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**Few layer graphene wrapped mixed phase TiO<sub>2</sub> nanofiber as a potential electrode material for high performance supercapacitor applications**

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**ABSTRACT**

A combination of favorable composition and optimized anatase/rutile mixed-phase TiO<sub>2</sub> (MPTNF) / Hydrogen exfoliated graphene (HEG) composite nanofibers (MPTNF/HEG) and anatase/rutile mixed-phase TiO<sub>2</sub>/reduced graphene oxide (rGO) composite nanofibers (MPTNF/rGO) have been reported to enhance the electrochemical properties for supercapacitor applications. These composite nanofibers have been synthesized by an efficient route of electrospinning together with the help of easy chemical methods. Both the composites exhibit good charge storage capability with enhanced pseudocapacitance and electric double-layer capacitance (EDLC) as confirmed by cyclic voltammetry studies. MPTNF/HEG composite showed maximum specific capacitance of 210.5 F/g at the current density of 1 A/g, which was mainly due to its availability of the more active sites for ions adsorption on a few layers of graphene wrapped TiO<sub>2</sub> nanofiber surface. The synergistic effect of anatase/rutile mixed phase with one dimensional nanostructure and the electronic interaction between TiO<sub>2</sub> and few layer graphene provided the subsequent improvement of ion adsorption capacity. Also exhibit excellent electrochemical performance to improve the capacitive properties of TiO<sub>2</sub> electrode materials which is required for the development of flexible electrodes in energy storage devices and open up new opportunities for high performance supercapacitors.

**Keywords:** Nanofiber, mixed phase TiO<sub>2</sub>, HEG wrapping, supercapacitors.

## 1. Introduction:

Supercapacitors, as an energy storage device, have attracted considerable interest over the past few decades due to strongly increasing demand in technology for high power density energy storage devices. This high power density is attributed to a charge storage mechanism on basis of which the supercapacitors can be classified in two categories: (i) electrical double layer capacitors that are non-faradaic electrode charge storage process, based on electrostatic charge diffusion and accumulation at the electrode/electrolyte interface, and (ii) pseudocapacitors that are dominated by faradaic reaction, for which charge displacement is based on reversible redox reaction at the surface of the electro-active materials [1,2].

Typically, Pseudocapacitors based on transition metal oxides ( $\text{RuO}_2$ ,  $\text{NiO}_x$ ,  $\text{CoO}_2$ ,  $\text{MnO}_2$ ), hydroxides and conducting polymers (polyaniline) have achieved higher capacitance (300-1200 F/g) through surface redox reaction than electric double layer capacitors (EDLC) (90 and 250 F/g) [3]. Limited charge accumulation in electric double layer restricts the specific capacitance of EDLCs. Thus, significant efforts have been focused on further improvement of the oxide pseudocapacitance materials. However, the electrochemical performance of the pseudocapacitance material is still not optimal due to its low power density and poor electrochemical stability issues because of the irreversible redox process, which causes gradual loss of capacitance [4]. Therefore, current research has been focused on the substantial improvement in electrochemical capacitance and stability of an electrode. The best way to improve the performance of supercapacitors is to develop nanostructure electrodes with the extremely large effective area. Recently, one dimensional (1D) nanostructure materials such as, nanotube, nano fiber, nanowire etc. have exhibited enhanced electrochemical performance than their bulk counterparts due to their large surface area and increased electroactive sites with in a small foot-print [5,6]. These properties provide an optimized ion diffusion path through the electrolyte and into the solid. To address these requirements, more recently a lot of investigations have been conducted on one dimensional  $\text{TiO}_2$  nanofibers for potential applications such as gas and humidity sensors, solar cell, lithium based batteries and photochemical catalysis [7-10]. Additionally, the fiber morphology can provide an adjustable geometry that serves as an easy path for fast ion and electron transport reaction, resulting in reduced internal resistance and improved pseudocapacitive performance.

A promising method to further enhance the capacitance is enhancing the electrical conductivity of electrode by mixing them with highly conductive materials. Graphene, a two dimensional (2D) carbon nanostructure consisting of a single layer of  $sp^2$  bonded carbon atoms has become one of the most promising electrode material for supercapacitors due to its excellent characteristics such as high chemical stability, electrical conductivity and surface area [11]. Among the different transition metal oxide, Titanium dioxide ( $TiO_2$ ) was investigated for electrode material in energy storage devices due to the pseudocapacitance behavior, excellent chemical stability, non-toxicity, natural abundance and low cost[12]. An ideal route to combine the advantage of the nanofiber features with an optimized exfoliated graphene and reduced graphene oxide (rGO) is either incorporated or wrapping on the surface of  $TiO_2$  nanofibers. This combined structure could provide an interconnected electron conducting pathway and could overcome the shortcomings of using graphene or  $TiO_2$  electrode separately.

Here, we report the fabrication of graphene wrapped one dimensional  $TiO_2$  nanofiber by simple electrospinning method. Wrapping by few layer graphene over mixed phase nanofibers were done by hot plate drying and annealing which is free from use of any toxic chemicals. This process leads to graphene wrapped mixed phase of  $TiO_2$  nanofiber that show significantly enhanced the pseudocapacitance properties. Therefore, graphene wrapped 1D  $TiO_2$  nanofiber composite could address aforementioned limitations and thus improve the specific capacitance of  $TiO_2$  material. These materials hold great potential as electrode material for high performance supercapacitors when compared to their counterparts.

## 2. Experimental

### 2.1 Materials Preparation

#### 2.1.1 Fabrication of $TiO_2$ Nanofibers

The electrospun solution was prepared by two steps. Initially, Titanium tetra isopropoxide was added to the mixed solution of ethanol and acetic acid to get a transparent solution. The second solution was prepared using a mixture of 10 ml of ethanol and 2 ml of N, N-Dimethylformamide (DMF) mixed with 0.5g of polyvinylpyrrolidone (PVP) under the magnetic stirring for 30 min. The above two prepared solutions were loaded into a 2 ml syringe having a stainless needle with diameter of 0.6 mm. A constant flow rate of fluid was set to 0.3

ml/h using a syringe pump. A high voltage power of 20 kV was applied to the needle tip. The charged nanofibers were deposited on Aluminium foil wrapped around the flat plate and placed 15 cm between the tip of the needle and collector of the aluminium plate. Finally, the mixed phase TiO<sub>2</sub> nanofiber can be obtained by calcined at 600 °C for 1h under air atmosphere.

