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Band gap reduction of titania thin films using graphene nanosheets

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ABSTRACT

Titania possesses a band gap of ~3.2 eV, whereas the work function of graphene ~4.5 eV exists near the lowest unoccupied molecular orbital (LUMO) of titania. The photoexcitation of electrons in titania (TiO_2) is possible only under the ultraviolet radiation. If such conversion is required in visible light range, band gap has to be lowered below 3.1 eV. This research work hence aims at lowering the band gap of titania thin films by incorporation of graphene nanosheets. Graphene was synthesized using modified Hummer's method. Oxidation of graphite was confirmed by X-ray diffraction (XRD) revealing a peak at 11.8° with interplanar distance of 7.5 Å and energy dispersive X-ray spectroscopy (EDS) analysis. Atomic force microscopy (AFM) analysis revealed exfoliation of single layer graphene oxide nanosheets having thickness of 0.6–1.0 nm. Fourier transform infrared spectroscopy (FT-IR) analysis confirmed the reduction of graphene oxide by revealing removal of carbonyl group ($C{=}O$). Titania sol was obtained using hydrolysis and condensation of titanium tetraisopropoxide. The TiO_2–graphene composite was prepared by liquid phase dispersion of graphene oxide into titania sol and reduction of deposited films was carried out by exposing hydrazine hydrate vapors. In the second method, nanoparticles of reduced graphene oxide were dispersed in titania sol; thin films were deposited on indium–tin oxide (ITO) coated glass using spin coating and subsequently heat treated. A scanning electron microscope (SEM) was used to reveal dispersion of graphene nanosheets among homogenously distributed titania nanoparticles of uniform size distribution (~30–50 nm). Surface roughness of about 16 nm was observed by AFM topographic images. The highest occupied molecular orbital (HOMO) and LUMO levels were calculated by cyclic voltammetry and subsequent band gap was calculated which came out to be as low as 2.9 eV. Ti–O–C chemical bonding between titania and graphene sheets resulted in enhanced electron transport in the obtained composite films.

1. Introduction

Titania, either in anatase or rutile phase, is considered to be one of important materials for various applications on account of its property of a photoexcitation phenomenon. Among the applications, efficiency of photocatalytic devices and photovoltaic solar cells could be enhanced if the band gap of the films made up of titania may be narrowed down [1,2]. Till now, several methods have been reported in which doping of titania is done to reduce the band gap and enhance the photocurrent by preventing photo-excitons recombination [3–5].

Carbon nanostructures have superior electrical properties and hence they can provide a medium for transport of electrons in semiconductor thin films. Use of carbon

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nanotubes in TiO_2, CdS and CdSe thin films has resulted in increase in the efficiency of photocurrent in such structures [6–8]. Graphene, a 2D carbon nanostructure, has high electron mobility (exceeding 2000 cm^2/V). Incorporation of graphene has shown enhancement in the charge transfer rate of electrons. This increased charge transfer rate resulted in increase in the photocurrent by preventing recombination of photo-generated electron–hole pair because of π–π interactions of graphene [9–11].

Originally, titania possesses a band gap of ~3.2 eV. Lowering of band gap is essential for maximum harvesting of sunlight and thus improvement of efficiency of devices hence produced. Graphene, having a work function of 4.5 eV, is explored in this research work for its effect on the band gap of titania thin films and also on photocurrent generated in such structures. In the past, much of the research have been performed for enhancement of photocatalytic activity of titania using graphene nanosheets, such as preparing composites through thermal reaction [5], solvothermal reaction [9], hydrothermal method [10,12,13], sol–gel method [14] etc. These methods have shown success in increment of photocatalytic activity by the composite; however none of the work actually reported the effect of graphene on the band gap of the semiconductor material. This work was hence developed to report the change in electrical properties of titania by incorporation of graphene nanosheets in two forms, i.e., graphene oxide (GO) and reduced graphene oxide (RGO). Sol–gel route was employed to obtain titania sol and graphene was dispersed in the sol. Thin films were obtained using spin-coating composite sol on the glass and ITO substrates. After heat treatment of the films, characterization and testing were performed.

