An Efficient Pseudocapacotpr Electrode Material Based On Magnesium And Sulphar Co-Doped Graphene Quantum Dots: Synthesis, Characterization And Energy Storage Applications

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Abstract:

An efficient pseudocapacitor electrode material has been found by using water soluble inorganic salt after doping in Graphene Quantum Dots (GQDs). Excellent results were obtained by using $MgSO_4.7H_2O$ powder and graphene oxide (GO) as source materials in a facile hydrothermal process. For electrochemical study, electrodes were prepared by using a dip coating in aqueous medium. The synthesized materials were analyzed by various characterization techniques such as Raman Spectroscopy, FT-IR Spectroscopy, High Resolution Transmission Electron Microscope (HRTEM), and Thermogravimetric Analysis (TGA/DTA). HRTEM results show that the hydrothermally prepared electrode material had a size of 5-30 nm. TGA/DTA results confirmed the high thermal stability of materials even at high temperature. Raman measurements were used to identify artificial disorder or defects in different forms of doped GQDs due to presence of Mg and S related defects. Strong interaction between graphene quantum dots with sulfur and magnesium enabled us to demonstrate fast and reversible redox reaction. The measured high specific capacitance for doped GQDs with Mg and S electrode was found to be 347.5 Fg^{-1}at $0.1mAg^{-1}$ due to enhancement in electrical conductivity and improvementintheelectrontransfer betweenelectrodesandelectrolyte.Thestabilityofthepreparedelectrodes wasdonebyusingcharging/dischargingcyclesat $0.1mAg^{-1}$in1MK_4FeCN_6electrolyte.Thenew insightonthe role of functional groups in Mg and S co doped GQDs turned out to be a better design of super capacitor device which showed good cyclic stability and energy storage capacities comparable to that of existing thin film ultra capacitors.

Keywords: GQDs, Defects, Hydrothermal Treatment, Magnesium Sulpate, Pseudocapacitor Electrode

1. Introduction

Super capacitors have attracted considerable attention in recent years because of high power density, long cycle life and fast charge/ discharge processes[1]. The major limitation of super capacitors is their low energy density as compare to recharge able batteries. To over come this limitation, we need appropriate materials which lead to satisfactory electrochemical performance and life cycles by controlling its specific surface area and pore size. Graphene Quantum dots (GQDs) are considered as one of the most promising materials for the next generation flexible thin film super capacitors due to it sun ique structural property features like large surface area, high conductivity, and superior mechanical property. Many more efforts havebeen done on novel capacitors including micro super capacitors, and solid state super capacitors super capacitors [2-4]. The electrochemical preparation of GQDs was firstly reported byLi et al. [5] in 2011. Zhang et al. [6] in 2012 showed yellow luminescent GQDs with an average diameter of 5–10 nmby electrolysis of graphite rod. TheLiu et al. [7] shows an excellent rate capability, higher specific capacitance ($1107.4\mu Fcm^{-2}$) and higher energy density ($0.154\mu Whcm^{-2}$) to built as GQDs//MnO_2 asymmetric super capacitor in aqueous electrolyte. Zhang et al. [8] proposed that GQDs can serve as

solution- and solid-type electrolytes for supercapacitors because of the fully ionization of the weak acidic oxygen bearing functional groups after neutralization. We really need more work to make an improvement of electrochemical performance of pseudo capacitors.

However, the commercial water soluble in organic salts with multiple valence state metalions have not explored in aqueous electrolyte to their pseudo capacitance. At present, most of the transition metal oxides with high specific capacitance are expensive. For high performance super capacitor applications, wepro poseda simple technique to prepare anelectrode material made by doping of the commercial water soluble inorganic salts in GQDs due to its good electrochemical performance, low cost, environmental friendly, easily scalable and highly economical.

