Graphene-Metal Oxide Based Nanocomposites for Supercapacitor Applications

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ABSTRACT

In this work graphene/TiO$_2$, WO$_3$ nanocomposites were synthesized by facile, surfactant free, in-situ microwave irradiation method, a quick but also are eco-friendly approach. The structure, morphology, composition and thermal stability of the composites were characterized by using XRD, SEM, Raman spectroscopy, and XPS analyses. The SEM and HR-TEM analyses demonstrate the spherical TiO$_2$ and WO$_3$ nanoparticles intercalated on the graphene sheets. XPS studies confirm the binding states of the composite structure. The nanocomposites used as the supercapacitor electrode in three electrode system exhibited higher specific capacitance. The enhanced capacitive performance is due to the intercalation of TiO$_2$ and WO$_3$ nanoparticles on the graphene sheet. The in-situ microwave irradiation method brings a viable, low-cost and facile synthesis of different metal oxide/graphene based composites with promising properties as supercapacitors for energy storage applications.

Key words: graphene oxide, microwave irradiation, supercapacitor.

1. INTRODUCTION

Rapid increase in industrialization has led to a number of severe problems, which in-turn might have a major social impact on issues such as increased usage of electronic devices, large memory back-up devices, renewable-energy power plants and electronic vehicles. This increased usage leads to an enhanced demand for energy storage devices. The need for the development of materials for electrochemical storage with improved performance has become an urgent requirement. Supercapacitors with their unique properties such as fast charging–discharging, high power density and long cycle life time are complementary to rechargeable batteries [1, 2].

Recent research is focused mainly on the development of supercapacitor with combined electrode containing redox active materials and porous carbon materials for achieving both high power and energy density [3]. Till date, the ever increasing growth of research activities in nanoscience and nanotechnology continually brings out new physical and chemical properties of TiO$_2$ and WO$_3$ nanomaterials and thus provides new opportunity for the growth of TiO$_2$ and WO$_3$ based wide-band gap semiconductor material for varied applications. TiO$_2$ and WO$_3$ have been studied for application in large scale energy storage owing to their high specific capacity and high current rate tolerance with various morphologies [4]. Conductive coating and/or adding conductive mediators were developed in order to improve the electronic conductivity of TiO$_2$, WO$_3$ nanoparticles [5, 6].

In recent years, various classes of carbon-based materials are being explored. Among them, graphene has emerged as one of the most interesting materials for supercapacitor applications. Incorporation of TiO$_2$ and WO$_3$ into conductive graphene electrode overcomes the drawbacks in the conductivity and mechanical flexibility of either graphene or TiO$_2$/WO$_3$ electrode. Hence, TiO$_2$ and WO$_3$ were used as additives to carbon materials, especially graphene for enhanced performance.

Recently, several attempts to synthesize TiO$_2$ and WO$_3$/graphene nanocomposites by different methods have been reported in order to fabricate suitable electrode material for supercapacitors applications. An eco-friendly and facile approach for the synthesis of TiO$_2$ and WO$_3$/graphene is essential. Microwave irradiation synthesis is one of the most popular techniques adapted in industries as well as in domestic applications due to the efficient and fast transfer of energy and influence on the size, shape and morphology of the prepared material [7, 8]. In the present work, TiO$_2$ and WO$_3$/graphene nanocomposites were synthesized by facile in-situ microwave irradiation method. In this method, homogeneous distribution of TiO$_2$ and WO$_3$ nanoparticles on the graphene sheet and simultaneous reduction of graphene oxide to graphene were achieved via microwave irradiation. This method enhances the specific surface area and the supercapacitor performance.

2. EXPERIMENTAL

2.1 Formation of TiO$_2$/WO$_3$/Graphene nanocomposite

Graphene oxide was synthesized by the modified Hummer’s method [9]. The TiO$_2$ and WO$_3$/graphene nanocomposites were synthesized by the facile in-situ microwave irradiation method. Initially 60 mg of graphene oxide was added to 60 ml of DI water and treated ultrasonically for about 1 h. Titanium (IV) n-butoxide (0.1 M) /sodium tungstate was added to graphene oxide solution followed by stirring for 1 h. The above mixed solution was kept in the microwave oven at 850W for 10 min. The reaction mixture was then allowed to cool down to room temperature and 2 ml of the reducing agent (H$_2$N$_2$O) was added and stirred for 2 h. The solution was kept in the microwave oven under the same conditions as mentioned above. Finally, the grayish-black product was collected, indicating the reduction of graphene oxide into the graphene. The final product was
filtered and washed using ethanol, water for several times and dried in vacuum oven at 60 °C for 12 h. The above protocol was followed for the synthesis of pure TiO$_2$ and WO$_3$ nanoparticles and graphene separately.

