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Self-assembled graphene oxide on a photo-catalytic active transparent conducting oxide

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ABSTRACT

For the first time, convective assembly technique was used for coating graphene oxide (GO) nano-sheets on an indium free, low cost and good conducting Nb doped TiO_2 (TNO) thin films as a transparent conducting oxide (TCO) template. This construction enhances the charge transport as well as getting the benefit of photocatalysis activity of graphene-TiO_2 structure. Surface morphology was investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM). TCO template showed a smooth surface with root mean square value (RMS) of 0.5 nm. The assembled GO thin layer has wide continuous area, with wrinkles, crumbles and folding at the edges. Raman analysis was used to investigate the phonon lattice vibrations within the films. According to photo-catalytic activity measurements, GO on TNO films exhibited better photo-catalytic efficiency. The proposed hybrid material structure exhibited transparent conducting property and photo-catalytic activity.

1. Introduction

It is convention to use Pt coated transparent conducting oxides TCO as a counter electrode because of its stability and electro-catalytic properties [1]. However, Pt is extremely expensive with diminishing supplies because of its applications in jewelry, catalyst, proton exchange membrane fuel cells (PEMFCs) and dye sensitized solar cells (DSSCs). Hence, Replacing Pt by low cost alternative materials is mandatory since Pt costs 40% of DSSCs price [2–5]. Economically, it is efficient to replace Pt counter electrode by multi-function carbonaceous materials due to their low cost, high electronic conductivity and reactivity [6–8]. Graphene based materials were first used in 2007 as a transparent electrode to replace fluorine doped tin oxide (FTO) at the photo anode [9].

Gratzel et al. reported a generation of photovoltaic devices with high efficiency, simple fabrication process and low cost DSSCs based on dye sensitized colloidal anatase titanium dioxide (TiO_2) films [10]. One of the strategies to facilitate the transport of photo generated electrons through TiO_2 and suppress the recombination is directing photo-generated electrons by introducing carbonaceous nano-materials as charge carriers [11,12].

Titanium dioxide has a wide range of applications, including semiconductor based photo-catalysts, pigments, catalysis, sensors, high-k material and resistive random access memory (RRAM) devices. Transparent TiO_2 thin films are characterized by high refractive index which is suitable for optical applications. There are three major structures of titanium dioxide; rutile (the most stable), anatase and brookite. Indeed, it is known that Nb doping of rutile TiO_2 decreases the resistivity (ρ) by a factor of more than 5500. The transport properties of rutile phase films were quite different from anatase one. However, anatase TiO_2 tends to be oxygen-deficient, less transparency. In addition to the oxygen deficiencies, the substitution of Nb for Ti could provide carriers since Nb impurities generates donor states near the conduction band [13–16]. TCOs are a key component in many optoelectronic devices including smart displays, flat panel displays, and photovoltaic devices [17]. TNO films are attracting attention as a new TCO, with comparable values of conductivity (σ) and transmittance (T) to those of Sn-doped In_2O_3 (ITO) [18]. Bhachu et al., reported that TNO thin films combines multifunctional properties (photo-catalytic activity, optical transparency, and electrical conductivity) within the same layer, making it a promising alternative to conventional TCO materials [19]. Horie et al., added Nb doped TiO_2 as a conductive agent to TiO_2 meso-porous layer in dye sensitized solar cells [20]. Hitosugi et al. have demonstrated that TNO films on a glass substrate, synthesized by PLD and annealed at 500 °C in a H_2 ambient, have high transmittance and low resistivity (ρ) values of 4.6×10^{-4} Ω·cm [21,22]. However, from a practical point of view, direct growth of TNO films on heated substrates without annealing is preferable because of simple preparation procedure and lower cost. Our group succeeded in the deposition of transparent conducting TNO films on glass substrates without annealing beside the epitaxial growth on GaN template [23–25].

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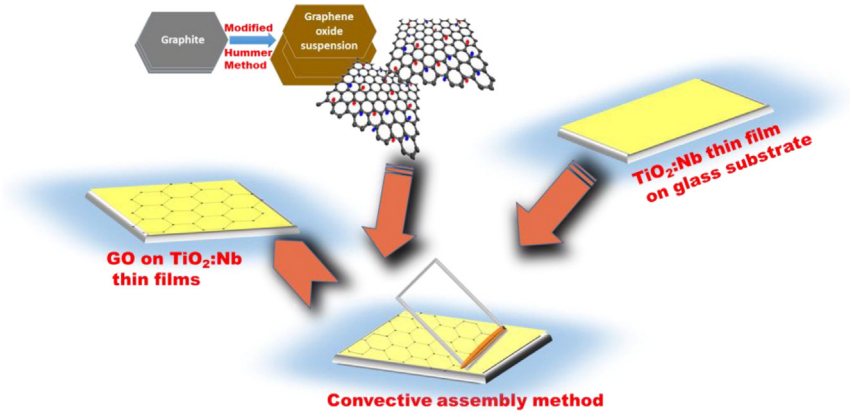

Fig. 1. Schematic diagram representing the experimental procedure. Step 1, GO nanosheets was synthesized by modified Hummer method. Step 2, Nb doped TiO_2 thin film was deposited on glass substrate. Step 3, GO continuous layer was prepared by convective assembly technique.