Herein, the commercial water soluble inorganic salt $MgSO_4.7H_2O$(~ 5.95 mg) was used to synthe size Mg-S/GQDs as it extends some functional groups after hydrothermal process. We believe, this work reports the synthesis of magnesium and sulphar codoped graphene quantumdots (Mg-S/GQDs) for the first time along with their morphology, optical properties and an efficient pseudo capactor electrode material. This work has implications for less expensive and next generation super capacitor applications of various metal oxide doped GQD materials with the presence of lotof artificial disorder and defects.

2. Experimental

2.1 Synthesis of Graphene Oxide (GO) and Mg-S/ GQDs

For the preparation of doped GQDs, initially graphene oxide was prepared by using commercially available graphite powder by Hummers and Offemann method [9]. Mg- S/GQDs were prepared with a similar hydrothermal method as earlier reported [10-12].

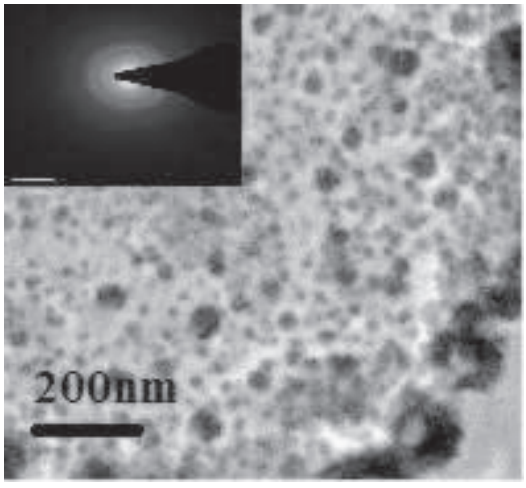
2.1 Characterization Techniques

Raman spectra were obtained by using a Renishaw spectrometer via microscope system equipped with an Ar^+ laser (Z=514.5nm). The presence of functional groups was confirmed by Fourier Transform Infra Red (FTIR) of samples using Perkin Elmer Spectrum-Two spectrometer with ATR & Specular reflectance operating with a resolution of 4 cm^{-1}in the frequencyrangeof400-4000cm^{-1}. Transmission Electron Microscope(TEM) was obtained using FEI Technai G2 20 electron microscope operating at 200 kV. Thermal analysis (TG/DTA) was carried out using a Thermal analysis (Perkin Elmer)at a heating rate of 10^0C min^{-1} from 300^0C to 800^0C in Ar.Thee lectrochemical measurements were carried out using a CHI-760C potentiostat- galvanostat instrument. The cyclic voltammetry (CV) curves were measure din1MK_4FeCN_6 electrolyte solution in a standard three electrode cell with a glassy as a working electrode (WE), an Ag/AgCl as a reference electrode (RE) and platinum as counter electrodes (CE),respectively.

3. Results and Discussion

3.1 Morphology and Optical Studies

Fig.1(a)showstheHRTEMimagesofMg-S/GQDs respectively. The majority of the Mg-S / GQDs are estimated to be narrow in the range of 5-30 nm in diameter. The distribution of Quantum dots (QDs) across the surface of GO suggests the hydrothermal method is the simple stand efficient way to synthesize QDs. The selected area electron diffraction (SAED) patternis show nininsetof Fig.1(a). The observed bright points reveal the trans formation of amorphous QDs to highly polycrystalline nature. Energy dispersive X-ray spectroscopy (EDX)analysis as mentioned in Table I indicate that the atomicratioof C/O/S/Mg showing that the carbon is the dominant element of the Mg-S / GQDs, and the small doping element is magnesium.