### 2.1.2 Fabrication of MPTNF/HEG and MPTNF/RGO Composites

Using the modified Hummers method the graphite oxide (GO) was prepared from graphite powder [13]. Graphene was obtained by thermally exfoliate GO at 200° C under hydrogen atmosphere in a tubular furnace and labelled as HEG (Hydrogen exfoliated graphene). Graphene was synthesized by hydrogen exfoliation technique which has wrinkled structure due to the rapid removal of oxygen containing functional groups [14]. To prepare the mixed phase of TiO<sub>2</sub>/HEG composites, first functional groups were introduced on HEG. For this purpose HEG was treated with concentrated H<sub>2</sub>SO<sub>4</sub> and concentrated HNO<sub>3</sub> in 3:1 ratio, which result in attachment of oxygen containing functional groups (–OH, –COOH) over the surface of HEG. The sample was washed several times till pH was neutral and further dried at 60 °C in a vacuum oven for 12 h. Final sample was labelled as f-HEG (Functionalized hydrogen exfoliated graphene) and it was added in 60 ml of deionized water. Then, sonicated for 1h to obtain the homogeneous dispersion of f-HEG. Furthermore, 5 mg of MPTNFs (Mixed phase TiO<sub>2</sub> nanofibers) was added into f-HEG and GO separately. These mixtures were dispersed under continuous stirring to mix homogeneously. The obtained brown colored product was annealed at 400°C for 1h under an argon atmosphere to produce HEG and rGO wrapped TiO<sub>2</sub> NFs by the reduction of functional group on HEG and reduction of GO. These two types of composites will be referred as MPTNF/HEG (Mixed phase TiO<sub>2</sub> nanofibers/ Hydrogen exfoliated graphene) and MPTNF/RGO (Mixed phase TiO<sub>2</sub> nanofibers/ reduced graphene oxide) throughout the manuscript.

### 2.2. Characterization

The surface morphology and elemental composition of the samples were examined using a Quanta 200 FEG field emission scanning electron microscope (FESEM) operating at 20 kV and a high resolution transmission electron microscope (JEOL JEM 2100) operating at 200

kV. The phase structure was characterized using a Rigaku Rintz Ultima X-ray diffraction unit. Raman spectra were recorded at room temperature using a LabRAM HP 800 UV with a 632 nm He–Ne laser as the excitation source, in the range of 100–3000  $\text{cm}^{-1}$ . Fourier transform infrared (FT-IR) spectral analysis was carried out using an FT-IR spectrometer (Nicolet FT-IR 4700) with KBr pellets in the frequency range 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$ .

### 2.3 Electrochemical characterization

Cyclic voltammetry and chronopotentiometry charge/discharge of the synthesized sample and its composites were investigated by scanning over the potential range of 0.0 to 1.0 V in an aqueous 1M  $\text{H}_2\text{SO}_4$  solution by using potentiostat/galvanostat (Ivium-Stat Technologies compactstat) with the standard three-electrode cell configuration. A platinum wire was used as counter electrode, Ag/AgCl was used as reference electrode. The working electrode material was prepared using a mixture of the material i.e. polyvinylidene fluoride (PVDF) as binder (15%), conductive carbon (10%) and active material (75 wt%). Then, N-methyl-2-pyrrolidone (NMP) solvent was added to the mixture to form a slurry using mortar and pestle. This slurry was coated on the carbon sheet (active surface 1  $\text{cm}^2$ ) and was dried at 120  $^\circ\text{C}$  which is used as working electrode and it was exposed to the electrolyte during electrochemical measurements.

## 3. Results and discussion

The crystalline structure and phase composition of GO, f-HEG, MPTNFs and MPTNF/rGO and MPTNF/HEG as shown in Fig. 1A. The dominant diffraction peak of GO centered at  $2\theta = 10.92^\circ$  corresponding to the d-spacing of 0.83 nm [15,16], indicating that the introduction of functional groups on the basal plane of graphite during the oxidization of natural graphite which increases the d spacing from 0.33 nm to 0.83 nm [13,15]. XRD pattern of f-HEG shows very less intense peak around  $24.4^\circ$  indicating the distorted graphite structure and additionally sharp peak appeared due to restocking of graphene sheets through the functional groups. In MPTNFs, the peaks located at  $25.35^\circ$ ,  $37.88^\circ$ ,  $48.04^\circ$ ,  $64.09^\circ$  and  $69.87^\circ$  correspond to (101), (004), (200) (204) and (116) planes of the anatase phase respectively (JCPDS card # 21-1272) [10], and the peaks located at  $27.61^\circ$ ,  $36.10^\circ$ ,  $39.27^\circ$ ,  $44.08^\circ$ ,  $54.38^\circ$ ,  $56.60^\circ$ ,  $62.92^\circ$  and  $69.05^\circ$  correspond to the (110), (101), (111), (210), (211), (220), (002) and (301) planes of the

rutile phase respectively (JCPDS card # 21-1276) [17], indicating the mixed phase of  $\text{TiO}_2$  nanofibers. All the identified peaks of the diffraction pattern of the composite exhibited a similar crystal structure of mixed phase of  $\text{TiO}_2$ . Notably, there is no typical rGO and HEG peaks were observed in the composite, apparently due to the overlap or screened by (101) the diffraction peak of  $\text{TiO}_2$  [18,15].

The FT-IR spectrum of GO, f-HEG, MPTNF, MPTNF/RGO and MPTNF/HEG composite in the wavelength range of  $400\text{--}4000\text{ cm}^{-1}$  were depicted in fig 1B. FT-IR spectrum of GO shows absorption bands at  $3386\text{ cm}^{-1}$ ,  $1732\text{ cm}^{-1}$ ,  $1611\text{ cm}^{-1}$ ,  $1370\text{ cm}^{-1}$ ,  $1227\text{ cm}^{-1}$  and  $1053\text{ cm}^{-1}$  which are attributed to the O-H stretching vibration, C-O-H stretching of COOH groups, C-C skeletal vibrations of un-oxidized domains, C-O-H deformation, C-OH stretching (epoxyl groups) and C-O stretching vibrations (alkoxy groups) respectively [10]. During the acid treatment, a significant amount of functional groups are attached which are observed in the FTIR spectrum of f-HEG. Moreover the entire composite exhibit the same absorption band at low frequency around  $516\text{ cm}^{-1}$  corresponds to the stretching vibration of Ti-O-Ti which is similar to the MPTNF. Conspicuously, most of the peaks arising due to the oxygen containing functional groups are disappear in the MPTNF/RGO and MPTNF/HEG composites. Additionally, a another band around  $442\text{ cm}^{-1}$  as observed in the FTIR spectra of the composites which indicates that the formation of Ti-O-C bonds during the synthesis process [19].