2.2 Electrochemical studies

The electrochemical performance of the nanocomposites was investigated by Chronopotentiometry (CP) analysis. For the preparation of working electrode, TiO$_2$, WO$_3$/graphene nanocomposite, ethanol and nafion solution were mixed homogeneously. The prepared material was coated onto the glassy carbon electrode and allowed to dry for a few minutes. Cyclic voltammetry (CV) measurements were carried out in 1 M H$_2$SO$_4$, Na$_2$SO$_4$ electrolyte (vs. Ag/AgCl) at different scan rates from 5 to 100 mV s$^{-1}$. The mass loading of the electrode active material was 3 mg. All electrochemical studies were performed at room atmospheric condition.

3. RESULTS AND DISCUSSION

Fig. 1 (a) shows the powder XRD pattern of synthesized graphene. XRD pattern of graphene with prominent (002) peak. The diffraction peaks match with the standard pattern (JCPDF NO: 75-1621) and confirmed the hexagonal phase of the graphene. XRD patterns of pure TiO$_2$ and TiO$_2$/graphene composite are shown in Fig. 1 (a). For TiO$_2$, the tetragonal anatase phase is in good agreement with (JCPDS NO: 211272). The characteristic peak of graphene (002) peak is not observed in the XRD pattern due to the overlapping with (101) peak of TiO$_2$ and low amount of graphene used for the composite formation [10]. The microwave reaction results in crystalline tungstic acid hydrates (WO$_3$.H$_2$O) as shown in Fig. 1 (b) and well matched with the JCPDS card No. 48-0719 [11]. Fig. 1(b) indicates the diffraction peaks correspond to the monoclinic phase of WO$_3$ (JCPDS: 43-1035) after calcining at 500°C. Fig. 2(d) depicts the diffraction pattern of WO$_3$/G composite, which is almost similar to the crystalline phase of WO$_3$ with reduced intensity. The inter-planar spacing of graphene (0.37 nm) is higher than that of graphite (0.34 nm) and lower than graphene oxide (0.83 nm).

Fig. 2. HR-TEM images of (a, c) TiO$_2$, WO$_3$/graphene nanocomposite. Insets in Fig. 2(b, d) show the FFT pattern of the composite.

Raman spectra shown in Fig. 3 (a) exhibits two peaks at 1334 (D band) and 1579 cm$^{-1}$ (G band). For TiO$_2$, three strong vibrational peaks are located at 402, 513 and 640 cm$^{-1}$ corresponding to B$_1g$, B$_1g$ A$_1g$, and Eg modes of anatase phase [14]. In TiO$_2$/graphene nanocomposite, TiO$_2$ characteristic peaks are observed along with graphene peaks at 1325 and 1596 cm$^{-1}$. The D/G ratio of graphene oxide and TiO$_2$/graphene composite are 0.809 and 0.865 respectively. The TiO$_2$/graphene composite shows an increased D/G intensity ratio compared to graphene oxide. This confirms the decrease in the average size of the in-plane sp$^2$ domains due to the reduction of the exfoliated graphene oxide, due to the presence of graphene in the TiO$_2$/graphene composite [15].

Fig. 3. Raman spectra of (a) TiO$_2$ and (b) WO$_3$ based graphene nanocomposite.
Fig. 3 (b) shows the WO$_3$ electrode bands at around 803 cm$^{-1}$ and 699 cm$^{-1}$ corresponding to the O–W–O stretching modes, which are the strong characteristic peaks of WO$_3$ crystallites. Additionally, the peak at 252 cm$^{-1}$ is related to the W–O–W bending mode and 944 cm$^{-1}$ is attributed to the symmetric mode of terminal W$^{6+}$=O bond. The D and G bands observed for the WO$_3$/G nanocomposite with less intensity reveal the formation of composite structure. The peak at 699 cm$^{-1}$ due to W=O bond was broadened and shifted to 686 cm$^{-1}$ in the WO$_3$/G, probably due to the formation of C–O–W bonds between the graphene and WO$_3$ nanopolaties [16, 17].

The XPS spectra of TiO$_2$ and WO$_3$/graphene nanocomposites are shown in Fig. 4. The survey spectrum (Fig. 4 (a)) of the TiO$_2$/graphene showed peaks of Ti, C and O confirming the presence of all elements in the composite. The Ti-2p core-level photoelectron spectrum reveals Ti 2p$_{1/2}$ (458.5 eV) and Ti 2p$_{3/2}$ (465.4 eV), which agree with the binding energy values of pure anatase Ti$^{4+}$.

