Flexible supercapacitor electrodes based on TiO$_2$/rGO/TiO$_2$ sandwich type hybrids

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ABSTRACT

The flexible nanostructured supercapacitors have gained vast majority of interests during recent years. In this article, flexible supercapacitor electrode based on TiO$_2$/rGO/TiO$_2$ sandwich is fabricated through a facile low cost solution process method based on pre-synthesized GO paper and titania sol. The XRD and FTIR spectroscopy analyses confirm the in-situ reduction of GO paper when faced with the titania sol. The Raman spectroscopy shows the coexistence of titania anatase phase beside rGO layers. Moreover, FESEM analysis demonstrates that the sandwich electrodes are composed of titania and rGO layers with thickness of about 660 nm and 15 µm, respectively. The optimum parameter for film deposition is 0.17 M concentration, water to Ti precursor ratio of 4, acid catalyst to Ti precursor ratio of 0.5, and solvent of I-propanol. The supercapacitor electrode based on this optimum deposited sandwich illustrates capacitance of 83.7 F/g at scan rate of 5 mV/s and appreciable charge-discharge behavior. These hybrid pseudo- and electric double layer capacitance behavior in this supercapacitor not only can dramatically improve the performance of the future energy storage devices but also can be applicable in cost-effective wearable electronics.

1. Introduction

Modern society needs of flexible tools including rollable and bendable devices and portable electronic papers, namely wearable sensors, and artificial body parts have dramatically increased in recent years. Devices for wearable applications need to be lightweight, flexible, and energy efficient. Flexible energy storage devices have recently attracted tremendous interest and are under growing studies for their potential applications in various electronic systems [1–3]. Supercapacitors are an important class of energy storage devices, considered as high-power systems given the fact that the charge storage occurs at the surface and is not limited by the diffusion process occurs in batteries. Ultra-capacitors typically store 10–100 times energy per unit volume than electrolytic capacitors, which can charge/discharge much faster, and tolerate more charge/discharge cycles compared to rechargeable batteries. However, they commonly do not have high energy density, which inhibits their large scale utilization. They are also ten times larger than conventional batteries for a given charge [4–7]. Carbon based supercapacitor electrodes such as activated carbon, carbon nanotubes (CNTs), and graphene have high power density, and are nowadays applicable in flexible electronics due to their high stiffness. However, they suffer from low energy density (a low electrode capacitance value) which is an obstacle to its development as electrode materials [8–10].

Among carbon based materials, graphene has higher intrinsic capacitance [11]. Graphene, single layer allotrope of carbon in the form of a two-dimensional, atomic-scale, honey-comb lattice has attracted increasing attention, since its first fabrication by Novoselov et al. [12,13] due to its exceptional electronic, optical, thermal, and mechanical properties. Graphene have been used in a variety of electronic applications such as sensors, catalysts, and energy storage applications due to its high charge carrier mobility and high specific surface area of approximately 2600 m$^2$/g [14,15]. There are various methods for graphene synthesis, such as micromechanical exfoliation [13,16], chemical vapor deposition [17], chemical routes [18], epitaxial growth by heating of silicon carbide [19], among which the chemical exfoliation of graphite by introduction of oxygen functional groups and graphene oxide (GO) preparation is known as one of the most popular methods because of its low cost and simplicity. The most common method for synthesis of GO was developed by Hummers and Offeman [20]. However, this method has gone through changes by Tour and co-workers which turned it to a safer and more cost beneficial route [21]. The free