In order to further confirm the crystalline quality and the formation of the chemical bonds in the MPTNFs and its composite, Raman spectrum was recorded in the range of  $200\text{ to }2500\text{ cm}^{-1}$ . Fig. 1C shows the Raman spectrum of GO, f-HEG, MPTNFs MPTNF/RGO and MPTNF/HEG. The characteristic D ( $1348\text{ cm}^{-1}$ ) and G ( $1595\text{ cm}^{-1}$ ) peaks of GO indicate the D-band corresponds to the defects induced in the graphitic structure, and G-band corresponds to the graphitic  $\text{Sp}_2$  carbon [19] respectively with an intensity ratio  $I_D/I_G$  is 1.04. Raman spectrum of f-HEG shows D band ( $1336\text{ cm}^{-1}$ ) and G band ( $1595\text{ cm}^{-1}$ ), which implies that the oxygen containing functional groups presented at the surface of the graphene sheets. Functionalization increases the defect on the graphene surface, which enhance the intensity of D band in the raman spectrum of f-HEG [20]. Hence, oxygen containing functional groups are presented at the surface of the few layers of graphene sheets which bring about a change in the reduced mass of



the harmonic oscillator [21]. For MPTNFs, Raman spectra shows three bands at 148, 436 and 612  $\text{cm}^{-1}$  corresponding to the  $E_{1g}$  (anatase),  $E_g$  (rutile) and  $A_{1g}$  (rutile) respectively and additionally, a broad band at 248  $\text{cm}^{-1}$  was observed due to second-order scattering feature [10]. Beside, All other composite exhibits the same bands with a slight shift compare to MPTNFs with D and G bands, it may attributed to the formation of the composite. The  $I_D/I_G$  intensity ratio of MPTNF/rGO and MPTNF/HEG was found to be 0.99 and 0.97 respectively (Fig.1D), which illustrate that the considerable de-functionalization of epoxide, hydroxyl and other oxygen containing functional groups during the reduction process of the composites [22]. The low value of the  $I_D/I_G$  ratio of the composite demonstrated the strong interaction between Ti and C via Ti-O-C bonds on the surface of the nanofibers by interacting carbon ions with surface of the  $\text{TiO}_2$  nanofiber for the formation of composites. Furthermore, after the removal of the oxygen containing functional groups, the defects were neutralized by making further bonds with Ti on the surfaces of the MPTNFs. Both the raman spectra of the MPTNFs and composites shows the similar vibration modes in the low frequency range, except for a shift that can be attributed to the strong interaction between the Ti atoms on the surface of NFs with C via Ti-O-C bonds [23]. Ergo, the reduction of the crystal defects and lattice distortion were occurred, during the formation of the composites, which helps in the restoration of  $\text{sp}^2$  hybridized domains [15].

The morphological properties of the GO, f-HEG, MPTNF, MPTNF/RGO and MPTNFG/HEG were analyzed using FE-SEM as shown in figure 2. The FE-SEM images of the as spun TNFs (Fig. 2C ) show a relatively smooth surface with the average diameter of 145 nm. After calcination (Fig.2D), the average diameter of the nanofibers shrank to 120 nm with a rough surface and porous nature. The FE-SEM image of the composites shows the similar morphology of the bare MPTNFs (fig 2 E& F). The elemental composition of the samples was evaluated by the energy dispersive X-ray analysis (EDXA). The MPTNF shows expected elements of titanium and oxygen as shown in fig.3. The illuminating electron beams on MPTNFG composites confirmed the existence of C, Ti, and O, which is listed in the table 1.

In order to determine the crystalline structure of GO, f-HEG, MPTNFs, MPTNF/rGO and MPTNF/HEG, TEM and HRTEM observations were carried out as shown in Fig. 4. Fig. (A & B) represent the TEM image of GO and f-HEG. The f-HEG shows the wrinkled nature is evident

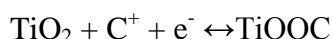


and these wrinkled region contain lots of defect and higher surface energy to improve the supercapacitor performance. The HRTEM image of MPTNFs reveals the formation of both anatase and rutile mixed phase nature of the nanofibers and also the inter-planar lattice spacing of about 0.35 nm corresponding to the (101) plane of the anatase phase and the inter-planar spacing of 0.32 nm corresponding to the rutile (110) plane of  $\text{TiO}_2$  (Fig. 4E). Fig. 4D and 4F show the TEM and HRTEM images of the composite MPTNF/HEG respectively. It can be observed from the HRTEM image (Fig. 4F) of the composite, that the HEG wrapped the surface of MPTNFs with the inter-planar spacing of about 0.37 nm, which is slightly higher than the inter-planar spacing of graphite (about  $\sim 0.34$  nm) but smaller than that of graphene oxide ( $\sim 0.83$  nm). Because of the removal of most of the oxygen containing functional groups from f-HEG.

### 3.1 Electrochemical properties

To evaluate the electrochemical properties of GO, f-HEG, MPTNF, MPTNF/rGO, and MPTNF/HEG, electrochemical measurements were conducted in a three-electrode electrochemical cell in 1M  $\text{H}_2\text{SO}_4$  electrolyte over the potential range 0.0 V to 1.0 V and scan rate of  $100 \text{ mV s}^{-1}$ . Fig. 5A shows the cyclic voltammetric (CV) curves of the GO, f-HEG, MPTNF, MPTNF/rGO, and MPTNF/HEG. CV curves of MPTNF displayed redox peaks (faradaic reaction), indicating the pseudocapacitive behavior of the electrodes. All other CV curves of the samples displayed a rectangular, symmetric shape with small redox peaks that resembles the electrical double-layer capacitance behavior (non-faradaic behavior) and fast charging/discharging process which indicate that both capacitive and redox reactions transpire in the hybrid supercapacitors [24, 25]. In comparison with other samples, MPTNF/HEG composite CV curves exhibit noticeable amount of variation in current. Therefore, the enhanced electrochemical performance of MPTNF/HEG could be attributed to the enhanced electrical conductivity of the composite electrode facilitating the transport of charge carriers. CV loop of MPTNF/HEG composite had shown the largest integrated area, indicating that this composite had the highest capacity. This high capacitive performance could be attributed to the conjunction of HEG with the  $\text{TiO}_2$  nanofiber, which caused high electrical conductivity of the composite. Also the fibrous structure of the composite had quick transfer of electrolyte into the electrode material. Additionally, HEG covered over the one dimensional morphology of  $\text{TiO}_2$  has a

considerable effect on electrochemical performance due to this unique morphology and high surface area consider both pseudocapacitance and double-layer behavior and enhance the ECS performance [26,27]. The pseudocapacitance behavior of  $\text{TiO}_2$  arises from the reversible redox transition involving the exchange of protons and/or cations with the electrolyte ( $\text{H}_2\text{SO}_4$ ). The redox peaks in the CV for the composite material resulted from the oxidation and reduction of  $\text{Ti}^{4+}$  ions in the  $\text{TiO}_2$ -HEG electrode [11]. The following equation is used to explain the proposed mechanism (Eq. (2)):



where  $\text{C}^+$  indicates the protons and alkali metal cations present in the electrolyte. Both protons and alkali metal cations are involved in the redox process. Additionally, one dimensional  $\text{TiO}_2$  structures increase the surface area and electro-active sites, which effectively reduces the diffusion length of the  $\text{H}^+$  ion in the electrode matrix. Due to high electronic conductivity of graphene and excellent interfacial contact between  $\text{TiO}_2$  and graphene, fast transportation of electrons promote in all aspects [28,29].

