Research Article

Facile and Novel in-Plane Structured Graphene/TiO₂ Nanocomposites for Memory Applications

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Here, we report a simple strategy for the preparation of graphene/TiO₂ nanocomposite by UV-assisted incorporation of TiO₂ nanosol in graphene oxide (GO) dispersion. The proposed method is facile and of low cost without using any photocatalysts or reducing agents; this can open up a new possibility for green preparation of stable graphene dispersions in large-scale production. X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy, and transmission electron microscopy (TEM) have been used to characterize carefully the as-prepared composites and to confirm the successful preparation of the nanocomposites. The average crystallite size of TiO₂ nanoparticles calculated from XRD pattern using Rietveld analysis is ~35 nm. TEM measurements show the adsorption of TiO₂ onto graphene (G) sheets, which prevents the restacking of graphene sheets. Current-voltage and capacitance-voltage measurements were used to investigate the electrical resistive memory properties of GO, GO/TiO₂, and G/TiO₂ thin films. Observed results show hysteresis behavior due to the charge trapping and detrapping process, indicating that the prepared thin films exhibit an excellent resistance switching memory characteristic for G/TiO₂ device.

1. Introduction

Carbon electronic devices have attracted a great deal of importance as promising electronic systems for modern high-performance computers. It is expected that electronic devices for the next generation will be lighter and foldable for applications in wearable computers, flexible displays, and cost effectiveness [1–4]. In particular, carbon nanotubes, graphene, graphene oxide (GO), or their composites have become a sparkling rising star on the horizon of material science in the last several years [5, 6]. The superior properties of graphene including large specific surface area, excellent mobility of charge carriers, and good electrical conductivity [7, 8] support graphene as a test bed for fundamental science.

As a promising application for graphene oxide, resistive random access memory (RRAM) has attracted a great deal of interest as a next generation nonvolatile memory (NVM) device for high-performance computer. Up to now, GO/TiO₂ nanoparticle RRAM devices have shown low switching voltage (about ±1 V) [9] and good endurance up to 10⁵ cycles and long retention time more than 5 × 10³ s [10]. Also, excellent

large flexibility area without degradation of memory performance for ~100 cycles has also been reported for GO-based device [11]. The optimization of the graphene-based materials for memory application passes through universal parameters such as preparation technique including the type of reduction method, additives/size, and device structure configuration.

Starting with the reduction of exfoliated GO, chemical [12] and thermal reduction [13] have been used for obtaining conductive graphene sheets or films. But here you must keep in mind that chemical reduction often uses hydrazine which is toxic chemical, while thermal reduction is not suitable for plastic substrates, intrinsic weaknesses. Recent researches focus on developing a facile and green reduction method that is suitable for various substrates. Radiation reduction of GO is deemed as the simpler, purer, and less harmful method that may overcome the shortcomings of other conventional reduction methods [14]. In practical applications, graphene nanosheets usually suffer from agglomeration or restacking giving rise to a great technical difficulty in the fabrication of graphene-based devices. These agglomerations are due to the strong van der Waals interactions between graphene sheets.

Thus, there has been a clear interest in the development of low cost and reliable synthetic methods for the preparation of the soluble-processable graphene derivatives [15]. On the other hand, the vast majority of the graphene-based RRAM devices reported in literature are made of metal-insulator-metal-(MIM-) type structures. A simple and effective alternative structure is the planar configuration where a significant lower intrinsic capacitance is performed compared to the MIM structure [16, 17]. In our present investigation, we report a facile preparation strategy of graphene/TiO₂ thin film for possible RRAM memory applications using planar configuration. UV irradiation is used as a green and simple tool for the reduction of GO/TiO₂ dispersion. Loading TiO₂ nanoparticles on the graphene nanosheets surface are anticipated to prevent the restacking of graphene nanosheets, thus resulting in enhanced electrical performance.

2. Experimental

2.1. Materials. Natural graphite flakes with an average diameter of $<50\ \mu\text{m}$ were supplied from Merck KGaA, Germany. Potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), H₂SO₄ (98%), and H₂O₂ (30%) were obtained from El Nasr Pharmaceutical Chemicals Co., Egypt. Titanium tetrakisopropoxide (TTIP) (98%) was purchased from Strem Chemicals Co., USA. All reagents were of analytical grade and used as received without further purification.