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Graphene were previously reported, the sandwich like TiO2/rGO/TiO2 was synthesized by using low cost and simple sol-gel method. Sandwich like poration induced self-assembly process, is dip coated by titania sol as the substrate for graphene-metal oxide hybrid as it surpasses many other paper like materials in mechanical properties namely flexibility, which is one of the most important factors concerned in wearable electronics. The flexible GO paper which would be reduced during the heat treatment in the presence of Ti, participates in charge transfer (therefore low conductivity of titania is no longer an issue) and the titanias plays the major role in providing high surface area for charge storage and high energy density of pseudocapacitor characteristic in this hybrid material. Direct growth of crystallized TiO2 shells on the surface of rGO would be difficult according to the fact that there is lack of chemical interactions between graphene and TiO2, as TiO2 nanoparticles, only grow on defects of rGO surface which forms discontinuous zone. This interferes with the electrochemical activity of the composite and impedes the materials from reaching their highest potential. This is an issue which would be solved by simultaneous reduction of GO paper and crystallization of TiO2 nanoparticles. Very recently, Ghorbani et al. have reported specific capacitance of 60.63 F g−1 at scan rate of 5 mV s−1 for ZnO/rGO/ZnO sandwich structure. Zhao et al. fabricated a uniform mesoporous TiO2/graphene/mesoporous TiO2 sandwich like structure for lithium ion battery electrodes with reversible capacity of 237 mAh g−1 after 100 cycles at a current density of 20 mAg−1. Xiang et al. have reported the specific capacitance of composite structure of rGO with TiO2 nanobelts and nanospheres, 225 F g−1 and 62.8 F g−1 at a discharge current density of 0.125 A g−1, respectively. Graphene–TiO2 hybrid nanostructure, using microwave assisted method, 30% H2O2, produced by evaporation induced self-assembly method[22,23]. The GO papers were synthesized using improved Hummers method based on our previous report[41]. Typically, 0.5 g of the graphite powder was dispersed in 60 mL H2SO4 and 6.6 mL H3PO4 and stirred for 2 h. Then, the mixture was put into a DI water bath and 3 g KMnO4 was added to the mixture, producing an exotherm to 40 °C. The reaction was then heated to 50 °C and stirred for 12 h. The color of the mixture changed from dark green to light brown. It was then, cooled to room temperature and poured onto 400 mL ice. There would be an obvious change in color of the mixture from light to dark brown in this section. 0.5 mL of 30% H2O2 was later added to the mixture and the color changed into light yellow. After the settlement of the mixture, the supernatant was decanted away and the precipitate was centrifuged by 200 mL of HCl and then water, at 12,000 rpm, until the mixture reached to higher pH. To separate the GO sheets from graphite oxide, the suspension was sonicated, followed by centrifugation at 4000 rpm for 45 min. The homogenous dispersion then was poured into a petri dish and allowed to dry overnight in air atmosphere. It was then peeled off from the petri dish. The obtained free standing GO paper can be seen in Fig. 1a showing the paper geometry is maintained after peeling off. It was then cut into pieces and restored for further deposition.

2.3. Titania sol preparation

A stable and transparent sol is indispensable for a high quality TiO2/rGO/TiO2 sandwich structure. The process of sol preparation is reported elsewhere[42]. Typically, the TTIP:DIW:Acid catalyst ratio is 1:4:0.5 and the concentration is 0.17 M. Primarily, TTIP was dissolved in the half volume of solvent under stirring for 10 min. In another beaker, solution of solvent, DIW, and acid catalyst was prepared and added drop wisely to the TTIP solution under vigorous stirring, and then stirred for 1 h. Various parameters of solvent type, concentration, acid type, Acid/TTIP (A/T) and Water/TTIP (W/T) molar ratio are considered and tabulated in Table 1. While one parameter is changed, the others are held constant.

2.4. TiO2/rGO/TiO2 sandwich preparation

The prepared sol was deposited on flexible GO paper substrate with dip coating method and dried at 100 °C for 10 min. The deposition of titania sol on GO substrate was repeated 10 times to achieve desired thickness of titania layer. All the coated substrates were calcined at 300 °C in air followed by 500 °C in argon atmosphere results in simultaneous reduction of GO to rGO paper and crystallization of TiO2 nanoparticles. This method, not only prevents the non-uniform growth of titania nanoparticles on the surface of rGO substrate but it also is very simple, low cost and safe unlike the reduction methods of GO paper by using hydrazine or applying heat treatment at high temperatures.

Although the flexible supercapacitor electrodes based on TiO2/graphene were previously reported, the sandwich like TiO2/rGO/TiO2 flexible supercapacitor electrode synthesized by this method has never been reported. This article may pave the way of the storage media for wearable electronic applications.