EIS analysis was carried out to evaluate the electrochemical behavior of the electrode materials for supercapacitors [28]. Typical Nyquist plots of the GO, f-HEG, MPTNF, MPTNF/RGO and MPTNF/HEG electrode are shown in Fig. 5C. Nyquist plots used to measure the  $R_s$  series resistance of the synthesis samples. The calculated  $R_s$  values for GO, f-HEG, MPTNF, MPTNF/RGO and MPTNF/HEG hybrid electrodes are 0.36, 0.29, 0.45, 0.26 and 0.23 respectively. MPTNF/HEG composite electrode has a low  $R_s$  value compare with the other electrodes, which indicating the wrapping of graphene nanosheets on the surface of the  $\text{TiO}_2$  nanofiber. As a result charge transfer performance of the electrode was improved. The electrochemical performance of the samples was further evaluated to find the specific capacitance using chronopotentiometry charge-discharge measurements (Fig. 5B) at the current densities of 1A/g in the potential range of 0.0–1.0 V. The following equation [28] used to calculate the The specific capacitance of the electrode material from the galvanostatic charge-discharge curve,

$$C_s = I\Delta t/m\Delta v$$

where,  $I$  is the discharge current in mA,  $m$  is the mass of the electro-active material,  $\Delta v$  is the potential window and  $\Delta t$  is the discharge time. MPTNF/HEG composite exhibited the best capacitive performance compare than other materials. The specific capacitance of MPTNF/HEG was calculated to be 210.5 F/g which is higher than the previous literatures reports and summarized in Table 1.

Fig. 6A shows the CV response of the composites with different mass ratio for MPTNF/rGO and MPTNF/HEG [ratios of 1:0.25, 1:0.5, 1:1] which will be referred to as MPTNF/rGO-1, MPTNF/rGO-2 MPTNF/rGO-3 and MPTNF/HEG-1 MPTNF/HEG-2 MPTNF/HEG-3 respectively. However, the use of an excessive amount of graphene in the MPTNF/HEG-3 and MPTNF/rGO-3 composites shows the less performance in the electrochemical properties. Thus, an optimal amount of graphene was considered in the preparation of the composites to enhance the electrochemical performance.

In order to evaluate the rate capability of MPTNF/HEG and MPTNF/HEG hybrid electrodes, Fig. 6B emphasizes the specific capacitance values at various current densities. We observed that, when increase the current density from 1 to 4 A/g, the specific capacitance for both composites electrodes were decreased. The cycling stability is one of the most important parameters for the application of supercapacitors. Fig.6C shows the charge/discharge measurement at a current density of 1A/g for 1000 cycles. Notably, the MPTNF/HEG electrode retained 97% of its initial capacitance after 1000 continuous charge/discharge cycles which demonstrate an excellent cycle stability.

These improved performance in MPTNF/HEG composite, presumably is associated with the combination effect of the specific surface area and high conductivity, which facilitates the transport of charge carriers.

#### 4. Conclusions

In summary, HEG and rGO wrapped mixed phase  $\text{TiO}_2$  as a electrode material for supercapacitors were prepared by using the electrospinning technique, along with easy chemical methods. More importantly, it does not require any toxic solvents or chemicals to reduce the graphene oxide. Fibrous morphology was clearly evident from the SEM observations.

Pertriculrly, the properties of both anatase rutile mixed phase of  $\text{TiO}_2$  and its composite with graphene greatly improve the supercapacitors performance. Our results showed that the HEG– $\text{TiO}_2$  hybrid electrode exhibited a maximum specific capacitance of  $210.5 \text{ F g}^{-1}$  in  $1\text{M H}_2\text{SO}_4$  electrolyte solution at the current density of  $1 \text{ A/g}$ . The improved specific capacitance of the MPTNF/HEG hybrid electrode was mainly attributed to the pseudocapacitance of the  $\text{TiO}_2$  phase and partially influenced by the intrinsic double layer capacitance of the graphene sheets. This kind of graphene– $\text{TiO}_2$  hybrid electrodes are a highly suitable, promising electrode materials, which may provide new possibilities of access high quality and reliable electrodes for next-generation high-performance supercapacitors.

