken using Pgstat30. Transmission electron microscopy (TEM) was conducted on a JEOL JEM 2010 operated at 200kV.

4. Results and discussions

Fig. 1. shows the FT-IR spectra of the CQD, PPy and CQD-PPy samples. The characteristic functional groups found in CQDs include hydroxyl, carboxyl and carbonyl groups. The presence of hydroxyl group is confirmed by observing a broad peak at a wavenumber of 3447.85 cm$^{-1}$. This value is close to 3418 cm$^{-1}$ which is the value found in literature[14]. According to literature, the presence of carboxyl group is indicated by the presence of peak at wavenumber close to 1600 cm$^{-1}$[15]. The peak at 1636.41 cm$^{-1}$ thus confirms the presence of carboxyl group. The peak at 1220.92 cm$^{-1}$ indicates the presence of carbonyl group.

The FT-IR spectrum of PPy showed all the characteristic peaks of the polymer. The peak at 789.19 cm$^{-1}$ confirms the presence of C-N bond. The peak at 1296.82 cm$^{-1}$ corresponds to C-H bond. Peaks at 1567.60 cm$^{-1}$ and 3419.83 cm$^{-1}$ corresponds to the C=C bond present in the PPy ring and the N-H bond respectively [16][17].

In the FT-IR spectrum of CQD-PPy, the characteristic peaks were obtained at 785.59 cm$^{-1}$, 1267.29 cm$^{-1}$, 1632.34 cm$^{-1}$ and 3416.25 cm$^{-1}$. These peaks were also observed in the FT-IR spectrum of CQD and FT-IR spectrum of PPy, and hence confirm the formation of CQD-PPy nanocomposite.

![Figure 1: FT-IR spectra for CQD (red), PPy (purple), CQD-PPy nanocomposite (blue)]

As it can be seen in Fig. 2, the XRD pattern obtained for PPy shows a broad peak at 25°. The sharp and narrow peaks in the pattern indicate diffraction from the crystalline component of the sample, whereas the broad peak shows diffraction from the amorphous component. This shows that the product formed is partially crystalline. The XRD profile of CQD-PPy nanocomposite also shows high intensity peak at 25° obtained due to presence of PPy, which also conforms to the literature reports[13]. At 15° a difference can be seen in the XRD patterns of both samples, which is due to the presence of CQD.

The corresponding interplanar spacing was calculated using Bragg’s law:

$$n\lambda = 2d \sin \theta$$  \hspace{1cm} (1)
\[ \lambda_{ex} = 1.54\text{Å} \]
And ‘d’ was calculated to be, 0.18 nm.

\[ \text{Figure 2: XRD pattern of PPy and CQD-PPy} \]

Fig. 3. shows the TEM images of CQD-PPy composite obtained by JEOL JEM 2010 operated at 200kV. The size of the nanoparticles was observed to be ranging from 20nm to 30nm. Agglomeration of particles was observed in the TEM images which could be the result of improper dispersion of composite in the solvent during TEM sample preparation.

\[ \text{Figure 3: TEM images of CQD-PPy (a) 50nm scale (b) 20nm scale} \]

The CV measurements were performed to analyse the electrochemical performance of PPy and CQD-PPy samples. The incorporation of CQD in PPy matrix has enhanced the electrochemical properties of
PPy. The CV curve for CQD-PPy can be seen in Fig. 4.b. The curves were obtained at three different scan rates i.e., 10mVs\(^{-1}\), 50mVs\(^{-1}\) and 100mVs\(^{-1}\). The CV curve of CQD-PPy exhibited quasi-rectangular shapes, which were observed to be unchanged for different scan rates, indicating a pseudocapacitive behaviour. The potential window was extended from -0.2 to 1.0 V. A wide potential window is a result of incorporation of CQDs.[5] The CQD-PPy composite shows better performance than PPy due to charge transfer between matrix and CQD.

To understand the electrochemical properties, GCD measurement was carried out in 1M H\(_2\)SO\(_4\) electrolyte solution and normal three electrode system was used at different current densities. The curves showed near-triangular shapes which indicate reversible and fast ion doping/de-doping process.[5] Fig. 5. shows the galvanostatic charge discharge (GCD) curve for CQD-PPy nanocomposite at different
current densities (5, 10, 15 μA g⁻¹). The specific capacitance of the material for electrode for supercapacitors was calculated using the equation given below [5], on the basis of GCD curve:

$$C_m = \frac{I \times \Delta t}{m \times \Delta V}$$  \hspace{1cm} (3)

Where, $C_m$ is specific capacitance, $I$ is the current, $\Delta t$ is the time for discharge, $m$ is mass of the sample coated, $\Delta V$ is potential window. The specific capacitance both samples was calculated using Eq. (3) and was found to be 240 mF g⁻¹ for CQD-PPy nanocomposite and 180 mF g⁻¹ for PPy sample.

5. Conclusion
This paper describes the synthesis of a CQD-PPy composite for application as a supercapacitor electrode material. The composite was characterized using transmission electron microscopy, which revealed carbon dots dispersed in the polypyrrole. FT-IR spectroscopy confirmed the synthesis of polypyrrole and suggests that the CQDs have hydroxyl, carboxyl and carbonyl functional groups. The electrochemical performance of the composite was studied using cyclic voltammetry and galvanostatic charge-discharge studies.

There was a 33% increase in the specific capacitance of CQD-PPy composite when compared with neat PPy, which could be due to an interfacial charge transfer between the two components. The low values of specific capacitance obtained could be due to insufficient dispersion of the composite during electrode fabrication leading to a lower surface area of interaction with the solvent during operation. Improved choice of solvent and dispersion methods is expected to improve the specific capacitance and performance of this material. Nevertheless, this study is a valuable initial step in developing CQD-PPy composite supercapacitor materials.
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