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Hafnium Oxide/Graphene Oxide Nanocomposites as Efficient Supercapacitor Electrodes

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ABSTRACT

This paper reports on the preparation of graphene oxide (GO) modified with hafnium oxide (HO) nanoparticles composites by a simple mixing and their use as efficient electrode in electrochemical supercapacitors. The technique relies on simple mixing the aqueous solutions of hafnium oxide (HO) nanoparticles and graphene oxide (GO) at different ratios of GO content (20, 30 and 40 wt%). The morphological studies, chemical composition and electrochemical behavior of the resulting HO/GO nanocomposites were investigated by using UV/vis spectrometry, X-Ray Diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM) and electrochemical respectively. The electrochemical performance, including the capacitive behavior of the HO/GO nanocomposites were investigated by cyclic voltammetry and galvanostatic charge-discharge curves. The HO/GO nanocomposites (40 wt%) ratio exhibited the best performance with a specific capacitance of 268 Fg^{-1} at a scan rate 5 mVs^{-1} in 1 M H_2SO_4 and it shows excellent long-term cycle stability.

1. Introduction

Over the past few years, the growing demand for portable systems and hybrid electrical vehicles requiring high power in short-time pulses, the electrochemical capacitors are gaining the increasing interest because of the up-coming depletion of fossil fuels. Carbon materials such as activated carbon, mesoporous carbon and carbon nanotubes usually display good stability, but the capacitance values are limited by the microstructures in the materials [1, 2]. Graphene, a two-dimensional all sp^2 hybridized carbon with unique electronic and mechanical properties, has received a rapidly growing interests as material in supercapacitors [3].

The metal oxide/graphene nanocomposite electrodes shows a better capacitive performance through a combined effect from pseudo capacitance (metal oxide) and electric double layer capacitance (graphene) [4]. HfO_2 being the metal oxide group can also be expected to enhance the capacitance when incorporate with graphene oxide. To study the potential of graphene based nanocomposites for supercapacitor applications, different approaches have been considered. The graphene based electrochemical double-layer capacitor with specific capacitance values of 135 Fg^{-1} in aqueous electrolytes is the first report using chemically reduced graphene oxide, synthesized through hydrazine reduction of graphene oxide (GO) [5].

Graphene oxide (GO), one of the most important derivatives of graphene, is characterized by a layered structure with oxygen functional groups bearing on the basal planes and edges [6-8]. Metal oxides depending upon their structural, geometries, and electronic structure play a very significant role in areas of chemistry, physics, biology and material sciences [9]. Supercapacitors in 21st century had attracted more in research interest as an auxiliary and clean source of power and energy [10].

First and third row transition metal oxides seems to be especially attractive as cathode materials in electrochemical energy storage systems due to their favorable electrochemical and solid-state properties. With the aspect of their low price, rich abundance, low toxicity, and diverse oxidation states many transition metal oxide nanoparticles alone and with carboneous filler have got special attention for supercapacitor applications [11-15]. GO provides an effective transportation of ions onto the material surface due to their large accessible surface area, thus accomplishing high electric-double layer capacitance in aqueous electrolytes [16].

The electronic properties of the metal oxide are effected by particle size of material, the quantum size or confinement effects are produced in nanostructured materials which essentially arise from the presence of discrete, atom like electronic state, and also nanosized material is observed to have small band gap in its lattice. Thus the metal oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites so metal oxide materials exhibit ionic or mixed ionic/electronic conductivity and are influenced by the nanostructure of the material [17].

Generally, there are two types of supercapacitors based on the electrode materials: (i) some redox active materials that use fast, reversible redox reactions at the surface of active materials, which is known as the pseudocapacitance and (ii) high surface area, inert and conductive materials that store and release energy by nanoscopic charge separation at the electrochemical interface between an electrode and an electrolyte [18-21]. The carbonaceous nanocomposites (like CNTs, active carbon and graphene) are commonly studied as electrodes for electrochemical double layer capacitors; while transition metal oxides, including HO, are promising material for pseudocapacitors. The introduction of GO into metal oxides can modify their chemical and physical properties and enhance the activity of supercapacitor. However, to the best of our knowledge, there are no earlier literature on HO/GO nanocomposite as efficient supercapacitor.