2.2. Preparation of GO. Graphite oxide was prepared from flake graphite powder by a modified Hummers method [18]. In brief, graphite oxide was synthesized by an oxidation of graphite with KMnO₄ and NaNO₃ in concentrated sulfuric acid. Then, the oxidation was performed by adding graphite powder (0.5 g) to 50 mL of 98% H₂SO₄ in an ice bath; then 5 g of NaNO₃ was added gradually while stirring. Subsequently, 2 g of KMnO₄ was added slowly avoiding a sudden increase of temperature. When the addition was finished, the resulting mixture was stirred for 2 h under ice-water bath to ensure that the temperature remains below 10°C. Later, the ice bath was removed and the reaction mixture was heated to 35°C for 2 h. The reaction was quenched by pouring 250 ml distilled water and 20 ml H₂O₂ (30%) at room temperature to dilute the solution and destroy unreacted KMnO₄. The graphite oxide was collected and washed with 10% HCl and distilled water three times. To prepare GO dispersion, 100 mg graphite oxide was dispersed in 100 ml of DI water and ultrasonicated for hours until the solution became clear. Then the GO dispersion was centrifuged with 4000 rpm for 10 min to remove any unexfoliated graphite oxide.

2.3. Preparation of TiO₂ Nanosol. In a typical procedure, 6.8 ml TTIP was added dropwise into 100 ml of 0.1 M HNO₃ under vigorous stirring. Then, the mixture was heated by water bath at 50°C for 24 h under stirring to form TiO₂ aqueous nanosol.

2.4. Preparation of Thin Films. GO dispersion and TiO₂ nanosol were mixed in the ratio 9:1 and sonicated for

15 min to get well dispersed GO/TiO₂ suspension (GOT). The reduction of GOT to graphene/TiO₂ (GT) was carried out by exposure to UV lamp (450W Xenon arc lamp) up to four hours. Thin films were grown onto ultrasonically cleaned glass substrates by employing solution casting of GOT and GT suspensions. Certain amount of GOT and GT suspensions were drop casted onto glass substrate and left for drying at room temperature. In order to avoid thick films, the casting of the prepared suspensions was controlled very carefully.

2.5. Characterization. The morphology of the as-prepared samples was characterized with transmission electron microscopy (JEM-100CS, JEOL Japan) operated at acceleration voltage of 80 kV. Fourier transform infrared spectrophotometer (FTIR) was carried out at room temperature with JASCO FT/IR-6300 (Japan) in the range of 400–4000 cm⁻¹ and used for the detection of chemical interaction in the as-prepared samples. Raman measurements were performed at room temperature using Witec alpha 300 R confocal Raman microscope, Germany. The crystalline phase of the products was characterized using X-ray diffraction (XRD) analyses by a Shimadzu machine (XRD-6000 series) with Cu K α radiation, operated at 40 kV and 30 mA. Electrical characterization of the as-prepared thin films was carried out by Keithley 2635A using finger type Ag electrodes onto glass substrate of area $2.5 \times 2.5\ \text{cm}^2$. The width of gap between two successive electrodes and the overlap electrode were 0.5 mm. The C-V characteristics were measured using Hioki 3532 LCR Hi-Tester at fixed frequency (100 kHz).

3. Results and Discussion

The overall procedure for the formation of GOT dispersion is illustrated in Figure 1. The TiO₂ nanoparticles, prepared through sol-gel process, absorbed a lot of hydroxyl groups on its surface, while GO sheets have high content of oxygen functional groups, such as carboxylic acid (–COOH) and hydroxyl group (–OH), in the basal planes and the edge sides that could provide enough chemical groups to accomplish the chemical bonding reactions with TiO₂ nanoparticles [19].

