

Synthesis of titanium decorated graphene for renewable energy applications

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Abstract

Reduced graphene oxide (RGO) was prepared from natural graphite by Hummers method. Few layers graphene was decorated with titanium by an incipient wetness impregnation method. The pristine graphene shows hydrogen storage capacity equal to 1.3 wt % while graphene decorated by titanium (RGO-Ti) enhanced hydrogen storage capacity to 1.4 wt%. We showed that titanium addition improved hydrogen storage capacity by chemical interactions. These interactions can be used for fabrication of different graphene-based materials as potential candidates for developing new adsorbents for energy application.

Keywords: Graphene, titanium, hydrogen storage, adsorption isotherm

Introduction

Hydrogen is the most abundant element in the universe and it can be generated from renewable energy sources. It has great potential to use as an energy source but its storage is one of the most challenging barriers in hydrogen system applications. Many experimental and theoretical methods were used to determine safe and effective hydrogen storage materials (Zhang et al. 2013). Various properties such as large gravimetric and volumetric storage capacity and low cost are necessary for practical storage of hydrogen (Vinayan et al. 2013). High surface area, low density and large microporosity make carbon-based materials good options to use as adsorbent in hydrogen storage systems. These materials including nanotubes, nanofibers and fullerene have attracted many attentions for efficient and safe storage (Chen et al. 2013).

Recently, graphene, a single atomic layer sheet of sp^2 bonded carbon, has gained tremendous attention because of its unique properties such as high surface area (Spyrou et al. 2013, Hong et al. 2012). It was proposed that graphene has the potential to become an ideal substrate for hydrogen storage application. Srinivas *et al.* (Srinivas et al. 2010) measured the capacity of graphene for hydrogen storage at different temperatures that is 1.2 wt.% and 0.1wt.% at 77 K and 298 K, respectively.

Doping graphene with appropriate chemical groups is a method to change the properties of graphene. Investigations show that dispersion of transition metals such as Pd on carbon materials improves hydrogen storage capacity by chemical adsorption (Chen et al. 2013). Lebon *et al.* (Lebon et al. 2013) studied hydrogen storage of graphene doped with 3d transition metals by using density-functional calculations. They found that the titanium-doped graphene sheets are capable of adsorbing hydrogen molecules and can meet hydrogen storage target of U. S. Department of Energy. Rojas and Leiva (Rojas et al. 2007) showed that each titanium atom can adsorb four hydrogen molecules with an average binding energy up to -0.42 eV/ H_2 molecule.

In this work, we prepared graphene by thermal exfoliation of graphite oxide obtained by Hummers method. We dispersed titanium on graphene sheets by incipient wetness impregnation method and measured hydrogen storage capacity by hydrogen adsorption isotherm. Effect of titanium addition on graphene sheets was studied by different methods.

Experimental

To form graphite oxide (GO), graphite flakes were first mixed with sulfuric acid (H_2SO_4) and sodium nitrate ($NaNO_3$) and then potassium permanganate ($KMnO_4$) was added slowly during 2 hours. After completion of oxidation stage, mixture was added to water and filtered. Then it is rinsed and redispersed in 5% HCl solution. Finally, mixture was washed with water till reaching neutral pH and dried at 60 °C under vacuum. RGO was obtained by thermal exfoliation/reduction of GO at 1000°C under controlled atmosphere for 12 min.

The decoration of graphene with titanium was performed with titanium chloride as the precursor. GO was dispersed in water and sonicated for 2 h and then mixed for 24 h with titanium chloride under vigorous stirring to form a stable suspension. RGO-Ti was obtained by the same thermal reduction method as RGO sample.

As-prepared samples were characterized by X-ray diffraction (XRD), Raman spectroscopic analysis, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) analysis. Specific surface area of samples was determined by analyzing the standard nitrogen adsorption isotherms (BET) at 77 K. To measure the hydrogen storage capacity, samples were degassed for 12h under high vacuum at 100°C. The hydrogen adsorption isotherms were measured at room temperature up to 10 bar.

Results and discussion

It has been reported that intensity of (002) diffraction line at $2\theta=26^\circ$ is inversely proportional to oxidation degree of the graphite oxide whereas absence of this (002) line implies a fully oxidized graphite. On the other hand, change of crystal structure from raw graphite to oxidized state results in appearance of (001) peak at $2\theta=10.5^\circ$. Fig. 1 shows XRD diffractograms of the graphite, GO, RGO and RGO-Ti. Intercalation of oxygen-containing groups between graphene layers changed the interlayer spacing (d-spacing) from 3.3 Å in graphite to 8.37 Å in GO. Observation of (002) peak and absence of (001) peak in XRD pattern of RGO suggest that this RGO sample is reduced completely and composed of free graphene-like sheets with poorly ordered structure along the stacking direction. Absence of titanium-characteristic peaks in RGO-Ti is an indication of too low metal content and/or extremely small metal particle size (Huang et al. 2011, Saner et al. 2010).