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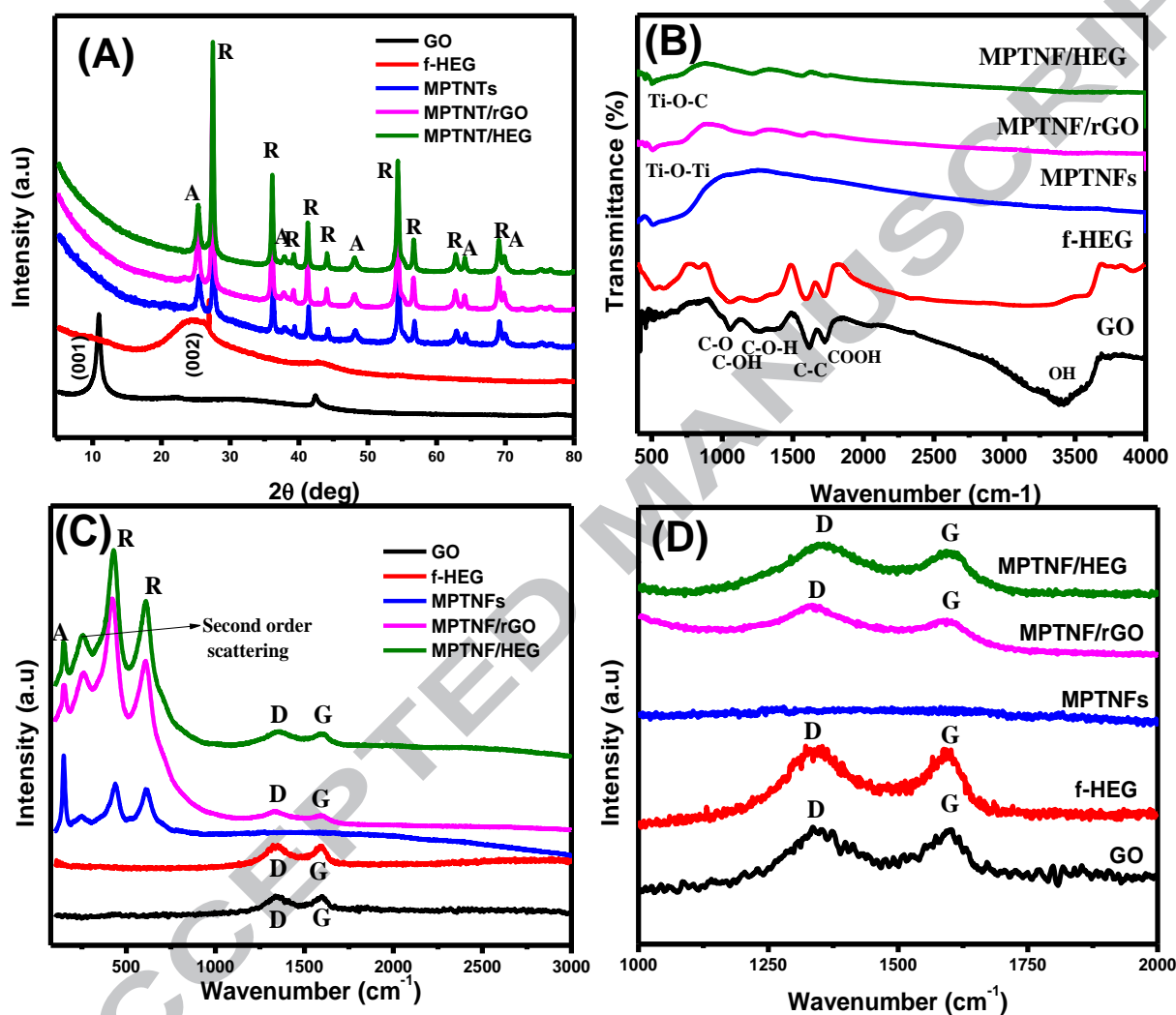
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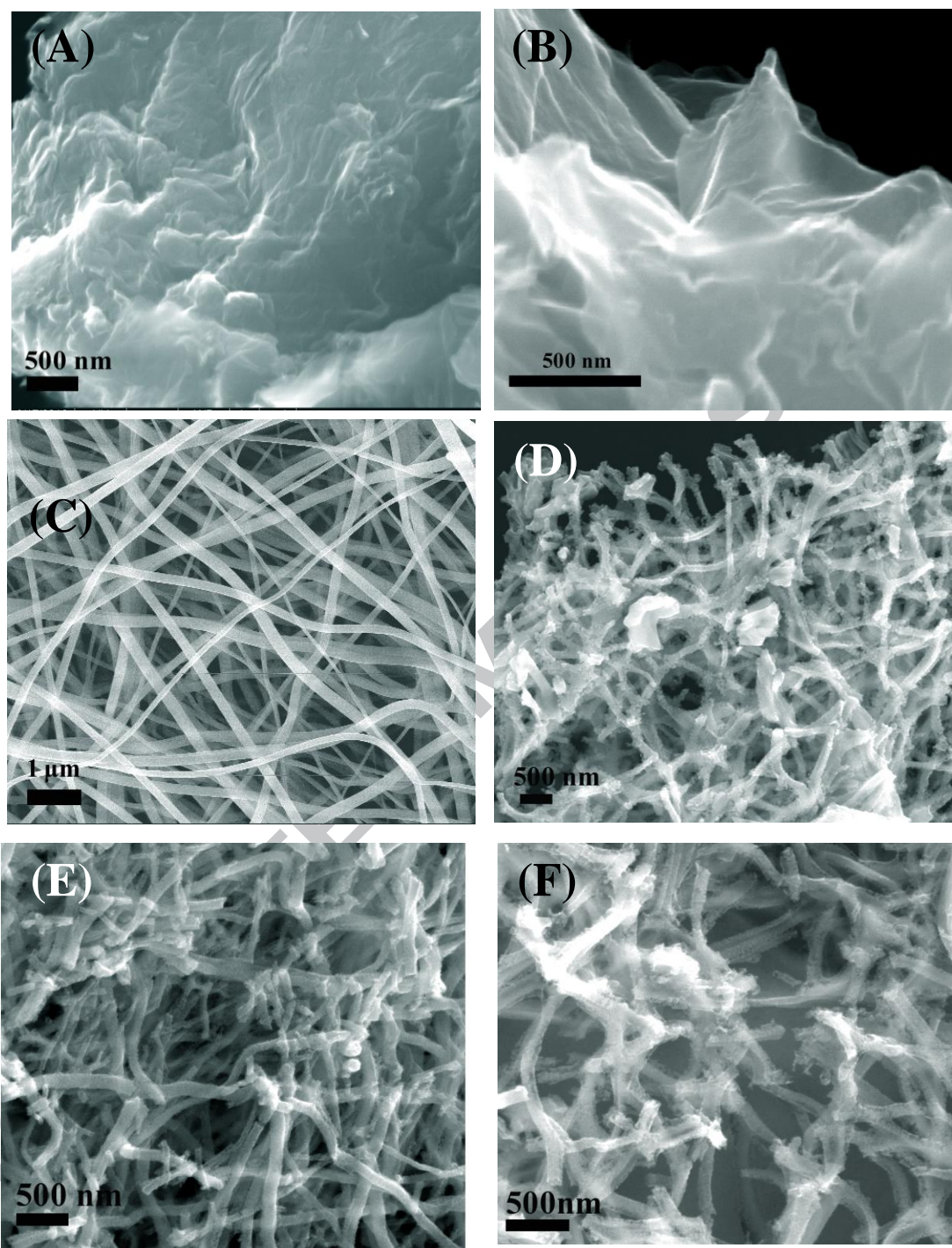
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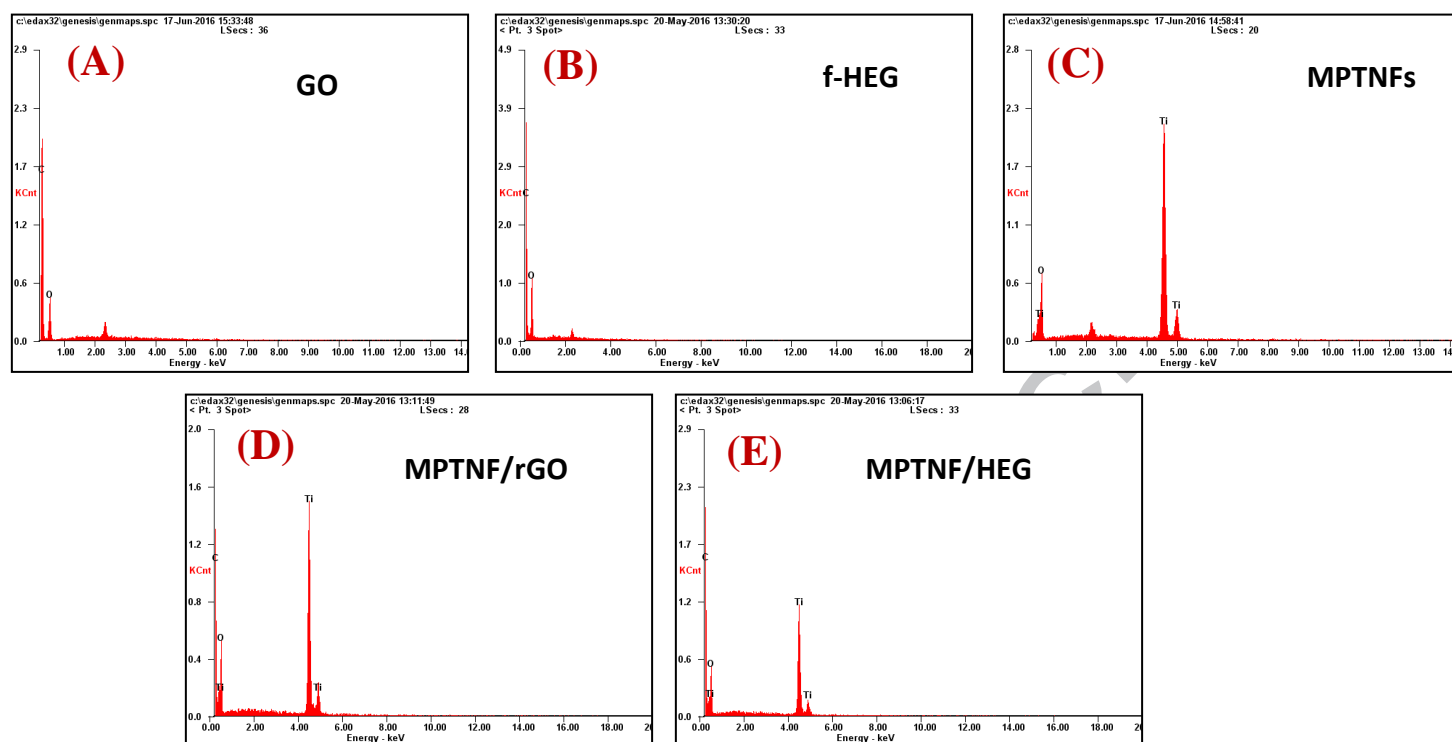