2. Materials and methods

2.1. Materials

Graphite powder (Sinchem, 150–200 mesh, 95%), sulfuric acid (H2SO4, Merck, 98%), potassium permanganate (KMnO4, Merck, 99%), hydrogen peroxide (H2O2, Merck.), and hydrochloric acid (HCl, Merck, 32%) were used for synthesis of GO paper. Materials including methanol (MeOH, analytical reagent grade), ethanol (EtOH, synthetic grade), 1-propanol (1PROH, analytical reagent grade), 1-butanol (1BuOH, analytical reagent grade), nitric acid (HNO3, 65%), hydrochloric acid (HCl, Merck, 32%), and titanium tetra isopropoxide (TTIP, Merck, 99%) were used for sol preparation and obtained from Merck chemicals. In all samples deionized water (DIW, 18.2 MV) was used.

2.2. GO paper synthesis

GO papers were synthesized using improved Hummers method based on our previous report[41]. Typically, 0.5 g of the graphite powder was dispersed in 60 mL H2SO4 and 6.6 mL H3PO4 and stirred for 2 h. Then, the mixture was put into a DI water bath and 3 g KMnO4 was added to the mixture, producing an exotherm to 40 °C. The reaction was then heated to 50 °C and stirred for 12 h. The color of the mixture changed from dark green to light brown. It was then, cooled to room temperature and poured onto 400 mL ice. There would be an obvious change in color of the mixture from light to dark brown in this section. 0.5 mL of 30% H2O2 was later added to the mixture and the color changed into light yellow. After the settlement of the mixture, the supernatant was decanted away and the precipitate was centrifuged by 200 mL of HCl and then water, at 12,000 rpm, until the mixture reached to higher pH. To separate the GO sheets from graphite oxide, the suspension was sonicated, followed by centrifugation at 4000 rpm for 45 min. The homogenous dispersion then was poured into a petri dish and allowed to dry overnight in air atmosphere. It was then peeled off from the petri dish. The obtained free standing GO paper can be seen in Fig. 1a showing the paper geometry is maintained after peeling off. It was then cut into pieces and restored for further deposition.

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2.5. Characterization methods

GO paper and the TiO2/rGO/TiO2 sandwich samples were characterized by means of X-ray diffraction, Philips X-pert pro PW1730, using Cu-Kα irradiation of 1.5405 Å, performed at 40 kV and 40 mA in 20 range of 5–80 degrees. The morphology of GO and TiO2/rGO/TiO2 sandwich structure was observed by field emission scanning electron microscopy (FESEM) using a VEGA-TESCAN-XMU. The transmission spectra of GO suspension in DIW, on UV–vis range obtained using an UV–Vis spectrophotometer, PG instrument, model T80+.
resolution transmission electron microscope (HRTEM), Philips CM30, 300 kV applied to study the GO structure. Fourier transform infrared spectroscopy (FTIR) was implemented by the NEXUS 670 Thermo Nicolet USA in the range of 400–4000 cm\(^{-1}\) with the use of KBr, to identify functional groups of the samples. Raman spectroscopy was utilized for investigation of GO formation and TiO\(_2\)/rGO/TiO\(_2\) structure, employing an Teksan instrument, model Takram P50C0R10 with laser wavelength of 532 nm.

2.6. Electrochemical tests

Electrochemical measurements of cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) performed using a SI 1287 Solartron. The system consisted of three electrodes: the working electrode, a platinum foil as the counter electrode, and a calomel as the reference electrode in 1 M KOH. Different scan rates of 5, 10, 20, and 50 mV s\(^{-1}\) in the potential range of \(-0.6–0.5\) V are applied. The surface area of the tested sample was 1 cm\(^2\). The synthesized TiO\(_2\)/rGO/TiO\(_2\) sandwich paper has been connected by an aluminum foil to a setup prepared for this experiment; the whole aluminum foil and the sandwich paper make the working electrode. During making connection between the wires and the working electrode, the wire is connected to the lowest part of the aluminum foil. The platinum electrode is placed in the setup in exact distance of 1 cm with working electrode. The sample is examined in different current densities of 600, 1000, 1400, and 1800 mA/g in potential window of 0–1 V.