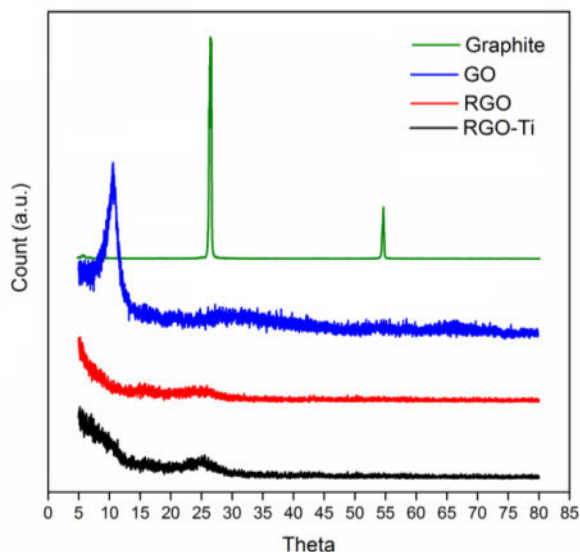


Fig 1. XRD pattern of (green), GO (blue), RGO (red) and RGO-Ti (black)

Raman spectroscopy was used to find the structural information required to define the density of defects in graphene sheets (Poh et al. 2012). Raman spectra (Fig. 2) of all samples display two characteristic bands at 1607 cm^{-1} (G-band) and 1373 cm^{-1} (D-band) related to vibration of the sp^2 -bonded carbon atoms in a two-dimensional hexagonal lattice and defects in the hexagonal graphitic layers respectively (Poh et al. 2012, Giovanni et al. 2012, Wang et al. 2013).

Thermal exfoliation and presence of various functional groups develop different degrees of disorder in carbon based material. Many researchers have used intensity ratio of the D and G bands (D/G ratio) to compare the degree of disorder of graphene sheets qualitatively (Poh et al. 2012, Giovanni et al. 2012, Ambrosi et al. 2011). Multilayer graphene structures such as graphite show a peak at $\sim 2720\text{ cm}^{-1}$ (2D band). Intensity of 2D peak in GO, RGO and RGO-Ti declined compared to that of graphite indicating the presence of structural defects. The intensity of D band in graphite is the lowest one among D bands of all samples. After oxidation a high $\text{D/G} = 0.88$ was observed in Raman spectrum of GO due to existence of large amount of oxygen containing functional groups. Reduced samples, RGO and RGO-Ti, exhibited higher D/G ratios of 1.02 and 1.1, respectively, showing that thermal reduction increased density of defects in these samples. These results are consistent with previous data published in literature (Ambrosi et al. 2011).

In addition to G and D bands, we observed an extra peak at 148 cm^{-1} in RGO-Ti. It has been reported that anatase TiO_2 exhibits Raman band at $\sim 144\text{ cm}^{-1}$ (E_g). Co-existence of E_g band from anatase and D and G bands from RGO confirms presence of TiO_2 on graphene sheets (Choi et al. 2005, Yoshitake et al. 2009, Kadam et al. 2014, Liu et al. 2014, Li et al. 2013).

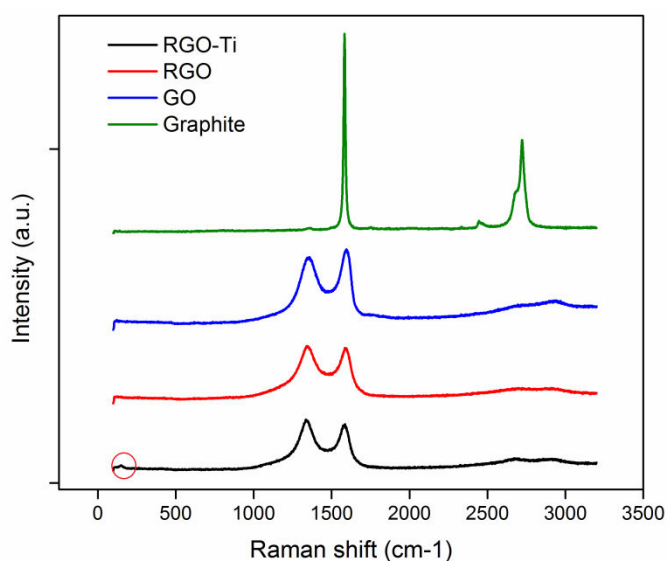


Fig 2. Raman spectra of graphite (green), GO (blue), RGO (red) and RGO-Ti (black)

