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Full Length Article

Effect of Al doping on the electrical and optical properties of TiO_2 embedded Graphene Oxide nanosheets for opto-electronic applications

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ABSTRACT

Exfoliated graphene sheets serve as a good candidate for high performance electronics as they display unique electrical properties. Owing to this, (GO) graphene oxide- Titanium dioxide (TiO_2) nanocomposites has been utilized as an electron transport layer (ETL) for photovoltaic applications. Incorporation of GO-TiO_2 nanocomposites in solar cells enhances the efficiency of the device by improving the electron transport. Moreover, metal doping to TiO_2 enhances the optical properties by passivating the defects. Metal doping improves charge transports of a TiO_2_ GO nanocomposite. This work, aims to study the role of aluminum as a dopant in TiO_2_GO nanocomposites. TiO_2_GO nanocomposites were synthesized by wet chemical method. The effect of aluminum and graphene oxide were investigated on the structural, morphological, electrical and optical characteristics of anatase TiO_2. The amount of GO added to Al doped TiO_2 was optimized and their impacts on carrier concentration, mobility and film resistivity were investigated. The results revealed that the synthesized Al doped TiO_2_ GO nanocomposites were of superior quality and is suitable material for energy-conversion and –storage applications devices.

1. Introduction

TiO_2 is a technologically important and naturally occurring, low cost material. It has good chemical and thermal stability, it is inexpensive and eco-friendly. It is used in photo catalysis and solar cells, electronic and optical devices, air and water purification and in numerous medical and technological applications [1,2]. Dye- sensitized solar cell (DSSC) and perovskite solar cell are highly promising in their performance and cost, they employ titanium dioxide (TiO_2) as nanostructured electron transporting layer and/or hole blocking layer [3–6]. Non-stoichiometry induced defects in TiO_2 has a negative impact on efficiency and the long-term photo-stability of the photovoltaic system [7]. Modification of TiO_2 by doping has significant effect on its band structure and trap states. Absorption in UV region prevents any visible light mediated transition in TiO_2. The efforts were made to enhance the absorbing capability of TiO_2 over the visible spectrum by doping it with metal [8–10]. Haspert et al. [11] doped Al with TiO_2 benefits of TiO_2's high dielectric constant, while minimizing leakage current as needed for nanocapacitor applications. Aluminum-doped TiO_2 has attracted much attention because of its low cost, good optical and electronic properties, heat stability and non-toxicity. Roose et al. [12] reported that dye-sensitized and perovskite solar cells employing Al-doped TiO_2 have increased device efficiencies and significantly enhanced operational device stability in inert atmospheres. They have reported that doping can shift the conduction band (CB), increase the charge transport and reduce the recombination and prolong the device lifetime. Li et al. [13] reported that the photo-anode modified with Al doped TiO_2 layer can improve the charge lifetime by inhibiting the recombination between electrons and electrolyte in DSSCs. Duan et al. [14] reported that Al doping in SnO_2 suppressed charge recombination and also tuned the bandgap. Recently, Zhao et al. [15] employed Al doped ZnO as electron collection layer in per-

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ovskite solar cells and obtained a thermally stable perovskite layers. S-H Lee [16], used the aluminum-doped zinc oxide (AZO) layer as a transparent conducting oxide (TCO) layer in ZnO nanowire (NW)-based DSSCs. Hence, the recent studies prove that Al doped metal oxides films are favorable candidate for photo energy conversion devices.

Recently reports have witnessed the graphene's photon-electron multiplication effect, using "ultrafast time- and angle-resolved photoemission spectroscopy" (trARPES) [17]. They revealed that doped graphene in combination with good photoactive layer allows it to generate two electrons for one photon it receives. Novel photovoltaic device using doped graphene can help improve the light conversion efficiency. Graphene, the ultra-thin material is famous for its strength, light weight and possess fascinating room temperature conductivity. A major bottleneck of anatase TiO_2, is the limited absorption of solar energy spectrum (absorbs in ultraviolet region), due to its large bandgap of 3.2 eV. If one could reduce the band gap of anatase to the visible region, TiO_2_ based nanocomposites could become the best material for solar cell applications. The identification of a TiO_2 anatase phase with a bandgap in the visible and high chemical reactivity has important implications for solar energy conversion, photocatalysis, and artificial photosynthesis. In view of this many papers has been published utilizing nanocomposites of graphene and TiO_2 nanoparticles as the electron collection layers in meso-super structured perovskite solar cells [18].

In the present study, considering the photon-electron multiplication effect of graphene, Al doped TiO_2_GO nanocomposites were prepared for the first time. Well crystalline TiO_2 nanofibers were synthesized hydrothermal method, Graphene oxide was synthesized by Hummer's method. The nanocomposites were synthesized for different weight percentages of Al and GO. The effect of Al doping on the optical and electrical properties of TiO_2_GO nanocomposites was extensively studied.

