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Facile *in-situ* microwave irradiation synthesis of TiO_2/graphene nanocomposite for high-performance supercapacitor applications

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ABSTRACT

In this work, TiO_2/graphene nanocomposite was 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, FT-IR, Raman spectroscopy, and TGA analyses. XRD result shows the tetragonal anatase phase of pure TiO_2, TiO_2 in the composite and their crystallite size were estimated to be 2.8 and 2 nm respectively. The SEM and HR-TEM analyses demonstrate the spherical TiO_2 nanoparticles intercalated on the graphene sheets. TGA results reveal higher thermal stability of the TiO_2/graphene nanocomposite over graphene oxide and TiO_2 nanoparticles. 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 value of 585 Fg^{-1} at a current density of 1 Ag^{-1} in 1 M H_2SO_4 as compared to graphene oxide (174 Fg^{-1}) and TiO_2 electrode (66 Fg^{-1}). The enhanced capacitive performance is due to the intercalation of TiO_2 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 for energy-storage applications in supercapacitors.

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 increased demand for energy storage devices. So 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].

Based on the energy storage mechanism, supercapacitors can be classified into two types, (i) electrical double-layer capacitors (EDLCs), and (ii) redox capacitors or pseudocapacitors. The EDLC is demonstrated from the charges that build up electrostatically at the interface of the electrode and electrolyte, while the pseudo-capacitance is obtained from the rapid Faradaic reactions that occur on either the surface or majority of an electrode [3,4]. EDLCs are mostly based on carbon-active materials of high electrical conductivity, large surface area, while pseudo-capacitors are based on redox-active materials of transition metal oxides and conducting polymers [5,6]. Compared with carbon electrode materials for EDLCs, pseudo-capacitive electrodes have higher electrochemical capacitances and energy densities, and they can satisfy the requirements of high-performance supercapacitors [7]. Therefore, 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 [8].

Till date, the ever increasing growth of research activities in nanoscience and nanotechnology continually brings out new physical and chemical properties of TiO_2 nanomaterials and thus provides new opportunity for the growth of TiO_2-based wide-band gap semiconductor material for varied applications such as photocatalysis [9], solar cells [10], Li-ion batteries [11], and sensors [12] due to its advantages such as large surface area, chemical stability, low cost, abundance in nature and eco-friendly. TiO_2 has been studied for application in large scale energy storage owing to its high specific capacity and high current rate tolerance with various morphologies [13]. Besides, the TiO_2 exhibits low electronic conductivity, poor electrochemical stability and low rate capability as well as relatively low theoretical capacity, which restricts the industrial application of TiO_2. Therefore, methods such as

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conductive coating and/or adding conductive mediators were developed in order to improve the electronic conductivity of TiO_2 nanoparticles [14].

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. Graphene is the sp^2 hybridized hexagonal arrangement of two dimensional honeycomb carbon lattice material, with good conductivity, excellent chemical stability, large surface-to-volume ratio, high mobility of charge carriers and good capacitive performance [15,16]. Incorporation of TiO_2 into conductive graphene electrode overcomes the drawbacks in the conductivity and mechanical flexibility of either graphene or TiO_2 electrode. Hence, TiO_2 is used as an additive to carbon materials, especially graphene for enhanced performance.

Recently, several attempts to synthesize TiO_2/graphene nanocomposites by different methods have been made in order to fabricate suitable electrode material for supercapacitors applications. Few such methods employed for the synthesis of TiO_2/graphene composite include hydrothermal synthesis [1], atomic layer deposition (ALD) [17], Ball milling and hydrothermal processing [18], vacuum-assisted filtration [19]. However, the aforesaid methods are always time-consuming and involve complicated reaction and high processing temperature. Moreover, the materials prepared using the above methods possess low specific capacitance. Henceforth, an eco-friendly and facile approach for the synthesis of TiO_2/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 [20,21]. In the present work, TiO_2/graphene nanocomposites were synthesized by facile *in-situ* microwave irradiation method. In this method, homogeneous distribution of TiO_2 nanoparticles on to 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. Materials

Graphite powder (99.999% Alfa Easer Laboratory Reagent fine power, USA), sodium nitrate (MERCK) and hydrogen peroxide (MERCK 30% GR Proanalysis), potassium permanganate (SRL, Extra pure AR Grade), hydrochloric acid, sulfuric acid (Fisher Scientific), and titanium (IV) n-butoxide, were used for the synthesis.