3. Results and discussion

3.1. GO paper characterization

Fig. 2a shows the XRD patterns of initial graphite powder and GO paper synthesized by Tour method. The XRD pattern of graphite powder consists of a sharp peak at about 26° attributed to (002) plane, which shifts to lower degrees of 2\(\theta\) = 10.15° through the introduction of oxygen functional groups to the basal plane in GO sample [21]. There is no trace of initial graphite powder on GO pattern which is a confirmation of the high quality of the synthesized GO. The d-spacing increases through the oxidation due to the presence of intercalated functional groups. The d-spacing is 8.43 and 3.42 Å for GO paper and graphite powder, respectively, which is consistent with other studies [21].

The UV–Vis spectrum of GO aqueous suspension is illustrated in Fig. 2b. This figure shows the main absorbance peak at 236 nm, \(\lambda_{\text{max}}\), which can correspond to the excitation of electron from a \(\pi\)-bonding orbital to a \(\pi\)-antibonding orbital (\(\pi^*\)) of carbon double bonds. As more electron transitions occur from \(\pi\) to \(\pi^*\), \(\lambda_{\text{max}}\) would appear in higher wavelengths which means less energy is required for the electronic transition [43,44]. Folded structure at the edges of GO paper is obvious in HRTEM image shown in Fig. 2c and d.

Table 1
Sol parameters for sandwich TiO\(_2\)/rGO/TiO\(_2\) samples.

<table>
<thead>
<tr>
<th>Sol no.</th>
<th>Solvent type</th>
<th>Concentration</th>
<th>Acid type</th>
<th>W/Tmol ratio</th>
<th>A/T mol Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>1-PrOH</td>
<td>0.17</td>
<td>HCl</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample 2</td>
<td>MeOH</td>
<td>0.17</td>
<td>HCl</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample 3</td>
<td>EtOH</td>
<td>0.17</td>
<td>HCl</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample 4</td>
<td>1-PrOH</td>
<td>0.085</td>
<td>HCl</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample 5</td>
<td>1-PrOH</td>
<td>0.34</td>
<td>HCl</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample 6</td>
<td>1-PrOH</td>
<td>0.17</td>
<td>HNO(_3)</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample 7</td>
<td>1-PrOH</td>
<td>0.17</td>
<td>HCl</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample 8</td>
<td>1-PrOH</td>
<td>0.17</td>
<td>HCl</td>
<td>6</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample 9</td>
<td>1-PrOH</td>
<td>0.17</td>
<td>HCl</td>
<td>4</td>
<td>0.25</td>
</tr>
<tr>
<td>Sample 10</td>
<td>1-PrOH</td>
<td>0.17</td>
<td>HCl</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

Fig. 1. (a) GO paper and (b) Flexible TiO\(_2\)/rGO/TiO\(_2\) sandwich paper (sample No. 1).

3.2. Sandwich characterization

Raman Spectroscopy has been proven to be an essential method for characterization of carbon based materials. Herein, Raman spectroscopy is used to confirm the formation of GO, its conversion to rGO, and coexistence of both phases in TiO\(_2\)/rGO/TiO\(_2\) sandwich structure. Fig. 4 shows a comparison of the Raman spectra of GO paper and TiO\(_2\)/rGO/TiO\(_2\) main sample (sample No. 1) sandwich structure. The Raman spectrum of GO paper has two peaks at 1386 and 1610 cm\(^{-1}\) corresponding to D and G bands. The D and G bands of rGO in sandwich structure is also detectable in Raman shifts of 1366 and 1591 cm\(^{-1}\), respectively. The D band is usually corresponded to topological defects in lattice structure and the G band relates to planar configuration sp\(^2\) bonded carbon (stretching of the C-C bond in graphite materials) [45].
These bands have been broadened and shifted to lower values after calcination, which is a confirmation for reduction of graphene oxide in the final composite structure [34]. The D/G intensity ratio which represents the disorder in the structure, has been calculated for both samples, and is equal to 0.98 and 0.86 for TiO2/rGO/TiO2 and GO paper, respectively. These relatively low values for D/G ratio in both cases suggest low disorder in the samples structure. The higher D/G ratio in the TiO2/rGO/TiO2 sandwich structure corresponds to higher structural disorder resulting from reaction between TiO2 nanoparticles and rGO nanosheets, which causes the decrease in sp² bonds in the lattice structure as GO converted to rGO through the removal of oxygen functional groups [46]. There are four other peaks located at 147(E1g), 397(B1g), 519(A1g), and 627 (Eg) cm⁻¹, which are related to vibrational modes of titania anatase phase [47]. There is no other peak corresponded to brookite or rutile phase which is favorable as it has been proven that the anatase phase would have faster charge transfer and be more beneficial for supercapacitor applications [48].