![XPS survey spectra of (a) TiO$_2$/graphene (b) WO$_3$/graphene nanocomposite.](image)

The deconvoluted spectrum of Ti 2p shown in Fig. 4 (a) revealed peaks centered at 465.8 and 460.2 eV, associated with the formation of Ti-C bonds in the TiO$_2$/graphene nanocomposite [18]. Fig. 4(b) represents the XPS of WO$_3$/G spectra of the W 4f doublet peaks. The binding energy states of W 4f$_{7/2}$ and W 4f$_{5/2}$ were observed at 37.79 eV and 35.74 eV, respectively. The separation between W 4f$_{7/2}$ and W 4f$_{5/2}$ core levels was 2.85 eV, indicating the normal state of W$^{5+}$ in the cubic spinel WO$_3$ structure. The BET studies revealed that the synthesized TiO$_2$/graphene, WO$_3$/G nanocomposites possess specific surface area of 529.99 m$^2$g$^{-1}$, 17.55 m$^2$g$^{-1}$, suggesting the successful reduction of graphene oxide into graphene and intercalation TiO$_2$, WO$_3$ nanoparticles in the graphene sheet.

The electrochemical properties of TiO$_2$, WO$_3$/graphene nanocomposite electrode were systematically analyzed in 1M H$_2$SO$_4$, Na$_2$SO$_4$ electrolyte by using three electrode system. electrodes. The CP curves of TiO$_2$ electrode at different current densities in 1M H$_2$SO$_4$ electrolyte are shown in Fig. 5 (a) reveal that the electrode has good capacitive behavior with superior electrochemical reversibility. The shape of CP curves, the derivative voltage-time profile and the symmetric charge-discharge curves indicate the non-Faradic redox reaction exhibited by the TiO$_2$/graphene electrode. Comparison of CP curves of TiO$_2$, graphene oxide, TiO$_2$/graphene composite electrodes at a current density of 1 A g$^{-1}$. The composite electrodes have higher charge-discharge time than pure TiO$_2$ and graphene oxide electrodes, which demonstrates that the composite electrode exhibit the highest specific capacitance and excellent electrochemical performance.

![Fig. 5. CP curves and specific capacitance (c) TiO$_2$ and (d) WO$_3$/graphene composite.](image)

The specific capacitance of the TiO$_2$, WO$_3$/graphene electrode was calculated using the equation

\[ C_s = I \frac{\Delta t}{\Delta V} \frac{\Delta t}{m} \]

where, I is the constant applied current, \( \Delta t \) is the discharge time, m is the mass of the electro-active material and \( \Delta V \) is the potential window. For TiO$_2$ and WO$_3$/graphene electrode, the specific capacitance values were calculated to be 585, 761 F g$^{-1}$ at current densities of 1 A g$^{-1}$ respectively. The specific capacitance values were higher than the other electrodes. The decrease in specific capacitance at higher current density may be ascribed to the large portions of the electrode surface that are inaccessible to the electrolyte [19].

The long cyclic stability is the most important requirement for supercapacitor applications. The specific capacitance retention of the TiO$_2$/graphene, WO$_3$/graphene electrode reached 100% at 5000 cycles, 100 %, 99.2 % of its initial capacitance, exhibiting good cycling stability.

\[ \eta = \frac{t_d}{t_c} \times 100 \]

where, \( \eta \) is the Columbic efficiency, \( t_d \) and \( t_c \) are the discharge and charging time derived from charge–discharge curves. The Columbic efficiency (\( \eta \)) of TiO$_2$ and WO$_3$/graphene electrodes were calculated to be 99.8% and 98.2%. Based on the electrochemical analysis, it was concluded that the composite electrode exhibited a higher specific capacitance, good rate capability, and highly efficient for supercapacitor applications.
4. CONCLUSION

The nanocomposites of TiO$_2$ and WO$_3$/graphene were synthesized by a facile in-situ microwave irradiation method without the assistance of any surfactant. The structure and morphology of the prepared composites were characterized by XRD and SEM analysis. Functional groups and phase formation of the synthesized material were further confirmed by and XPS and Raman spectroscopy studies. Based on the electrochemical studies, the enhanced specific capacitance values of composite electrodes are attributed to the combination of pseudocapacitance of the metal oxides and partially influenced by the inherent double layer capacitance of the graphene sheet. The composite electrode revealed excellent cyclic stability indicating that the nanocomposite can be used as a potential electrode material for supercapacitor applications.

REFERENCES