2. Experimental work

Graphene oxide was synthesized from flake graphite (average+100 mesh ($\geq$75% min), SigmaAldrich) by a modified Hummers method reported elsewhere [15]. All other chemicals were of analytical reagent grade and used without further purification. Sonication of the resultant solid was carried out in water to exfoliate graphene oxide nanosheets. Chemical reduction of GO was carried out by adding hydrazine hydrate (1.00 ml, 32.1 mmol) (Merck) in the exfoliated GO dispersion and the solution was heated at 100 °C for 24 h under a water-cooled condenser for 24 h. The reduced GO slowly precipitated out as a black solid. The subsequent nanoparticles were washed with water and methanol and finally vacuum dried.

For thin film fabrication, titania sol was prepared by hydrolysis and condensation of 97% titanium tetraisopropoxide (TTIP) (Aldrich) in the acidic mixtures of glacial acetic acid and 37% hydrochloric acid. The solution, whose composition is shown in Table 1, was heated at 60 °C under vigorous stirring for 2 h [16].

Table 1
Titania sol composition.

Chemical	Amount (ml)
TTIP	10
Glacial acetic acid	5
HCl	1.4
Water	83.6

Table 2
Titania–GO composite sols.

Precursor composite sol	Titania sol (ml)	GO (5 mg ml^{-1}) (ml)
TGO-1	50	0
TGO-2	50	2
TGO-3	50	4
TGO-4	50	6
TGO-5	50	8

Two approaches are used for composite thin film processing. In one method, graphene oxide was mixed with various concentrations (Table 2) in titania sol and resulting spin coated composite films were exposed to an atmosphere that has been saturated with vapor of hydrazine hydrate at 100 °C for 2 min. In another approach, already reduced graphene oxide was mixed in various amounts (Table 3) in titania sol and films were prepared using a spin coating method. In both cases, after addition of graphene precursor in titania sol, the solution was sonicated for 30 min before film deposition. Films were pre-annealed at 80 °C for 2 min followed by annealing at 450 °C for 2 h at 2 °C/min of heating rate.

3. Results and discussion

Fig. 1 shows a comparison of the X-ray diffractograms of precursor graphite and graphite oxide. Pristine graphite shows a high degree of crystallinity with a sharp diffraction peak at $2\theta=26.47^\circ$, that has an interplanar distance of 3.37 Å of (002) diffraction plane. However the degree of crystallinity of graphite oxide is very low with a minor broad-diffraction peak at 11.8°, which is due to a conserved graphene-like honeycomb lattice in graphite oxides [17]. Hence the shift of the diffraction peak position from 26.47° to 11.8° is due to increase in the interplanar distance from 3.37 Å to 7.5 Å. This is confirmed from Braggs equation which inversely relates interplanar distance 'd' to the diffraction angle '2θ' [18]. The increase in interplanar distance is due to trapping of oxygen atoms between the graphene sheets in graphite structure [19].

Scanning electron microscope (SEM) images (Fig. 2a and b) reveal exfoliation of graphite oxide into individual (single or multi-layer) graphene sheets. A closely packed "tilting" of graphene oxide platelets having an even contrast was detected on the substrate. The lateral dimensions of the sheets ranged from several hundred nanometers to several micrometers. Fig. 2c shows the thickness of exfoliated graphene oxide sheets investigated by atomic force microscopy in a tapping mode. The graphene oxide height profiles typically ranged between 0.6 nm and 1 nm which is reported to be single layer graphene oxide sheet [20].

From the AFM topographical image (Fig. 3), graphene nanosheets can be seen lying on glass slide. Overall, roughness (RMS) is about 0.5 nm indicating that the features are very small in dimension along the 'z' axis. The only factor