In the present scenario, we report on the preparation of HO/GO composites using the simple mixing with different ratios of GO content (20, 30 and 40 wt%) gave the corresponding nanocomposites with enhanced electrochemical properties. The HO/GO nanocomposites have been successfully used as electrodes in supercapacitors with a maximum specific capacitance of 268 Fg^{-1} in 1 M H_2SO_4 at a scan rate of 5 mVs^{-1}.

2. Experimental Methods

2.1 Materials

Graphite powder, hafnium tetrachloride ($HfCl_4$), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4), sodium nitrite ($NaNO_3$), potassium permanganate ($KMnO_4$), polyvinylidene fluoride (PVDF) and hydrochloric acid (HCl) were purchased from Sigma Aldrich and used as received.

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2.2 Preparation of Hafnium Oxide/Graphene Oxide (HO)/(GO) Nanocomposites

Hafnium oxide (HO) Nanoparticles were synthesized using precursor of hafnium tetrachloride ($HfCl_4$) and sodium hydroxide (NaOH) by simple precipitation method. Initially, 0.4 M (100 mL) aqueous solution of NaOH was slowly added drop wise into 0.1 M (100 mL) aqueous solution of $HfCl_4$ and subjected to continuous stirring using teflon coated magnetic bar for 24 h, which gives a white coloured precipitate containing hafnium hydroxide. The $Hf(OH)_4$ precipitate was washed thoroughly with millipore water and centrifuged at 2000 rpm for 10 minutes to remove the residuals. This process was repeated many times until the precipitate was free from any trace impurities. Finally, the obtained product was dried in a hot air oven at 100 °C for 24 h and further calcined at 800 °C for 4 h which results in the formation of HfO_2 NPs [22].

Graphene oxide was synthesized from graphite powder by a Hummers method [23] and the detailed experimental conditions are reported earlier [24]. The HO/GO nanocomposites were prepared by mixing aqueous solution of GO into aqueous solution of HO at different ratios of GO (20, 30 and 40wt %) to form the HO/GO nanocomposites, then the mixture was heated at 100 °C for 12 h. The resulting black precipitate was separated from the aqueous supernatant by centrifugation 2000 rpm for 15 min. Then the precipitate was dried at 100 °C.

2.3 Electrode Preparation

Prepared electrode material (HO, GO, HO/GO (30 wt%) and HO/GO (40 wt%), activated carbon and PVDF binder were mixed together in the ratio of 85:5:10 (wt%) were deposited onto a platinum foil (A=0.5 cm^2). The active mass is around 400 µg.

2.4 Instrumentation

2.4.1 X-Ray Diffraction

The crystal structure, orientation and crystalline size of the HO/GO nanocomposites were examined by Rigaku X-ray diffractometer using Cu k_α (λ =1.5406 Å) radiation.

2.4.2 UV/Vis Spectroscopy

The absorption spectra were recorded using Perkin-Elmer Lambda UV/vis 35 spectrophotometer in plastic cuvettes with an optical path of 10 mm. The wavelength range was 200 – 800 nm.

2.4.3 Scanning Electron Microscopy (SEM)

SEM images were taken using a scanning electron microscope VEGA3 TESCAN (Germany) equipped with a thermal field emission emitter and two different detector.

2.4.4 Transmission Electron Microscopy (TEM)

TEM images were obtained using Hitachi H-7650 (Singapore) microscope at maximum acceleration voltage of 120 keV.

2.4.5 Electrochemical Measurements

Cyclic Voltammetry (CV) experiments were performed using a CHI 661 C. The electrochemical cell consisted of HO/GO as the working electrode, Standard calomel electrode (SCE) as the reference electrode, and platinum (Pt) wire as the counter electrode. Cyclic voltammetric measurements were performed using aqueous 1 M H_2SO_4 solution at ambient conditions. All electrochemical experiments were performed at room temperature.