**Fig.1.** (A) XRD, (B) FTIR, (C) Raman, spectra of GO, rGO, MPTNFs, MPTNF/rGO and MPTNF/HEG composites. Figure D shows Raman spectra of GO, rGO, MPTNFs, MPTNF/rGO and MPTNF/HEG composites in the range of 1000-2000  $\text{cm}^{-1}$ .



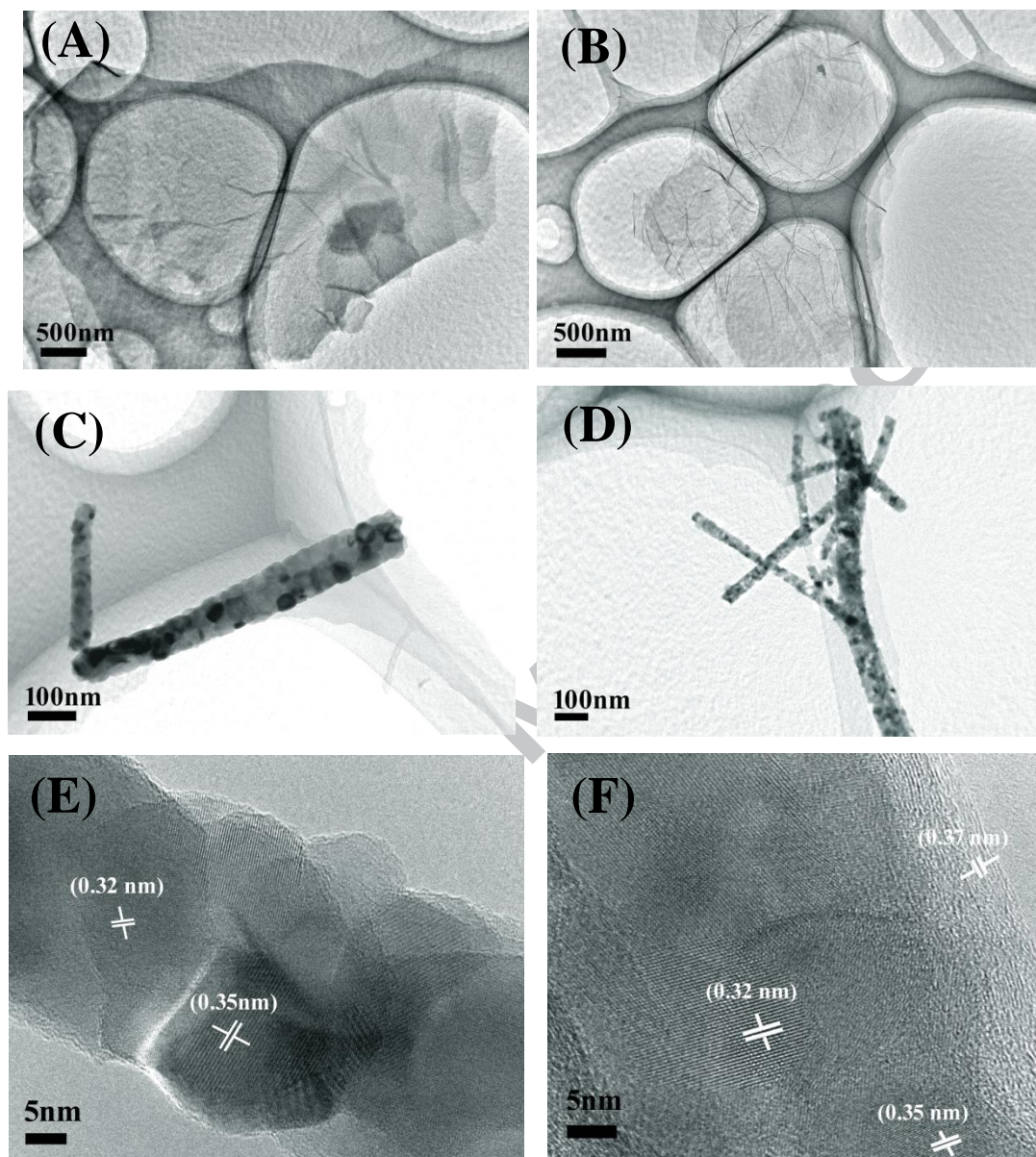
**Fig. 2.** FE-SEM images of (A) GO, (B) f-HEG, (C) as-spun NFs (D) MPTNFs after calcination (E) MPTNF/rGO and (F) MPTNF/HEG.