Fig. 5 demonstrates the FTIR spectra of bare GO paper and TiO2/rGO/TiO2 main sample sandwich calcined at 300 °C in air atmosphere followed by 500 °C in argon atmosphere. GO paper spectrum confirms the presence of functional groups namely O-H stretching vibration at 3438 cm⁻¹, C=O stretching vibration in carboxylic acid and carbonyl groups at 1740 cm⁻¹, C=C remained from unoxidized carbon-carbon bonds (under oxidized graphitic domains) at 1619 cm⁻¹, C-OH and C-COOH stretching vibrations at 1423 cm⁻¹, and C-O vibrations of epoxy groups at 1041–1047 cm⁻¹ [49]. There are two small peaks at 2915 and 2848 cm⁻¹ corresponded to CH2 stretching vibrations. By comparing the two spectra, it could be said that the peak related to C=C remained from unoxidized carbon–carbon bonds is located at 1638 cm⁻¹ in the spectrum of sandwich sample. The C=O and C-OH stretching vibrations almost disappear as graphene oxide reduces through calcination process. The intense peak at 610 cm⁻¹ can be corresponded to envelope of phonon bands of Ti-O-Ti or Ti-O-C vibrations which may be due to the formation of chemical bonding between titania nanoparticles and rGO nanosheets [32,50]. The band corresponded to O-H stretching vibration still exists in FTIR spectrum of TiO2/rGO/TiO2 sandwich structure showing the graphene oxide has been partially reduced and these remained oxygen functional groups make the sandwich structure more likely to interact with functional groups of titania.

Fig. 6 shows XRD patterns of different TiO2/rGO/TiO2 sandwich samples. Fig. 6a shows the XRD patterns of TiO2/rGO/TiO2 sandwiches deposited by titania sol with 1-propanol as the solvent, 0.17 M, A/T = 0.5, HCl catalyst, and W/T = 4 (sample No. 1) calcined at 300 °C in air atmosphere and the same sample but calcined at 300 °C in air followed by 500 °C in argon atmosphere. The non-calcined sandwich sample with the same parameters is also compared with others in this figure. The calcination of same sample directly to 500 °C in argon atmosphere may cause the low organic residual removal rate in TiO2 and GO deterioration, respectively. Also, the calcination in 300 °C in air or argon atmosphere, may not lead to the complete crystallization of TiO2 nanoparticles. The (101) plane of anatase structure could be detected in XRD patterns of all samples according to JCPDS card No. 21–1276, which is in line with Raman spectroscopy results [30]. The (002) plane of GO can be seen near 10° due to the existence of unreduced GO plates in sample without calcination. This peak can be still detected in lower intensity in sample calcined at 300 °C. However, it seems that the sample calcined at 300 °C in air and then 500 °C in argon atmosphere is converted to rGO due to the disappearance of peak around 10° in this sample. Since the (002) plane broad peak of rGO has an overlap with that of (101) anatase peak at 25°, this peak cannot be thoroughly distinguishable [51]. The presence of rGO did not affect the position of
**Fig. 3.** FESEM images of GO paper: (a, c) cross sectional and (b, d) surface view in low and high magnifications.

**Fig. 4.** Raman spectra of GO paper TiO$_2$/rGO/TiO$_2$ sandwich (sample No. 1) calcined at 300 °C in air atmosphere followed by 500 °C in argon atmosphere.

**Fig. 5.** FTIR spectra of GO paper, and TiO$_2$/rGO/TiO$_2$ sandwich (sample No. 1) calcined at 300 °C in air atmosphere followed by 500 °C in argon atmosphere.
(101) anatase peak. The defects of GO nanosheets act as nucleation sites that facilitate the formation of TiO$_2$ grains as they trap the residual Ti atoms from titania sol. As the Ti atoms interact with the oxygen functional groups of GO, the in situ reduction of GO in high temperatures occurs without addition of any other material such as hydrazine. The thermal treatment assists not only the reduction of rGO but also the completion of TiO$_2$ crystallization through the calcination process [24–26].