2. Materials and methods

2.1. Materials

All the chemicals were of analytical grade and used without further purification. Titanium tetra isopropoxide (TTIP), Aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), *n*-butanol ($C_4H_{10}O$), Graphite powder, Sodium nitrate ($NaNO_3$), Sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), Hydrogen peroxide (H_2O_2), Hydrochloric acid (HCl).

2.2. Synthesis of the Al doped TiO_2nanocomposites

Al doped TiO_2 nanoparticles (Al wt% – 0.5, 1, 2,) were prepared by hydrothermal method using titanium tetra isopropoxide (TTIP) and aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) as precursors. First, TTIP and aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) were added to 60 mL of butanol. The solution was maintained at room temperature under constant stirring for 30 min 18 mL of deionized water was slowly added to the above solution and then stirred for one hour. The white-colored solution was then transferred to a 100 mL Teflon-lined stainless steel autoclave. This autoclave was maintained at 180 °C for a period of 12 h. The resulting products were centrifuged several times. Finally, the product was kept for annealing at 350 °C for 3 h in a furnace.

2.3. Preparation of GO

GO was prepared from graphite flakes by using Hummer's method [19]. 2 g of Graphite powder and 1 g of $NaNO_3$ and 92 mL of H_2SO_4 (98%) were mixed in a 1000 mL volumetric flask kept in an ice bath (0–6 °C) under continuous stirring. 6 g of $KMnO_4$ was added to the suspension very slowly. The addition rate was controlled carefully to preserve the reaction temperature lower than 10 °C. Then the ice bath was removed, and the sample mixture was stirred at 35 °C till it became brownish paste. Then the reaction was weakened with the slow addition of 92 mL of water. The reaction temperature was increased to 96 °C with effervescence, and the color changed to brown. The mixture was then decanted into 280 mL of deionized water and the unreacted $KMnO_4$ was removed by adding of 3% hydrogen peroxide. The reaction mixture was then allowed to settle down. The obtained graphite oxide was purified by using 1 M of HCl in deionized water until a neutralized pH was achieved. Finally, the resulting graphene oxide (GO) was dried at 60 °C in a vacuum oven.

2.4. Preparation of Al doped TiO_2_GO composites

The Al doped TiO_2_GO composites were obtained via hydrothermal method. Graphene oxide was ultrasonicated in a 70 mL of deionized water. Two different calculated amounts of the GO solution was taken and added to two beakers containing 1 g of Al doped TiO_2 sample each. These solutions were continuously stirred for 2 h to obtain a homogeneous suspension. Later the suspensions were transferred to 100 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 12 h. The resulting products were centrifuged several times. Finally, the products were dried at 60 °C for 12 h in an oven. Thus, the obtained Al doped TiO_2_GO nanocomposites with 1 wt% GO and 5 wt% were processed and stored for future use.

2.5. Characterization techniques

X-Ray Diffraction (XRD) patterns were obtained using PANalyticalX'Pert pro with CuKα radiation (λ = 1.5406 Å). Surface morphologies were obtained by Field emission scanning electron microscopy (FESEM) images using a JEOL JSM 7001F microscope at an accelerating voltage of 15 kV. UV–vis absorption spectroscopic studies were studied using Shimadzu, UV-2600 Spectrophotometer. Raman Spectroscopy was studied using JASCO-NRS-7100. Transmission electron microscopy (TEM) images were obtained using JEOL JEM 2100F microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed via a Kratos analytical instrument (Shimadzu Corporation, ESCA 3400, Japan). The photoluminescence (PL) spectra were recorded at room temperature using Fluorocube – JOBIN- VYON. The electrical resistivity, carrier concentration, and mobility were measured at room temperature in a van der Pauw (VDP) four – point probe configuration by using automated Hall Effect measurement using ECOPIA HMS – 3000.

3. Results and discussion

Figs. 1 and 2 portrays the X-ray diffraction patterns of the undoped TiO_2, Al doped TiO_2, GO and Al doped TiO_2_GO nanocomposites. Phase analysis reveals the dominance of, anatase phase (JCPDS card no. 21–1272) of TiO_2 for all the sample [20]. In addition to the anatase, a weak peak corresponding to brookite is also observed at 2θ value of 30.8° for pure TiO_2. Brookite phase was dormant for 0.5% and 1% of Al doping, but the peak intensity slightly increased for 2% of doping. A slight shift in anatase peak corresponding to (101) plane was also observed for 2% Al doping. Peaks related to Aluminium-phase were not seen in any of the synthesized samples [21,22]. However, the effect of Al-substitution in Ti-position was confirmed by the small displacement of peaks and the reduction in peak intensities of the Al doped samples. Manu et al. [23] reported similar observations, the intensity of the XRD

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