The supercapacitor behavior of HO/GO was investigated using a three-electrode system comprised of HO/GO nanocomposites as the working electrode, Pt foil as the counter electrode and SCE as the reference electrode. The CV curves were recorded from 0 to 0.8 V with a scan rate of 10 mVs^{-1}.

The specific capacitance (C) was calculated by integrating the area under the CV curve according to Eq.(1):

$$Cs = \frac{1}{mv(VU-VL)}\int_{VL}^{VU} I(V)dV \qquad (1)$$

where m is the mass of active material (g), v is the scan rate (mVs^{-1}), V_U and V_L are the upper and lower voltage limits (V) and I is the current (A).

The specific capacitance was in addition calculated from the slope of the galvanostatic charge-discharge curve at the different densities using the following Eq.(2) [25].

$$Cs = \frac{I\Delta t}{m\Delta V} \qquad (2)$$

where I is the discharge current (mA), m is the mass of the electro-active material (mg): Δt is the discharge time (t).

3. Results and Discussion

3.1 Preparation and Characterization of Hafnium Oxide/Graphene Oxide (HO/GO) Nanocomposites

The preparation method of HO/GO nanocomposites is given in Fig. 1. First, hafnium oxide was synthesized which was reported by Ramadoss et al. [26]. Second, graphene oxide was prepared using a Hummers method. Third, the aqueous solution of GO is mixed with aqueous solution HO at three different ratios of GO content (20, 30 and 40 wt%). The resulting three different ratios of HO/GO nanocomposites were tested.

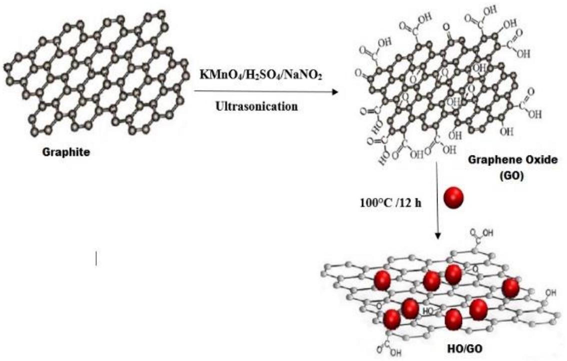

Fig. 1 Schematic illustration of the preparation of HO/GO nanocomposites

X-Ray Diffraction (XRD) analysis were performed on GO and HO before and after its reaction with each other to gain further knowledge on its crystal structure, purity and particle size. The XRD patterns of pure HO, GO and HO/GO nanocomposites at three different ratios were shown in Fig. 2. The crystalline structures of HO, GO, HO/GO (20%), HO/GO (30%) and HO/GO (40%) samples were studied by XRD. The XRD spectrum of HO (Fig. 2b) exhibited a sharp diffraction peak at (2θ = 24.55°) with preferential orientation of the (-111) plane. The mean particle size of HO can be found using the Debye Scherer's formula, with the help of full width half-maximum of the peaks belongs to HO and is found to be nearly ≈20 nm. All the peaks of HO obtained in the XRD pattern were exactly matched with the monoclinic HO phase (JCPDS card No: 06-0318). The XRD pattern of GO (Fig. 2a) exhibited a strong and broad peak at (2θ = 23.39°) which is compatible with the literature data (JCPDS, 75-2078) degree corresponding to d spacing of 3.842 Å which might be attributed to very thin GO layer due to high degree of exfoliation. However, the apparent diffraction peak of GO sheets was discerned in the XRD pattern of HO/GO (20%, 30% and 40%) composites, this suggests that the layer-stacking regularity of GO sheets would be disrupted and low fraction of GO sheets did not influence the lattice structure of HO crystal, which is similar to that of HO/GO composites.