We characterized the chemical structure of GO, RGO and RGO-Ti by using XPS. We observed four peaks (Fig 3a) at 284.56, 285.02, 286.8 and 288.8 eV in the C 1s XPS spectrum of GO that are related to the C–C (aromatic) (Liu et al. 2013), C–OH (Compagnini et al. 2012, Kim et al. 2014), C (epoxy/alkoxy)/C=O (Wang et al. 2011) and O=C–O (carboxylic) (Liu et al. 2013) groups, respectively. Presence of these peaks implies occurrence of high degree of oxidation during the oxidation process. Fig. 3b shows C 1s XPS of graphite oxide after thermal reduction. The absence of C-OH peak and

decrease of intensity in oxygen-containing group components demonstrated that most of the functional groups were removed from graphene sheets (Liu et al. 2013, Kim et al. 2014). The survey scan result of the RGO-Ti (Fig. 3c) indicates a sharp peak at 285 eV and two low intensity peaks at 458 eV and 530 eV that are in agreement with the C1s, Ti2p3 and O1s spectra of RGO-Ti. Fig. 3d displays Ti2p XPS spectrum of RGO-Ti in which the peaks located in 464.58 and 458.75 eV correspond to Ti 2p_{1/2} and Ti 2p_{3/2}, respectively. It has been reported titanium atoms react with any available oxygen to form TiO₂ with the bonding energy similar to what we observed. Many researchers (Felten et al. 2009, Pisarek et al. 2012, C. Biesingera et al. 2010) suggested that above mentioned bonding energies belong to titanium in fully oxidized state (Ti⁺⁴).