**Fig. 3.** EDAX spectrum of (A) GO (B) f- HEG (c) MPTNFs (D) MPTNF/rGO and (E) MPTNF/HEG.

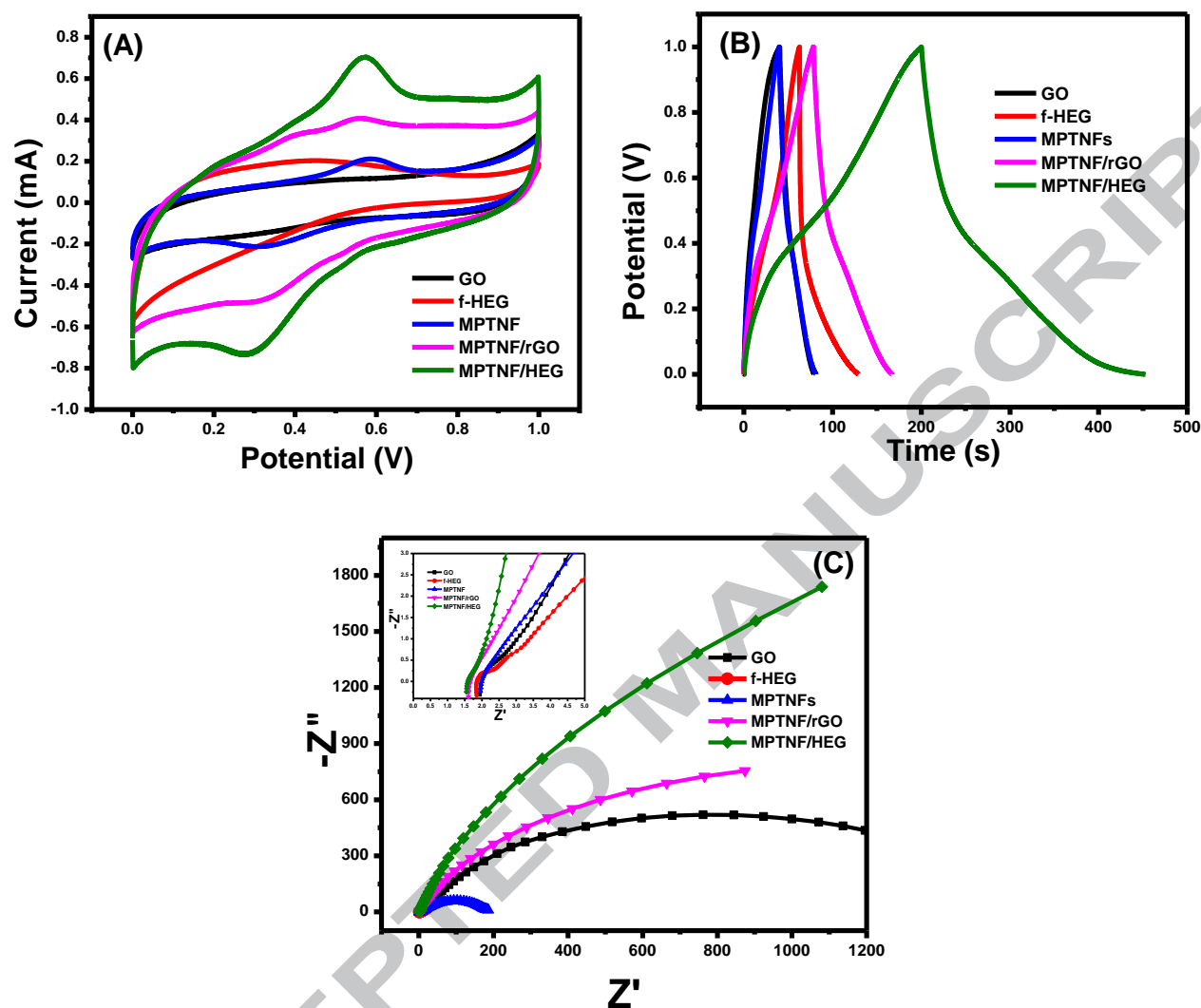
**Table:1**

Sample	Element weights%			Atomic%			Total
	Ti	O	C	Ti	O	C	
GO	-----	36.52	63.48	-----	30.16	69.84	100
f-HEG	-----	26.75	73.25	-----	21.52	78.48	100
MPTNFs	55.88	44.12	-----	29.73	70.27	-----	100
MPTNF/rGO	50.78	32.24	16.98	23.62	44.89	31.49	100
MPTNF/HEG	31.75	28.91	39.34	11.54	31.45	57.01	100