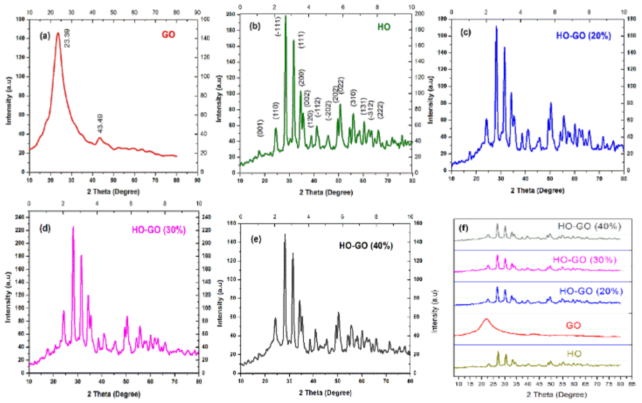

Fig. 2 XRD pattern of (a) GO, (b) HO, (c) HO/GO(20 wt%), (d) HO/GO (30 wt%), (e) HO/GO (40 wt%) and f) all the samples (Comparison)

The UV-vis absorption spectra of HO, GO and HO/GO nanocomposites are depicted in Fig. 3. The absorption peak at 205 nm can be assigned to the absorption of HO [27]. GO dispersed in water exhibits a maximum absorption at 226 nm, attributed to the $\pi - \pi *$ transition resulting from C=C bonds from carboxylic acid functions. The absorption peak at 270 nm [28] is attributed to n-$\pi *$ transition of aromatic C-O bonds i.e. graphene oxide (GO). The spectrum of HO/GO nanocomposite varies significantly with different wt% of HO/GO employed. The absorption band at 196 nm is relatively small for HO/GO (20%), but is significantly increased for higher ratios 206 nm for HO/GO (30%) and 214 nm for HO/GO (40%).

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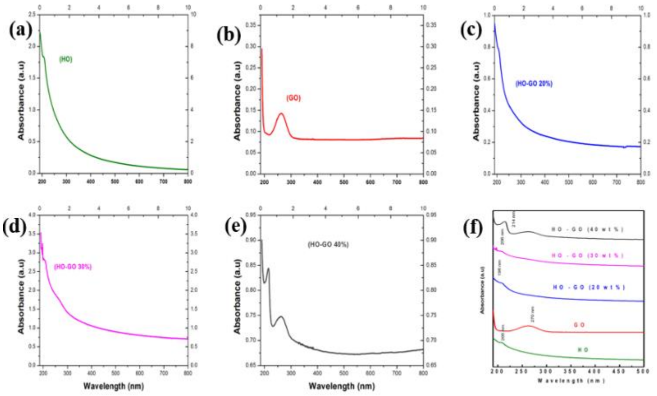

Fig. 3 (a-e) UV absorption spectrum of GO, HO, HO/GO(20 wt%), HO/GO (30 wt%) and HO/GO (40 wt%) respectively and (f) UV absorption spectrum of all the samples (Comparison)

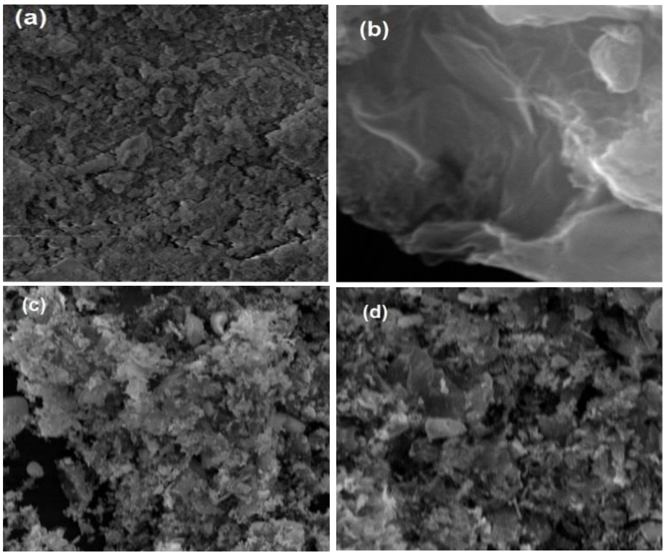

Fig. 4 (a-d) SEM images of HO, GO, HO/GO (30 wt%) and HO/GO (40 wt%) respectively