Fig. 6b shows the XRD patterns of TiO$_2$/rGO/TiO$_2$ sandwiches deposited by titania sol using methanol, ethanol, 1-propanol and 1-butanol as solvents, concentration of 0.17 M, A/T = 0.5, HCl catalyst, and W/T = 4 calcined at 300 °C in air followed by 500 °C in argon atmosphere. A peak located around 25° confirms the formation of the (101) plane of anatase phase. The other peaks of anatase cannot be detected which may be attributed to the low thickness of titania on GO paper substrate. In some samples, there are small peaks with very low intensity around 10°, which suggest the presence of residual GO structure. It can be perceived from these patterns that as carbon chain length of solvent increases, both the viscosity and gel time of titania sol increase, which leads to higher thickness of titania layer on the substrate during the deposition process and higher intensity of anatase peak in the final structure of the composite [52]. The XRD patterns show that the sample deposited by 1-butanol sol (sample No. 4) has the highest intensity of (101) plane due to its longest carbon chain length. Fig. 6c shows the sandwich structure synthesized by HNO$_3$ and HCl as the acid catalyst (stabilizer). Both samples show the formation of anatase titania phase. Due to the fact that the formation of slight amount of rutile phase is encouraged beside anatase phase in the presence of HNO$_3$, HCl would be more suitable for supercapacitor applications [48,52,53].

Three samples have been prepared using 1-propanol as the solvent, A/T = 0.5, HCl catalyst, and W/T = 4, employing different concentrations of 0.085, 0.17 and 0.34 M calcined at 300 °C in air followed by 500 °C in argon atmosphere and the XRD patterns of these samples are represented in Fig. 6d. XRD patterns confirm the presence of titania anatase phase. With the same explanation as before, the increase in the concentration of the sol can cause notable changes in the viscosity of the sol, which brings on changes in the thickness of titania layer. The sample prepared using the sol with the highest concentration of 0.34 (sample No. 6) have the highest intensity of (101) peak.

The effect of W/T ratio has been investigated on the TiO$_2$/rGO/TiO$_2$ sandwich structure calcined at 300 °C in air followed by 500 °C in argon atmosphere and the related XRD patterns are displayed in Fig. 6e. Three W/T ratios of 2, 4 and 6 have been studied in this research. Other parameters of titania sol remained constant (1-propanol as the solvent,
concentration of 0.17 M, A/T = 0.5, HCl catalyst). Since the water content accelerates the hydrolysis reactions, it is predictable that with an increase in water content, the gel time of titania sol dramatically decreases, which can lead to the higher thickness of titania in samples with higher W/T ratio. The intensity of anatase peak in the sample with W/T ratio of 6 (sample No. 9) is the highest compared to those of W/T = 2 (sample No. 8) and 4 (sample No. 1).

The effect of A/T ratio could be seen in Fig. 6f. All the samples again consist of anatase titania phase. However, the intensity of the (101) peak enhances by acid content. The acid is used as catalyst for the condensation reactions during the sol formation process. As the acid content increases, due to the higher crystallinity, it causes higher intensity of anatase (101) peak in XRD patterns would be obtained [54].