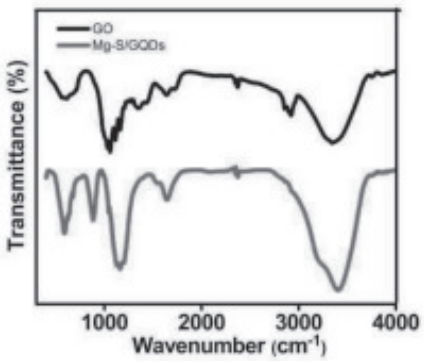
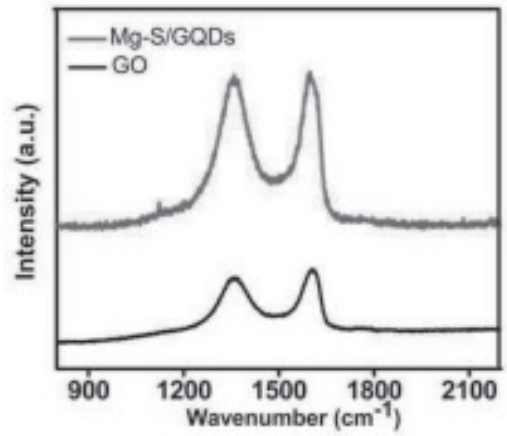


Figure 1: HRTEM images of GO and Mg-S/GQDs



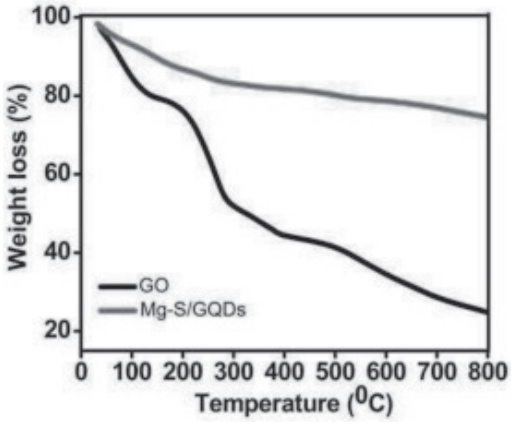


Figure1: (a) HRTEM images(b) FTIR Spectros copy, (c)Raman Spectroscopy, and(d) TGApatterns of GO and Mg-S/GQDs

Fig. 1 (b) shows that the Fourier transform infrared (FTIR) spectrum of GO and Mg-S / GQDs. The pristine GO shows the presence of C-O (v_{C-O} at 1040 cm^{-1}), C-OH (v_{C-O} at 1389 cm^{-1}), C=O (v_{C-O} at 1639 $cm^{-1}$and 1726 cm^{-1}) which are similar as earlier reported in refs [10- 12]. After hydrothermal treatment with $MgSO_4.7H_2O$, the strong vibrational bands were observed at 448, 580, 660, 874, 1043, 1154, 1535, 1647, 2911, 3205, and 3396cm^{-1}. The emerging peaks of doped GQDs were assigned at 448cm^{-1}, 660cm^{-1} (stretching vibrations of C-S) and 1154cm^{-1} (C = S) [13] which indicates the effect of doping of sulfur in the carbon matrix. The observed peaks at 1154 cm^{-1} were assigned to vibrations of S = O. [13-16]. These results confirm the formation of the more dominant excellent quality of S to compare to Mg in GQDs. It should be noted that both the two absorption peaks at 1043cm^{-1} (C-O) and 1647cm^{-1} (C = O) of the Mg-S / GQDs have appeared due to more defects related to oxygen- containing functional groups as compared with GO The strong absorptions at 874 cm^{-1} (C-H) and 2911 cm^{-1} (C-H) suggest that the presence of hydrogen contentin Mg-S/GQDs. In addition, an increase in intensity of band at the 3465$cm^{-1}$was observed due to the presence of the oxygen-containing functional groups and defects.

Raman spectra of GO and Mg-S/ GQDs are shownin Fig.1(c). Fig.1(c) shows that the prominent G peaks located at 1585 cm^{-1} and a slightly less intense D band at 1354 cm^{-1}[12].The D band is attributed to the disordered nature due to reduction in size and the G band is related to the inplane vibration of the sp^2 carbonatoms[12].The observed Intensity(I_D/I_G) ratioof the Mg-S/GQDs is 0.86 which is higher than GO(0.84). Asmallin crease in intensity ratio which is a measure of defects arise in doped GQDs after hydrothermal method, not only due to doping, but also due to reduction in size [17] It also suggests that the intercalation of S and Mg atoms in conjugated carbon which has more defects on surface of GQD

Table 1. EDAX pattern of GO and Mg-S/GQDs

	Carbon	Oxygen	Sulphur	Magnesium
Graphene Oxide(Weight %)	51.82	46.18	0	0
Mg-S/GQDs(Weight%)	77.95	18.11	3.41	0.51

smay possibly improve the electronic and chemical properties of GQDs.