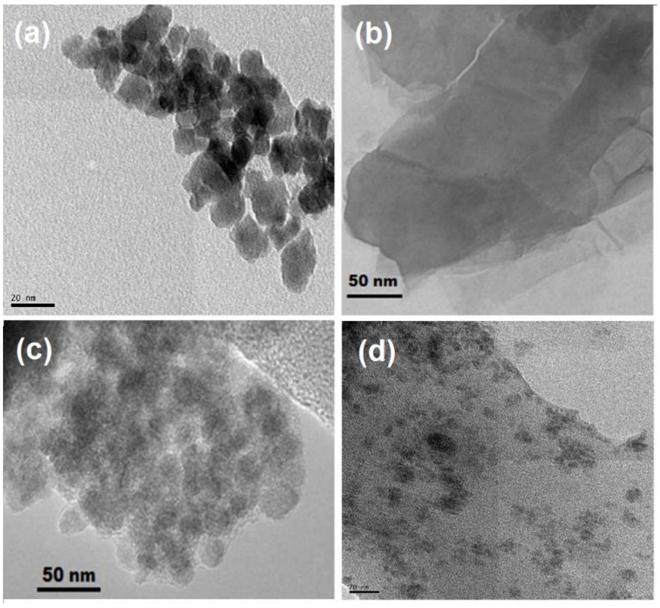

Fig. 5 (a-d) TEM images of HO, GO, HO/GO (30 wt%) and HO/GO (40 wt%) respectively

Fig. 4 shows the SEM images of pure HO, GO and HO/GO composites. Pure HO is possess a uniform distribution of dense particles spherical in shape (Fig. 4a). From the Fig. 4b it is clearly revealed that the GO has a two dimensional sheet-like structure, also it is evident that GO has a multiple lamellar layer structure and it is possible to distinguish the edges of individual sheets from the SEM images. The films are stacked one above the other and also show wrinkled areas. It can also be noted that the GO sheets were thicker at the edges, why because the oxygen-containing functional groups were mainly combined at the edges of GO [29]. It can be observed from the SEM image (Figs. 4c and d) that the GO sheets are covered the surface of HO particles.

For further characterize, the morphology of the HO, GO and HO/GO composites, TEM were investigated. Samples were prepared by dipping carbon mesh grids into the ultrasonicated suspension and drying them in air. The TEM investigations shown in Fig. 5 revealed that the HO densely bound on the surface of the GO sheets, as it can be seen from TEM images, the average size of the HO particles were in the range of 20 nm, which was in good agreement with XRD measurements. The EDS analysis suggests that the presence of hafnium (Hf), carbon (C) and oxygen (O) elements in the HO/GO nanocomposites (Fig. 6).

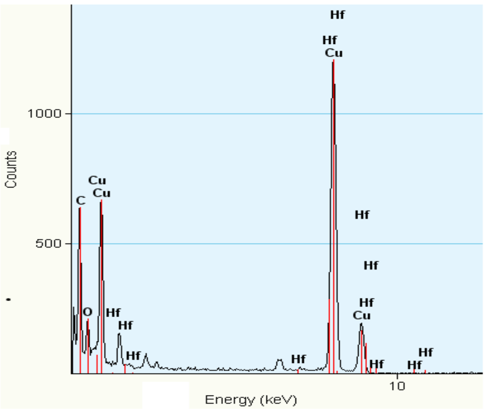

Fig. 6 EDS Spectrum of HO/GO nanocomposites

3.2 Electrochemistry of Hafnium Oxide/Graphene Oxide Nanocomposites

The electrochemical activity of the HO/GO nanocomposites was studied by measuring cyclic voltammetry and galvanostatic charge-discharge cycles of these nanomaterials. Full range CV of all the samples were scanned on CHI 661 C electrochemical workstation. All the electroactive material show I/V compliance in one anodic and one cathodic step; redox transition between a semiconducting state and a conducting state are responsible for cathodic and anodic peaks. With scan rate, all such I/V compliances were found to consist of increasing peak current and a shift in the voltage to higher values. In a CV, the higher the redox peak, the greater is the electrochemical reaction activity [30].