By exposing GOT dispersion to UV irradiation, its color changes from light brown to black (Figure 2(a)). This change in color indicates that GO is reduced to graphene due to the partial restoration of the π network within the carbon structure. The photo-assisted reduction of GO at the surface of TiO₂ nanoparticles was believed to be associated with photocatalytic reactions [20]. Electron–hole pairs were generated upon UV irradiation of the TiO₂ nanoparticles [21, 22]. The electrons could be efficiently captured by the sp² regions of GO, whereas the holes reacted with surface-adsorbed water to generate oxygen and protons [23]. Moreover, electrons delocalized in the sp² regions of GO together with protons may initiate the reactions to dissociate oxygenated functional groups at the boundary of sp² regions. The drop casted GOT and GT thin films over glass substrate were shown in Figure 2(b). It can be noted that well-adhered and uniform thin films can be conveniently prepared by this method.

FIGURE 1: Illustration of the fabrication schematics of graphene oxide/TiO₂ (GOT) suspension.

3.1. TEM Images. The morphological structure of the as-prepared composites was investigated by TEM and displayed in Figure 3. Figure 3(a) shows GO sheets with flat and smooth surface that indicates the successful exfoliation of GO sheet from graphite containing ordered stacking graphene layers. On the other hand, Figure 3(b) reveals the surface of GT nanosheets that is uniformly covered by high dense TiO₂ nanoparticles. It is especially noteworthy to mention that the GT suspension has been sonicated in deionized water before being performed by TEM and no individual TiO₂ nanoparticles were observed. The attachment of TiO₂ nanoparticles on the surface of graphene sheet indicates that most of the TiO₂ nanoparticles would not be peeled off during the sonication process and the restack of graphene nanosheets could be effectively prevented.

3.2. FTIR Spectra. FTIR spectroscopy was used to characterize the interaction between GO and TiO₂ nanoparticles before and after UV irradiation. The FTIR spectrum of GOT (Figure 4(a)) shows absorption peaks at 3280 cm⁻¹ assigned for O-H stretching vibration [24, 25] and 1384 cm⁻¹ for C-O stretching vibration [26, 27], and the peak at 1627 cm⁻¹ can be assigned to the C=C ring stretching or H-O-H bending band of the adsorbed H₂O molecules [28]. Moreover, the entire obvious characteristic for oxygen-containing functional groups (i.e., -COOH) can also be observed in the FTIR spectrum of GOT. This reveals a considerable chemical bonding reactions, like dehydration condensation reaction, between TiO₂ and GO [28]. The strong band around 585 cm⁻¹ is attributed to Ti-O-C vibration indicating the successful

FIGURE 2: (a) Picture of graphene oxide/ TiO_2 (GOT) suspension before and after UV irradiation; (b) picture of the GOT and graphene/ TiO_2 (GT) thin films on glass substrate.

FIGURE 3: TEM images of (a) graphene oxide sheets and (b) graphene/ TiO_2 (GT) composite.

FIGURE 4: FTIR spectra of (a) graphene oxide/ TiO_2 (GOT) and (b) graphene/ TiO_2 (GT) composites.

adsorption of TiO_2 nanoparticles onto GO nanosheets through chemical interaction between the surface hydroxyl groups of TiO_2 and the functional groups of GO [19, 29]. Additionally, the bands related to the oxygen functional groups of GO were reduced in the spectrum of GT, revealing that the functional groups were almost removed under the effect of UV irradiation and thus GO was reduced successfully into graphene. Moreover, a new band at $\sim 1580 \text{ cm}^{-1}$ can be noted in the spectrum of GT that may be attributed to the skeletal vibrations of the graphene sheets [30].

3.3. Raman Spectra. Raman spectroscopy is a technique based on the analysis of the inelastically scattered light from the medium, produced by the interaction of the light with the atomic vibrations. This spectroscopy technique is generally used to characterize the crystal quality of carbonaceous materials. The position and width of the peaks are highly dependent on the sample temperature [31]. Figure 5 shows the

FIGURE 5: Raman spectra of (a) graphene/TiO₂ (GT) and (b) graphene oxide/TiO₂ (GOT) thin films.