The TGA (shown in Fig.1d) analyze shave been used to investigate the thermal stabilities of GO and Mg-S / GQDs. From the Fig.1 (d), GO shows the maximum weight loss (74%) followed by Mg-S/ GQDs(24%). The TGA analysis of Mg-S/GQD sex hibitsa quantitative weight loss of ~ 50% in single step hydrothermal methods with respect to source material GO.

3.2 Electrochemical Characterization:

Fig.2(a) shows CV of Mg-S/GQDs with different canrates of 20,40,60,80,100,200 and 500 mVs^{-1} from an operating potential window from -0.6 V to +0.2 V. This study shows that the codoped GQDs contributed pseudo capacitive behaviour with prominent redox cathodic and anodic peaks. The oxidation peaks were observed at 0.1 V, while the reduction peakswere found at 0.42 V with different scan rates. Anodic peaks shift toward more positively in Mg-S / GQDs (at 0.1V) as compared to GQDs [12] and shift in cathodic peaks toward more negatively in Mg-S / GQDs (0.42V) as compared to GQDs [12]. We speculate that it may be attributed to the presence of the defect in the site and disorder of graphene quantum dots after Mg and more dominating S-doping, resulting in improving the capacitance current.

Fig. 2 (b) shows that the galvanostatic charge-discharge curves of Mg-S/GQDs at different current densities of 0.1mA/g, 0.2mA/g, 0.4mA/g and 0.9mA/g. The value of the specific capacitance was obtained from the discharge curve according to the followinge quation C=(I/m) (dt/dV) [12], where I is the constant discharge current, m is the mass of active materials within the Electrode and dv/dt can be obtained for the discharge curve. The specific capacitance at different current densities from galvanostatic charge-discharge curves was found to be $44Fg^{-1}$, $44Fg^{-1}$, $54Fg^{-1}$and $347.5Fg^{-1}$. The obtained high specific capacitance at lower current density caused by doping with S and Mg is due to increase in electrical conductivity and surface area. The high conductive nature of prepared electrode can provide better transport-pathways during the fast charge-discharge process. The specific capacitance of Mg-S/GQDs electrodes decreased with increase in current densities due to slow diffusion of electrolyte in the pores of prepared electrode material.

To obtain the information on the internal resistance of the electrode material and the resistance between the electrode and electrolyte, electrochemical impedance spectroscopy (EIS) was carried out. Fig. 2 (c) shows that the obtained internal resistance of the doped samples is very low at high frequency. Therefore, sulphar and other magnesium moities in Mg-S/GQDs are not responsible for increase in resistance. As frequency increased in Mg-S/ GQDs, asemi circle loop is observed which is not seen clearly in GQDs[12].