CV curves of all the electrodes clearly shows redox reactions, which exhibits anodic peaks associated with oxidation of material and a cathodic peak corresponding to reduction (Fig. 7). All of the among nanocomposites HO/GO (40 wt%) had the greatest redox activity while the redox activity is the least for HO.

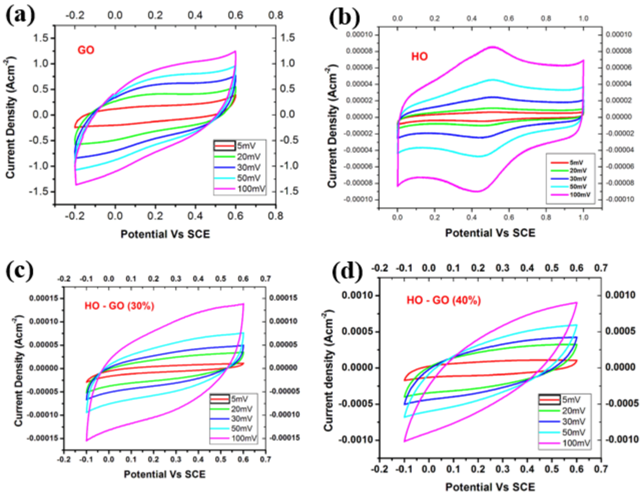

Fig. 7 Cyclic voltametric curves of a) HO, b) GO, c) HO/GO nanocomposite (30%) and d) HO/GO nanocomposite (40%)

3.3 Super Capacitive Characterization

To check if the observed electrochemical conductivity is elevated enough to enable current collection, we investigated the supercapacitor behavior of the HO/GO (30 and 40 wt%) composite electrodes. In contrast to conventional high surface area materials such as conducting polymers and nonporous electrode materials like carbon nanotubes, the effective

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surface area of graphene and its derivatives is not solely dependent on the distribution of pores in the solid state [31]. The presence of oxygen functional groups enhances generally the wettability and the capacitance values of graphene-based supercapacitor [32]. Graphene oxide is known to comprise of well capacity and a potential material to store energy [33]. Two mechanisms are responsible for the specific capacitance of metal oxide electrode: the surface adsorption/desorption and the intercalation/deintercalation of alkali metal ions [34]. Fig. 7 shows the cyclic voltammograms of the different interfaces in 1 M H_2SO_4. Beside the HO/GO (40 wt%) composite (Fig. 7d), rectangle-like shaped curves characteristic of capacitive behavior are observed with specific capacitance varying between 66 Fg^{-1} and 268 Fg^{-1}, depending on the HO/GO nanocomposite (Table 1). The rectangular shape indicates that the main contribution to the capacitance is the charge and discharge of the double layer, which is enhanced by the presence of HO working probably as spacers. We observed that the specific capacitance for both electrodes decreased with an increase in the scan rate from 5 mVs^{-1} to 100 mVs^{-1}. This is a common phenomenon and is caused by the insufficient time available for ion diffusion and adsorption inside the smallest pores within a large particle at high scan rate [35]. Similar results have been reported for GO/MO (Manganese oxide) nanocomposite with a specific capacitance of 211.2 Fg^{-1} at a scan rate of 5 mVs^{-1} [36]. Qi wang et al. [37] reported reduced graphene oxide (rGO)/ (ND) nanodiamond with 10/1 ratio showed the best performance with a specific capacitance of 186±10 Fg^{-1} at scan rate 10 mVs^{-1}.