Graphene, a two dimensional (2D) honeycomb flat monolayer of carbon atoms, has attracted attention due to its superior structural and electronic properties with wide range of applications [26–28]. Graphene can be prepared by several methods, including thermal expansion [29], micromechanical exfoliation [30], chemical vapor deposition [31], reduction from GO [32,33]. Transparent graphene films can be obtained by chemical vapor deposition (CVD) as transparent conductive electrodes (TCE) in organic photovoltaic cells [34]. Recently, graphene oxide-TiO_2, and graphene-TiO_2 are considered as the next generation of high-performance photocatalyst [35]. A considerable effort has focused on the application of TiO_2 with graphene in photo-degradation [36].

In the open literatures, there are many attempts to introduce different materials like conducting polymers (polyaniline, polypyrole and PEDOTIPSS), carbon nanotubes and graphene as Pt free cathode materials in DSSCs [37–42]. However, most of Pt free cathode materials use an expensive TCO (ITO). The advantages of selecting TNO thin films as TCO are relatively low cost, photocatalytic activity, high refractive index as well as its good conductance and transmittance. Here we open the gate to use GO on TNO films as a promising cathode material in DSSCs. To the best of our knowledge, there is no report of using TNO thin films as a template for GO.

2. Experimental

Fig. 1 summarizes the experimental work, which can be described in three steps. In the first step, GO was synthesized using modified Hummer method. More details about the preparation procedure can be found elsewhere [32,33]. In the second step, TNO thin films were deposited on non-alkali glass substrate using radio-frequency magnetron sputtering technique as described in reference [23]. $Ti_{1-x}Nb_xO_2$ films with x value of 0.09 were deposited on non-alkali glass substrate at deposition temperature of 500 °C, deposition pressure of 5 Pa and oxygen fraction of 0.02%. In the third step, TNO thin films were covered by a continuous thin layer of GO (11 nm) using convective assembly technique. The convective assembly set up is as follow: a cleaned glass substrate was used as a knife blade which oriented (45°) with respect to TCO template. 100 μL of a well dispersed GO solution (1 mg/mL) was injected between the blade and the template to make a meniscus. Then, the blade was moved slowly with step motor at a speed of 1 cm/h.

The samples were characterized using XRD, AFM, FE-SEM, TEM, Raman spectroscopy and UV–vis spectrophotometer (JASCO 570). Philips X-ray diffractometer (Model X-Pert) utilized monochromatic (CuK_α) radiation operated at 40 kV and 25 mA. The surface morphology of our samples were investigated using Helios 400 FE-SEM. In non-contact mode, AFM was used to study the roughness and surface morphology of the deposited films. High resolution transmission electron microscopy (HRTEM) images were monitored using Model JEM 1230 (JEOL, Japan) to investigate the nano-scale structures. The lattice vibration modes have been investigated by Raman spectroscopy measurements at room temperature (Model Renishaw system 2000) using Ar + laser with power of 3 mW and at wavelength of 514 nm. The electrical conductivity were investigated by Van der Pauw Hall measurement system (HMS-3000), using ohmic contacts formed by silver paste. In order to investigate the photo catalytic activity of the prepared samples, 0.2 mM of methylene blue (MB) was spin coated on the prepared samples and kept overnight in dark. Spin coater was rotated at

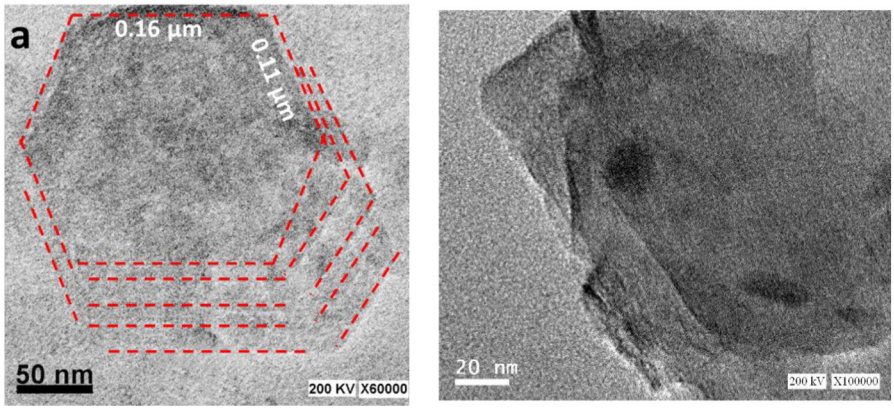

Fig. 2. TEM images of GO nanosheets.