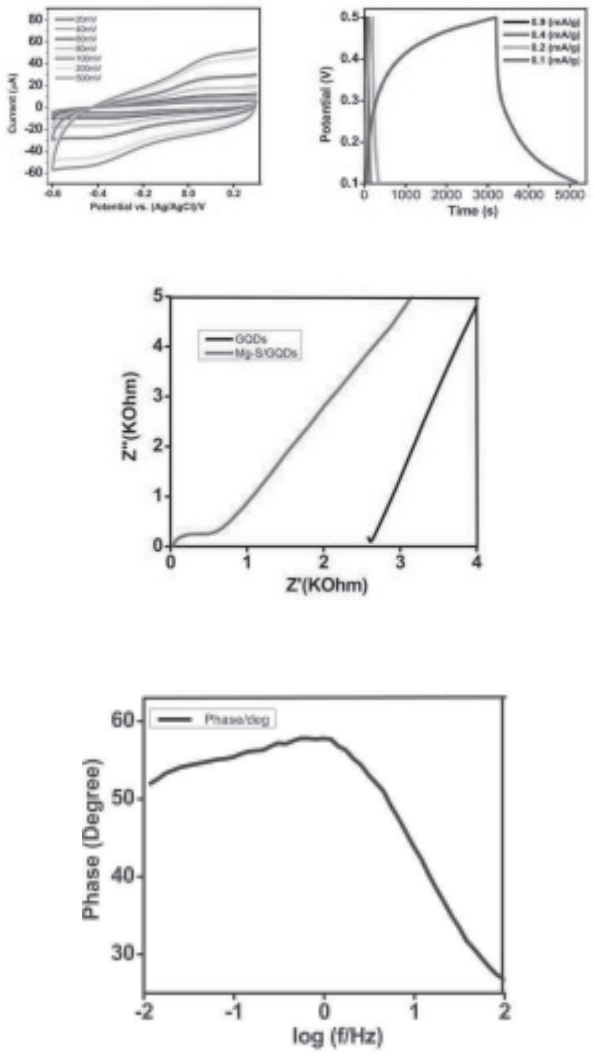


Figure 2: (a) Cyclic Voltammetry at different scan rates,(b) Galvanostatic charge-discharge with current densities, (c) Impedance Spectroscopy, and (d) Phase angle ofMg-S/GQDs.

It is well known that the semicircle reflects the electrochemical reaction impedance of the electrode, and a small semicircle means low charge transfer resistance. Therefore, the doped samples have the lowest charge trans ferresistance as compared to GQDs[12]. According to EDAX pattern as shown in Table I, a large amount of sulphur exists on the surface of the carbon surface, which leads to increase the polarity of the carbon surface and facilitate its contact with aqueous electrolyte leading to reduced charge transfer resistance for doped samples. There sults shows that the diffusion rate of Mg-S/GQD sis higher than that of GQDs due to observed low charge transfer resistance (Rct) in Mg-S / GQDs (0.2 kfi) as compared to GQDs(2.5 kfi)[12]].There sponse time(ýR)(Fig.2 (d)) determined from on set frequency is found to be 17ms suggests that most of the stored energy is still present at frequency of 57Hz[18]. Its houldbe noticed that the phase angle of Mg-S/GQD sisclose to 60^0 effectively improved the capacitive behaviour. Most of the commercially available super capacitors operate at frequencies less than 1 Hz was reported so far [19]. From Fig. 2 (d), the phase angle decreased from 57 to 28 degrees, shows the transition to more pseudo capacitive nature. To see the resistive behaviour for Mg-S/GQDs electrodes, The relaxation time constant at a phase angle of $45^0$is observed about 0.1ms (Freq = 11124Hz) and this frequency is much higher than those reported high super capacitors rGO (ýR=33ms)[20],RGO-CNT (ýR=3.4ms)[20].The obtained extremely small corresponding relaxation time constantin Mg- S / GQDs reveals the excellent power response of super capacitors.

4. Conclusions

In summary, more dominating sulphur doping element in Mg-S/GQDs were successfully synthesized through a hydrothermal method by using water soluble inorganic salt $MgSO_4.7H_2O$ and GO as precursor materials. Interestingly, FTIR, Raman, and TGA spectroscopic measurements were found to be strongly influenced by the doping process to form Mg-S/GQDs. The simultaneous malgamation of Sand Mgspecies with the presence of oxygen- containing functional groups and defects significantly improved the surface chemistry of GQDs. The obtained results show a fast and reversible redox reaction of co-doped GQDs electrode and deliver a very high specific pseudo capacitance of 347.5 F/g at 0.1mAg^{-1}. The results obtained here indicate that co-doped samples in GQDs are promising for future electro chemical applications.

5. Acknowledgement

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