S. Xiang et al. [38] reported TiO_2 and graphene nanocomposites revealed a maximum specific capacitance 84 Fg^{-1} at a scan rate of 10 mVs^{-1}. Graphene/TiO_2 nanocomposite exhibited a high specific capacitance of 165 Fg^{-1} at a scan rate of 5 mVs^{-1} in 1 M Na_2SO_4 electrolyte solution reported by Ramadoss et al. [39]. RuO_2/graphene, TiO_2/graphene and Fe_3O_4/graphene nanocomposites observed a maximum specific capacitance of 265 Fg^{-1}, 60 Fg^{-1} and 180 Fg^{-1} respectively with 1 M H_2SO_4 as the electrolyte at scan rate of 10 mVs^{-1} are reported by Mishra et al. [40]. The prepared HO/GO nanocomposite electrode, which exhibited a maximum specific capacitance value is 268 Fg^{-1} at a scan rate 5 mVs^{-1}. The specific capacitance of HO/GO nanocomposite is higher than that of above mentioned reported values.

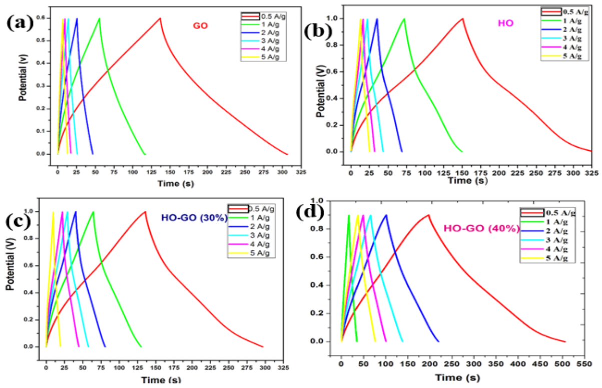

Fig. 8 Galvanostatic charge-discharge curve of the a) GO, b) HO, c), HO/GO nanocomposite (30 wt%) and d) HO/GO (40 wt%)

To further evaluate the specific capacitance of our HO, GO and HO/GO nanocomposite electrode, galvanostatic charge-discharge measurements (Fig. 8) were performed in the current densities of (0.5 Ag^{-1} to 5 Ag^{-1}). It can be seen that all of the curves were linear and exhibited a typical triangular shape, which revealed good electrochemical capacitive characteristics. The specific capacitance of the electrode can also be calculated from the galvanostatic charge-discharge curve at different densities using the Eq.(2).

Table 1 Specific capacitance of HO, GO, HO/GO (30 wt%) and HO/GO (40 wt%) nanocomposites using cyclic voltammetry with different voltage sweep rates and using the galvanostatic charge-discharge technique

Product	Specific Capacitance (Fg^{-1}) (Cyclic Voltammetry)					Specific Capacitance (Fg^{-1}) (Galvanostatic)					
	Voltage Scan Rate (mVs^{-1})					Current Density (Ag^{-1})					
	5	20	30	50	100	0.5	1	2	3	4	5
HO	147	134	128	123	118	91	78	69	62	56	53
GO	200	131	118	107	94	145	102	73	42	40	37
HO/GO (30 wt%)	231	128	95	62	34	156	121	117	109	98	83
HO/GO (40 wt%)	268	171	137	103	66	165	133	127	117	115	93

4. Conclusion

The present study shows that the HO/GO hybrid nanostructure as an electrode material for supercapacitors was successfully synthesized using a simple mixing method. The surface morphology, microstructure, composition and capacitive behaviors of the prepared nanocomposite were well investigated. SEM and TEM images confirmed the uniform distribution of HO nanoparticles on the surface of GO sheets. While XRD confirm the nanosized materials with layered matrix. Our results showed that the HO/GO hybrid electrode exhibited a maximum specific capacitance of 268 Fg^{-1} at a scan rate of 5 mVs^{-1} in 1 M H_2SO_4 electrolyte solution. The remarkable performance of HO/GO nanocomposite could be credited to the nanosize and surface area of HO particles along with good electric conductivity of GO. Moreover, the material exhibited excellent electrochemical stability (long cycle stability) for specific capacitance. These results suggest that HO/GO hybrid electrodes are highly suitable, promising electrode for next generation high performance supercapacitor.

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