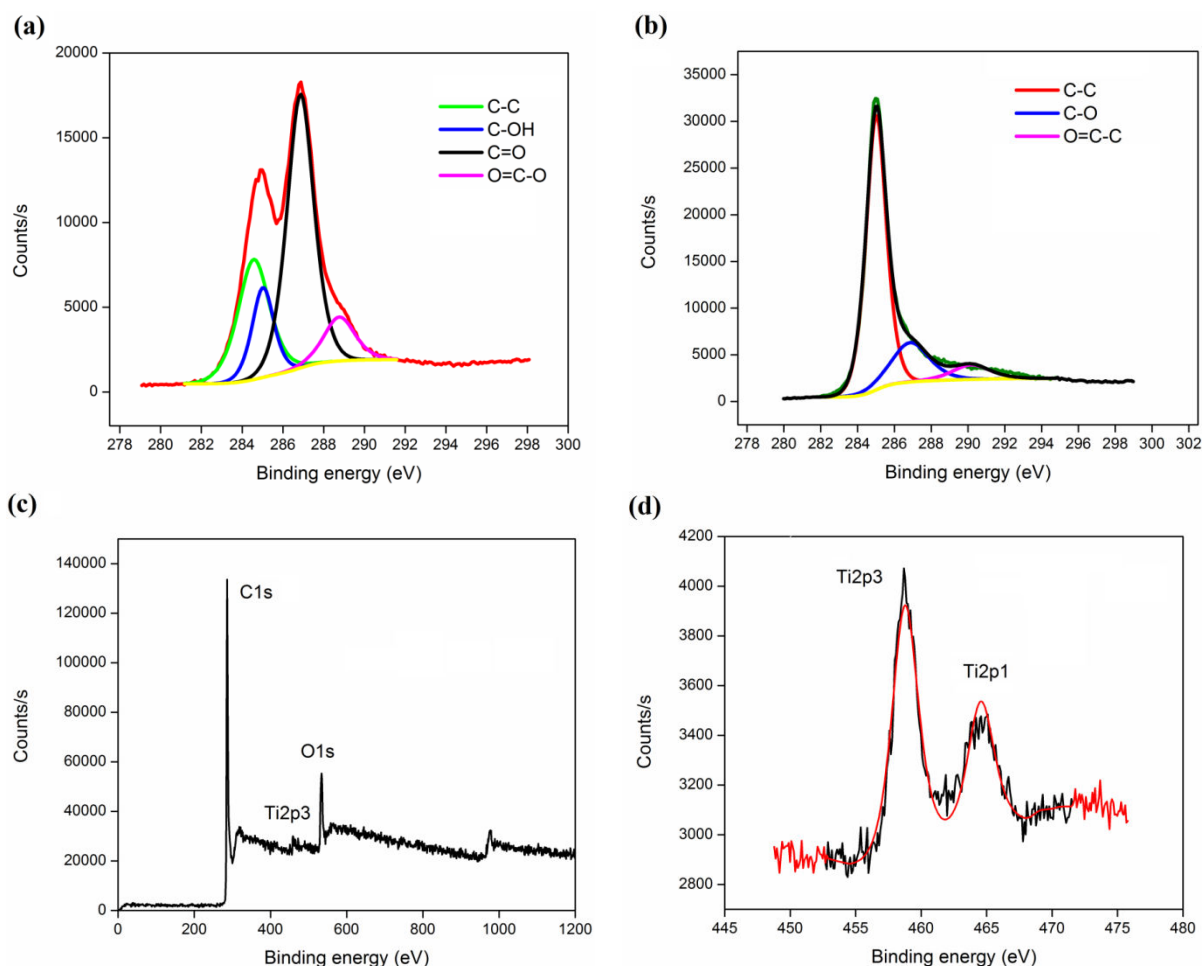


Figure 3. XPS spectrum of C 1s of GO (a), C 1s of RGO (b), survey scan(c) and Ti 2p (d) of the RGO-Ti

We compared BET surface area of reduced samples by using nitrogen adsorption-desorption isotherms at 77 K (Fig. 4). The nitrogen isotherms on RGO and RGO-Ti show that the graphene adsorbs more N₂ than graphene containing titanium. The reasons behind of this observation are higher surface area and lower density of RGO compared to RGO-Ti (Wang et al. 2011). Surface area and total pore volume of RGO were measured to be 655.799 m²/g and 2.41 cc/g compared to 371.144 m²/g and 1.25 cc/g for those of RGO-Ti.

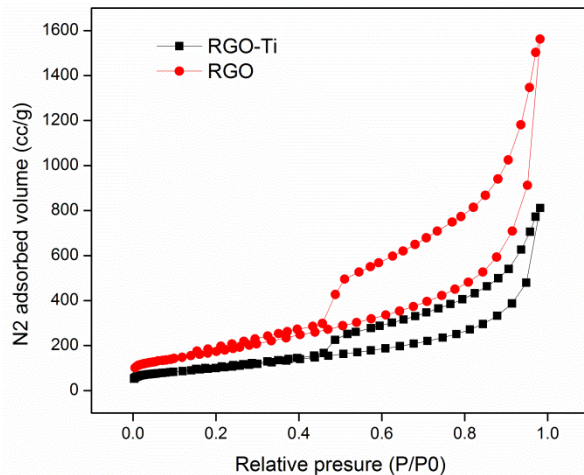


Fig 4. Nitrogen isotherms measured for RGO and RGO-Ti.

We monitored morphological structure of graphene sheets in different specimens by using SEM. Fig. 5 exhibits exfoliated graphene sheets with layered and transparent structure. Higher degree of exfoliation was detected in RGO compared to RGO-Ti that can be ascribed by restacking of graphene sheets in mechanical mixing of graphene with titanium (Parambath et al. 2012). This observation is in agreement with decrease of BET surface area that was extracted from N₂ adsorption-desorption measurement. Fig. 5b shows SEM micrograph of RGO-Ti sample. Since results of XPS and Raman spectroscopy confirmed existence of TiO₂ in this sample, we conclude that bright points with diameter of less than 25 nm (shown with the box in Fig. 5b) illustrate titanium-containing particles.