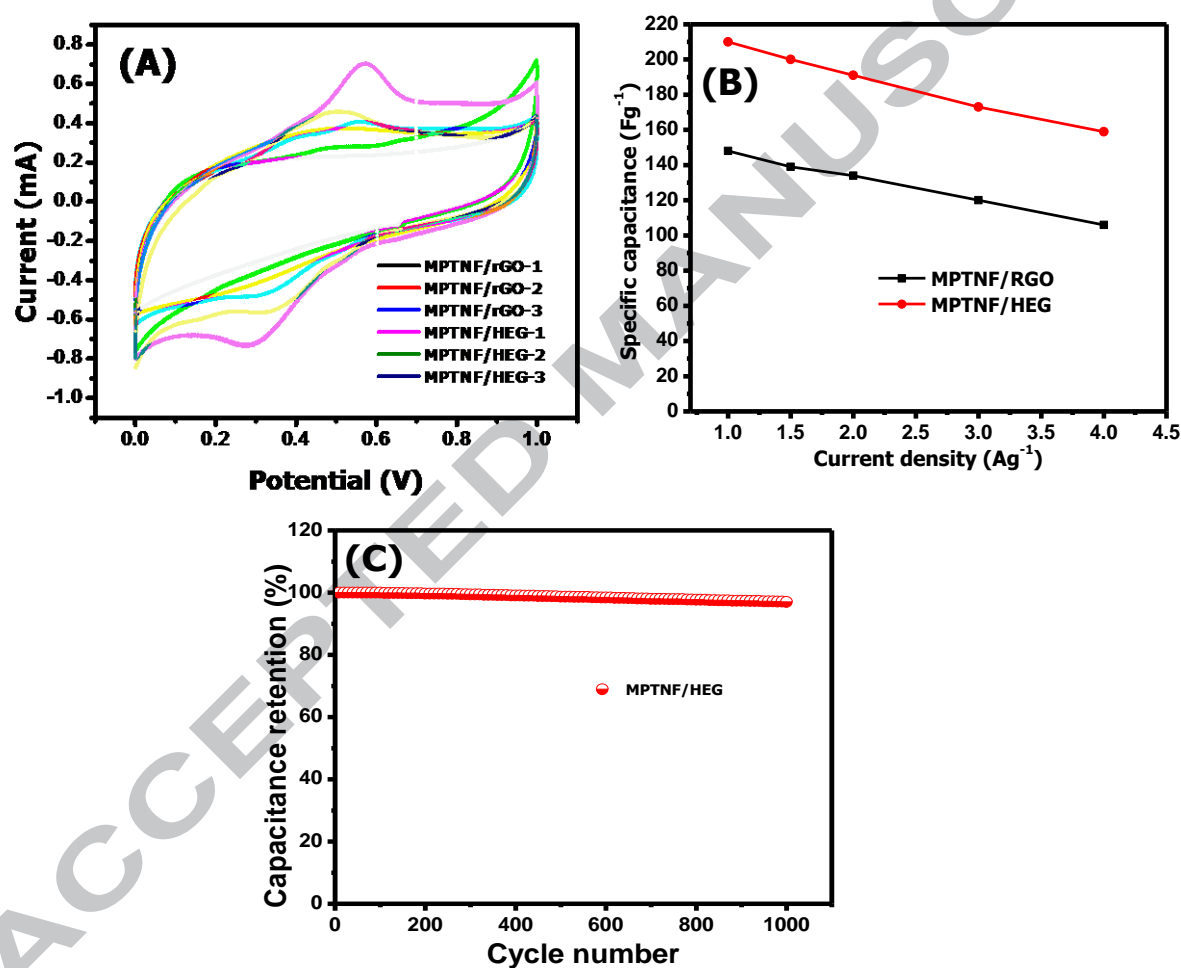


**Fig. 4.** TEM image of (A) GO, (B) f-HEG, (C) MPTNFs and (D) MPTNF/HEG composite. nanofiber, (E) and (F) shows HRTEM images of MPTNFs and MPTNF/HEG composite nanofiber respectively.





**Fig. 5.** (A) CV curve of GO, f-HEG, MPTNFs, MPTNF/rGO and MPTNF/HEG composite nanofiber, (B) CD curves of GO, f-HEG, MPTNFs, MPTNF/rGO and MPTNF/HEG composite nanofiber and (C) shows EIS of the GO, f-HEG, MPTNFs, MPTNF/rGO and MPTNF/HEG composite nanofiber respectively.



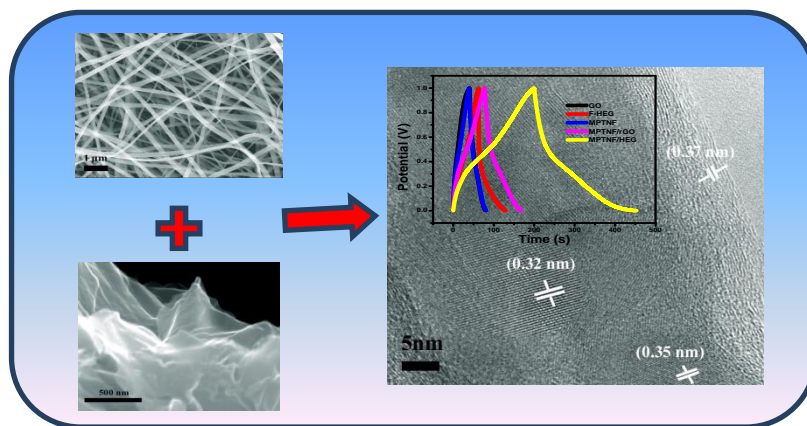
**Fig. 6.** (A) CV curve of MPTNF/rGO and MPTNF/HEG composites nanofibers with different mass ratio (B) Specific capacitance of MPTNF/rGO and MPTNF/HEG composites as a function of different current densities and (C) Cycle stability measurement of MPTNF/HEG composites at the current density of  $1\text{Ag}^{-1}$ .

Table 1

S. No	Materials	Current density	electrolyte	Specific capacitance	Ref
1	carbon/TiO <sub>2</sub> /rGO	0.0001 A	0.5 M Na <sub>2</sub> SO <sub>4</sub>	23.6 mF/cm <sup>2</sup>	[30]
2	Three-dimensional TiO <sub>2</sub> –graphene hydrogel electrode	1 A g <sup>-1</sup>	1 M Na <sub>2</sub> SO <sub>4</sub>	175 F g <sup>-1</sup>	[4]
3	p/p -TiO <sub>2</sub> /activated carbon composite electrodes	2 mvs <sup>-1</sup>	0.1N Na <sub>2</sub> SO <sub>4</sub>	122 Fg <sup>-1</sup> .	[31]
4	graphene–TiO <sub>2</sub> hybrid electrode	2.5 mAcm <sup>-2</sup>	1 M Na <sub>2</sub> SO <sub>4</sub>	136 F g <sup>-1</sup>	[28]
5	TiO <sub>2</sub> /C NTAs	1 mA/cm <sup>2</sup>	1.0 M H <sub>2</sub> SO <sub>4</sub>	20.1mf/cm <sup>2</sup>	[32]



## Graphical abstract



Few layer graphene wrapped one dimensional  $\text{TiO}_2$  nanofibers were synthesised by simple electrospinning method together with the hot plate method. These composite showed maximum specific capacitance of 210.5 F/g at the current density of 1 A/g, which was mainly due to its availability of the more active sites for ions adsorption on a few layers of graphene wrapped anatase/rutile mixed phase  $\text{TiO}_2$  nanofiber surface.

**Highlights:**

1. Synthesis of high performance electrode materials.
2. Wrapping by few layer graphene over mixed phase nanofibers were done by hot plate drying and annealing which is free from use of any toxic chemicals.
3. The HEG-TiO<sub>2</sub> hybrid electrode exhibited a maximum specific capacitance of 210.5 F g<sup>-1</sup> in 1M H<sub>2</sub>SO<sub>4</sub> electrolyte solution at the current density of 1 A/g.