2.2. Synthesis of graphene oxide

Graphene oxide was synthesized by the modified Hummer's method. The natural graphite powder (2 g) and $NaNO_3$ (1 g) were added to 50 ml of H_2SO_4 maintained in an ice bath. The mixed solution was stirred continuously for 1 h. After adding 8 g of $KMnO_4$ to the reaction mixture, a colour change to dark greenish black was visualized while the reaction mixture was still maintained in an ice bath at 5 °C. Furthermore, the solution was stirred at room temperature for 24 h, until the colour changes from greenish black to brown. Subsequently, 50 ml of distilled water was added drop wise into the reaction mixture and maintained at 30 °C. In addition, 100 ml of distilled water and 3 ml of hydrazine peroxide (H_2O_2) were introduced into the solution, which led to a sudden change in the colour to brilliant or royal yellow, indicating the conversion of natural graphite into graphene oxide. The solution was then filtered and washed several times with HCl, distilled water and ethanol to remove residual functional groups. Finally the product was dried at 60 °C for 24 h in a vacuum oven and brownish colored graphene oxide powder was collected as the product [22].

2.3. Formation of TiO_2/graphene nanocomposite

The TiO_2/graphene nanocomposite was 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) was added to graphene oxide solution followed by stirring for 1 h. The above mixed solution was kept in the microwave oven at 850 W for 10 min. The reaction mixture was then allowed to cool down to room temperature and 2 ml of the reducing agent (H_6N_2O) 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 nanoparticles and graphene separately.

2.4. Characterization studies

The crystalline structure of the prepared materials was analyzed by XRD using CuKα radiation (Rigaku, MiniFlex II-C). The morphology was studied using SEM (TESCAN, VEGA3) and HR-TEM (HI-TACH). Thermal behavior of the synthesized material was studied by TG-DTA (SII-TG/DTA6300) analysis. The FT-IR spectra were recorded by the KBr pellet technique using Alpha Bruker FT-IR spectrophotometer (Bruker optics systems). Raman spectra were recorded using Lab RAM HR micro Raman system using He-Ne laser of 632 nm wavelength. The binding energy of the material was analyzed by XPS spectra recorded using ESCA 3400 spectra photometer (SHIMADZU). The surface area was measured by ASAP 2420 V2.09 (V2.09 J) Unit1 Port1 Serial #: 203. The electrochemical behavior of the materials was analyzed by three electrode system using Bio Logic electrochemical work station. The prepared composite coated with glassy carbon, Ag/AgCl and platinum wire were used as the working electrode, a reference electrode and the counter electrode respectively.

2.5. Electrochemical studies

The electrochemical performance of the nanocomposites was investigated by Cyclicvoltammetry (CV), Chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) techniques. For the preparation of working electrode, TiO_2/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_2SO_4 electrolyte in the potential range between 0.0 and 0.8 V (*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. The charge -discharge studies were performed to calculate the specific capacitance at different current densities applied between 0.0 and 0.8 V. The electrochemical impedance spectroscopy was also studied in the frequency range 1 Hz to 1 kHz. All electrochemical studies were performed at room atmospheric condition.

The two-electrode device was also fabricated by mixing the as-prepared samples, carbon black, and polyvinylidene fluoride (PVDF) in the mass ratio of 80:15:5 and dispersed in 1-methyl-2-pyrrolidone (NMP), resulting in a homogeneous paste. The resulting solution mixture was coated onto a nickel foam substrate (1 cm^2) for the positive electrode and activated carbon coated substrate as negative electrode with PEDOT as the separator. The electrodes were dried at 120 °C for 12 h in a vacuum oven. The mass loading of the electrode active material was 8.5 mg·cm^{-2} [23–25]. The cyclic voltammetry and charge/discharge response of the device were performed between 0 and 1.0 V at different current densities.