Raman measurements of GOT films, carried out at room temperature, before and after UV irradiation. The typical modes of TiO₂ anatase phase are clearly observed in both films at 152 cm⁻¹, 408 cm⁻¹, 511 cm⁻¹, and 631 cm⁻¹, attributed to E_{g(1)}, B_{1g}, A_{1g}, and E_{g(2)}, respectively [19, 32]. Moreover, two characteristic peaks at about 1349 and 1601 cm⁻¹ for graphitized structure are also observed, ascribed to the D and G bands, respectively. As a result of edge defects, internal structural defects, and dangling bonds, the D band is known to be attribute to the disruption of the symmetrical hexagonal graphitic lattice, while the G band is due to the E_{2g} vibrational mode of the in-plane stretching motion of symmetric sp² C-C bonds [33, 34]. The UV irradiated composite shows an increase of the D/G intensity ratio from 0.95 for unirradiated film to 0.99. The D/G intensity ratio has been widely used in the literature to quantify the defect density in sp²-bonded carbons. The increase of the D/G intensity ratio in our work is attributed to the formation of defects and removal of oxide functional groups that suggests the successful UV reduction of GO [35]. Both FTIR and Raman emphasized the well samples preparation compared with other green and direct synthesis methods [19, 29].

3.4. XRD Results. Figure 6 shows the XRD spectrum of the as-prepared thin films. The main XRD peaks are attributed to pure tetragonal anatase phase structure at 25°, 37°, 48°, 53°, 55°, 62°, 69°, 70°, and 75° that can be indexed to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes, which is in a good agreement with (JCPDS- 21-1272). The main crystal structure of the anatase TiO₂ is the crystal facet (101). Due to the low reaction temperature employed during the preparation no rutile phase was detected [36]. Based on Rietveld analysis refinement patterns carried out by using MAUD program (red line in Figure 6) the average crystal size of the TiO₂ nanoparticles was calculated to be ~35 nm. For GO, a strong peak centered at 2θ = 11.4° assigned to (001) plane is observed. This peak corresponded to an interlayer spacing of about 0.77 nm, indicating the presence of oxygen

FIGURE 6: XRD patterns of (a) TiO₂, (b) graphene oxide (GO), and (c) graphene oxide/TiO₂ (GOT) thin films.

FIGURE 7: XRD patterns of graphene oxide/TiO₂ (GOT) thin film after UV exposure for different hours from (a) 1 hour up to (d) 4 hours.

functionalities that facilitated the hydration and exfoliation of GO sheets in aqueous media [37]. After mixing TiO₂ nanosol and GO dispersion the diffraction peaks intensities for both TiO₂ and GO weakened in composite state.

Figure 7 shows the XRD patterns of GT thin films after UV irradiation for different hours. Notably, the typical diffraction peak of graphene was not observed in the XRD pattern and a slight change in FWHM of (101) peak of anatase TiO₂ was observed. A possible reason for this observation was that the characteristic (002) peak at 25.9° of graphene [38, 39] might be overlapped with the (101) peak of anatase TiO₂ (25.3°). Interestingly, sharp peak was observed after exposing GOT suspension to UV irradiation for four hours. This indicates that the UV exposure time affects the crystallinity of GT nanocomposites and the average crystal size of TiO₂ nanoparticles has been changed from ~35 nm up to ~75 nm which will affect their electrical properties.

FIGURE 8: Current-voltage characteristics of (a) graphene oxide (GO) and (b) graphene oxide/ TiO_2 (GOT) devices; the inset is the planar structure of prepared devices.

FIGURE 9: Current-voltage characteristics of (a) graphene oxide/ TiO_2 (GOT) and (b) graphene/ TiO_2 (GT) devices.

3.5. Electrical Measurements. Typical I - V curves of Ag/GO/Ag, Ag/GOT/Ag, and Ag/GT/Ag devices measured at room temperature (300 K) are shown in Figures 8 and 9. The voltage was swept from +20 V to -20 V and then -20 V to +20 V with a constant voltage sweeping rate. Hysteresis loops are clearly observed in the forward and reverse voltage scan in all I - V curves. This indicates that all devices have two distinct conductivity states at the same voltage, ON state and OFF state, corresponding to the high-current and the low-current states, respectively. Figure 10 shows I - V curves of Ag/GOT/Ag measured at different sweep voltages, a represented example. The electrical hysteresis behavior is independent of the sweep voltage. Furthermore, the behavior shown in the I - V characteristics is the required feature for any memory device [40]. It can be postulated that the

FIGURE 10: Current-voltage characteristics of graphene oxide/ TiO_2 (GOT) device measured at different sweep voltages from 8 V (1st Run) to 20 V (6th Run).

conductivity memory behavior of the as-prepared devices is strongly correlated with the presence of GO and graphene.