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Fig. 7e, the acid catalyst of nitric acid causes serious cracking on the film (sample No. 7) due to the large exothermic reaction of this catalyst during drying, resulting very high gas evolution through the non-calcined film layers [55]. This sample has also been rolled up. Fig. 7f and g show the samples with different A/T ratios. It is perceivable from the Fig. 7f and g, that as the acid content increases in sample No. 11 (Fig. 7g) and decrease of pH of the sol, the crystallite size of nanoparticles decreases, which can be attributed to the slower hydrolysis reactions compared to condensation reactions in this condition. As the acid content increases, the prepared sample would have denser structure and higher crack formation tendency due to the inhibition of nanoparticles agglomeration [56]. The effect of concentration on sandwich structure can be seen in Fig. 7h and i. As the concentration of titania sol increases, the viscosity of corresponding sol increases as a consequence. Therefore, the low boiling point solvents (such as MeOH and EtOH in Fig. 7a and b) result in very high drying rate during dip coating, which induces large internal tension in the film and cause the films more likely to roll, which is an unfavorable quality for the use of these papers in flexible supercapacitor applications [52]. Among these solvents, the 1-PrOH based sol (sample No. 1) not only shows appreciable surface quality, but also survives the rolling during drying step. According to Fig. 7e, the acid catalyst of nitric acid causes serious cracking on the film (sample No. 7) due to the large exothermic reaction of this catalyst during drying, resulting very high gas evolution through the non-calcined film layers [55]. This sample has also been rolled up. Fig. 7f and g show the samples with different A/T ratios. It is perceivable from the Fig. 7f and g, that as the acid content increases in sample No. 11 (Fig. 7g) and decrease of pH of the sol, the crystallite size of nanoparticles decreases, which can be attributed to the slower hydrolysis reactions compared to condensation reactions in this condition. As the acid content increases, the prepared sample would have denser structure and higher crack formation tendency due to the inhibition of nanoparticles agglomeration [56]. The effect of concentration on sandwich structure can be seen in Fig. 7h and i. As the concentration of titania sol increases, the viscosity of corresponding sol increases as a consequence. Therefore, the
high sol concentration should be avoided in order to minimize the crack formation. The sample with the highest concentration of 0.34 M (sample No. 6) has more cracks on its surface in comparison with the two other samples (Fig. 7b-c). It is detectable that the nanoparticles size increases with the increase in the concentration of the sol. The optimum concentration of the sol based on FESEM images is 0.17 (sample No. 1). The water content can also affect the gel time of the sol. As mentioned before, the higher the water content, the higher the thickness of the film and hence the higher the probability for crack formation (Fig. 7j and k). Furthermore, the particle size is smaller in samples with lower W/T ratio, as the increase in water content results in higher growth rate of nuclei which can be seen in Fig. 7c, j, and k in higher magnifications.

Fig. 8a shows the thickness of GO paper which is about 15 µm. As the GO converted to rGO, the layer distance between the sheets is reduced, which is attributed to the partial removal of functional groups from GO paper layers. Cross sectional images of main sample of TiO2/rGO/TiO2 sandwich structure shows that the thickness of 10 layers of titania deposited on GO paper is about 660 nm.

3.3. Electrochemical tests

The electrochemical performance of TiO2/rGO/TiO2 in hybrid structure with TTiP:DIW:HC1 ratio of 1:4:0.5 and concentration of 0.17 M in 1-PrOH (sample No. 1) is studied using the flexible sandwich structure as the working electrode (anode). The flexibility of the hybrid decreases as the thickness of the TiO2 layer increases. Thus, samples No. 4, 6, and 9 would not have proper flexibility properties compared to the main sample due to thicker titania layer. However, other factors should be also considered. Samples No. 2 and 3 may have appropriate thickness, while due to the low boiling point of MeOH and EtOH, the paper rolled up and it is not suitable for the electrochemical tests. Sample No. 7 (using HNO3 as catalyst) is not tested due to the improper properties of the sample (too many cracks and rutile phase of titania were formed). Samples No. 5 and 8 have very low thickness of titania phase and sample No. 10 has very large grains, which again make them improper for supercapacitor application of the sandwich paper and the presence of titania would be less effective. Sample No. 11 has too many cracks. Therefore, the main sample (sample No. 1) is chosen for electrochemical test.

Fig. 9a shows the CV curves of TiO2/rGO/TiO2 hybrid structure (sample No. 1) in different scan rates. The shape of CV curves is quasi-rectangular without any redox peaks, which represents proper capacitive behavior. The asymmetric curve can be due to the contribution of both pseudocapacitance behavior of TiO2 and double layer performance of rGO to the total capacitance of hybrid. The faradic mechanism is caused by the reversible redox reactions of TiO2 by exchanging protons/cations with KOH electrolyte. The presence of rGO facilitates the redox transitions and the electron transfers between TiO2 and rGO is much faster due to high charge mobility of rGO. It can be seen that the area under CV curves increases as the scan rate increases along with the current density. The distortion of the CVs in high scan rates can be referred to the increased resistance of the electrode. The specific capacitance of the TiO2/rGO/TiO2 sample can be calculated by Eq. (1) [26,57]:

$$C_{sp} \approx \frac{\int_1 v dv}{m \Delta V}$$

(1)

where I is the average current (A), v is the scan rate (V s⁻¹), ΔV is the potential window (V), and m is the mass of the electrode (g). The specific capacitance for this sample at different scan rates of 5, 10, 20, and 50 mV s⁻¹ is equal to 83.7, 69.8, 43.28, and 29 F g⁻¹ of the electrode, respectively (Fig. 9b). More information acquired using GCD measurements on the same sample (Fig. 9c). The charge and discharge curve are almost linear and symmetric (triangular shape), which shows a good capacitive behavior. The slight curvature may again be due to the contribution of pseudocapacitance activity of TiO2 along with rGO double layer mechanism.