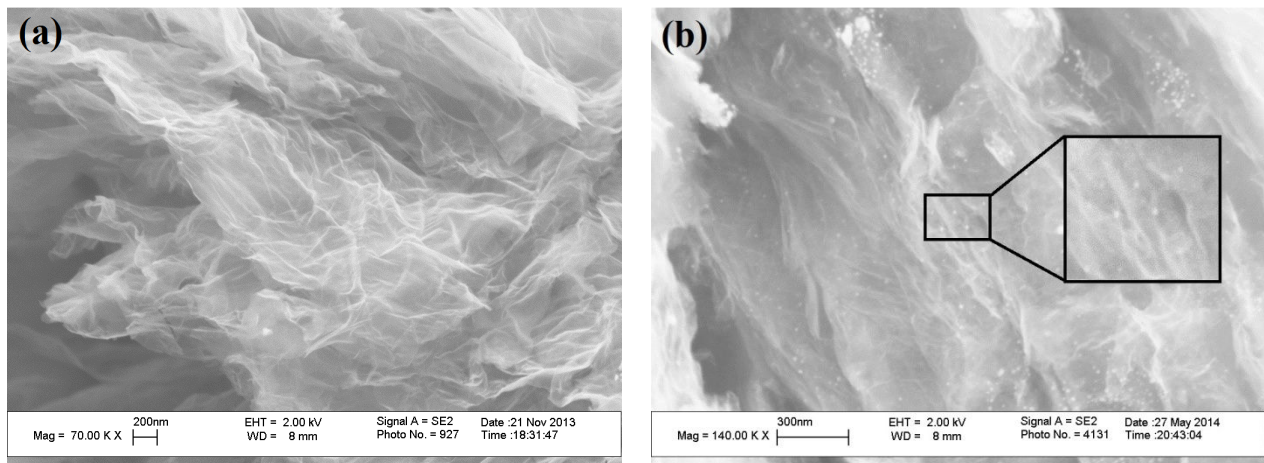


Fig 5. SEM image of (a) RGO and (b) RGO-Ti

Elemental analysis of RGO-Ti sample was shown in Fig. 6. Appearance of a peak at 4.5 keV indicates presence of titanium in the sample (Ullah et al. 2013).

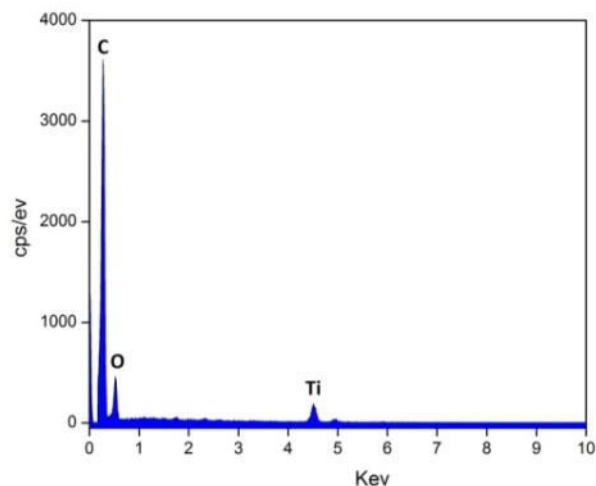


Fig 6.EDX spectra of RGO-Ti

Fig. 7 presents the hydrogen adsorption isotherms at room temperature for RGO and RGO-Ti up to 10 bar. Increasing pressure of hydrogen improved hydrogen uptake of samples. The pristine graphene shows hydrogen storage capacity equal to 1.3 wt % while decorating of graphene with titanium enhanced hydrogen storage capacity to 1.4 wt%.

According to BET results, decrease of surface area and total pore volume, we can conclude that hydrogen uptake via physisorption mechanism is lowered in RGO-Ti but based on Wang *et al.* (Wang et al. 2011) work on Ni-B nanoalloy doped graphene; we suggest that decoration of graphene with titanium improves hydrogen storage capacity by chemisorption of hydrogen.

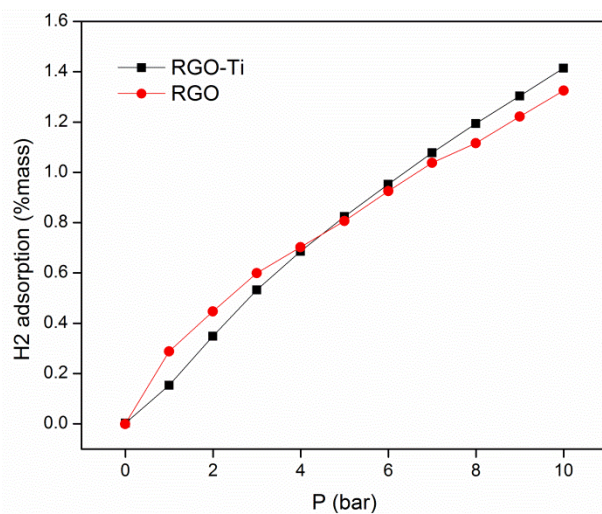


Fig 7. H₂ adsorption of RGO and RGO-Ti

Conclusion

Graphene and graphene supported by titanium were prepared by chemical method. XPS results showed that titanium reacted with any available oxygen atoms at first to form TiO₂. Analysis of nitrogen isotherm indicated decrease of surface area and total pore volume in titanium decorated sample, however, we found that decorating of graphene by titanium increased hydrogen storage capacity by chemisorption mechanism.

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