The resistive memory mechanism is quite complicated especially in the planar structure of our devices, while the memory behavior has been reported in devices with sandwich structures and explained by formation and rupture of metallic filaments [41]. The findings in the planar structures reported here seem to discharge this process, because the electrodes are considerable apart. Furthermore, migration of metallic species from electrodes is unlikely to occur. The memory behavior here might be attributed to the charge trapping and detrapping process. The interfacial defects in GO can act as trapping sites [42, 43] that capture electrons injected from the electrodes. Ag electrode is used because Ag is an electrochemically active material. When a positive voltage is applied, oxidation reaction may occur resulting in Ag^+ cation and the electrons are injected from Ag to the LUMO level of graphene matrix. The electrons existing at the LUMO level are transported along the direction of applied voltage [44]. As a result, the conductivity of the device increases indicating the ON state. In reverse applied voltage, tunneling of the holes through the valence band of the graphene matrix occurs. Graphene is charged positively and negatively depending on the polarity of the applied voltage. Thus the graphene matrix can act as charge trapping element and is responsible for the low conductivity switching mechanism of the devices, thus indicating the OFF state.

Addition of TiO_2 nanosol to GO and graphene causes enhancement in the memory behavior of the as-prepared devices. The maximum current differences between the high-current ON state and low-current OFF state for GO, GOT, and GT devices are 0.14 mA, 0.81 mA, and 18 mA, respectively, as shown in Figure 11.

FIGURE 11: Variation of current difference between up and down sweeps in forward bias (F) and reverse bias (R) for graphene oxide (GO), graphene oxide/TiO₂ (GOT), and graphene/TiO₂ (GT) devices.

TiO₂ is an oxygen-vacancy doped semiconductor [45] because in TiO₂ lattice each oxygen atom is surrounded by three titanium atoms and when an oxygen atom is removed from its original position the oxygen vacancies are created [46, 47]. The removal of the oxygen atoms enhances the Ag electrode oxidation and increases the injected electrons. Moreover, TiO₂ causes an increase in the structural defects of GO and graphene that act as charge trapping sites. As a result, the conductivity of the thin films increases, which positively affects the memory behavior of the as-prepared devices.

To further understand the carrier transport mechanism, the forward C-V measurement is done for the best device that is GT device as shown in Figure 12. The C-V characteristics show hysteresis under voltage scan from 0.2 to 5 V and back, in both forward and reverse voltage sweeps. This means that the charge carriers, electrons (clockwise), and holes (anticlockwise) are involved in the charging and discharging processes of this device. Moreover, under applied voltage, the charged state of the composites or the ON state of the device is represented when the capacitance magnitude is large and vice versa [40].

4. Conclusion

In conclusion, we have successfully prepared GT nanocomposite via UV irradiation. TEM images reveal the uniform attachment of TiO₂ nanoparticles on the surface of graphene sheets. Simple solution casting technique has been employed to fabricate three coplanar devices (Ag/GO/Ag, Ag/GOT/Ag, and Ag/GT/Ag). These devices have been characterized with I-V and C-V measurements. I-V characteristics show hysteresis loops in both positive and negative applied voltages. In comparison, the ON/OFF ratio is 0.14 mA and 18 mA for GO and GT devices, respectively. This increment is due to the addition of TiO₂ nanoparticles that increase the charge

FIGURE 12: Capacitance-voltage characteristics of graphene/TiO₂ (GT) thin film measured at 100 kHz.

trapping sites and enhanced the conductivity of the thin film. In addition, the C-V measurement confirmed that both electrons and holes take part in the charging and discharging processes of these devices. The easy processing technique and simple device structure provide an opportunity to develop the next generation electronic RRAM memory devices.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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