The specific capacitance using charge-discharge curve can be calculated by using Eq. (2) [26,58]:

$$C_{sp} = \frac{\Delta t \times I}{m \times \Delta V}$$

(2)

where Δt is the discharge time (s), I is the discharge current, m is the mass of active electrode, and ΔV is the potential drop during discharge. The discharge specific capacitance of sandwich structure is consistent with the results gained from CV curves. As expected, the specific capacitance decreases as the current density increases. Fig. 9d shows the flexibility of TiO2/rGO/TiO2 sandwich structure (sample No. 1), as it remains almost stable with a very slight change in specific capacitance under bending angle of 90°. Recently, very high capacitance supercapacitors based on graphene/Ni(OH)2 have been reported by Liu et al. [59] with specific capacitance of 1382 F g⁻¹. Ding et al. [60] have reported a 3D structure of TiO2/rGO composite used as supercapacitor electrode with high capacitance of 397 F g⁻¹. Zhang et al. [61] also reported a 3D structure of TiO2/graphene composite materials, using hydrothermal technique with specific capacitance of 206.7 F g⁻¹. Among flexible supercapacitors, solution-processed poly (3,4-ethylenedioxythiophene) nanocomposite paper electrodes can be mentioned reported by Wang et al. [62] with specific capacitance of 90 F g⁻¹.
Ghorbani et al. [38] also reported a flexible supercapacitor electrode based on rGO/ZnO sandwich hybrid with specific capacitance of 60.63 F g$^{-1}$. The specific capacitance of 83.7 F g$^{-1}$ obtained in this study is among the appreciable capacitances in flexible supercapacitors and give great promises for wearable devices.

4. Conclusions

The TiO$_2$/rGO/TiO$_2$ sandwich structure as an electrode for flexible high performance supercapacitors has been successfully synthesized, using facile and low cost sol-gel deposition. Unlike other methods which apply high temperature, employ hydrazine for reduction of GO, or involve high cost methods, here we report a novel and simple route, in which in-situ reduction of GO paper occurs along with crystallization of TiO$_2$ nanoparticles under thermal treatment without utilization of any binder or surfactants. FESEM images of sandwich structure show that titania nanoparticles cover rGO surface uniformly. The reduction of GO paper is proved by Raman spectroscopy. The results obtained from CV and GCD curves for hybrid structure with optimum parameters of 1-ProOH as solvent, HCl as stabilizer, concentration of 0.17 M, W/T ratio of 4, and A/T ratio of 0.5 confirms the cooperation of both pseudocapacitance behavior of TiO$_2$ nanoparticles and double layer activity of rGO, which brings up its good capacitance among flexible hybrid structures of TiO$_2$/graphene. The hybrid structure demonstrates good specific capacitance of 83.7 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$ in 1 M KOH solution. This material has outstanding potential to be used as flexible electrode in wearable electronic applications.

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References

Graphene oxide

S. Park, J. An, J.R. Potts, A. Velamakanni, S. Murali, R.S. Ruo

X. Li, W. Qi, D. Mei, M.L. Sushko, I. Aksay, J. Liu, Functionalized graphene sheets as

M. Ghorbani, M.R. Golobostanfard, H. Abdizadeh, Flexible freestanding sandwich

C. Xiang, M. Li, M. Zhi, A. Manivannan, N. Wu, A reduced graphene oxide/Co3O4

A. Ramadoss, S.J. Kim, Improved activity of a graphene


M. Sonochemical synthesis of TiO2 nanoparticles on graphene for use as photocatalyst, Ultrason.

S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu,

P. N. First, W.A. de Heer, T. Seyller, C. Berger, J.A. Stroscio, J.S. Moon, Epitaxial


