In-situ fabrication a thin-film nanocomposite photo-anode electrode for the dye-sensitized solar cell

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ABSTRACT
Here, the performance of dye-sensitized solar consisting of the TiO₂ anatase phase of nanoparticles and its nanocomposite (TiO₂/G) were successfully fabricated via the electrophoretic method as thin films on the ITO conductive glass. Thin films were characterized by the X-ray diffraction, Fourier-transform infrared spectroscopy (FTIR), Diffuse Reflectance Spectroscopy (DRS), and Raman spectroscopy. All of these techniques have confirmed the formation of nanocomposite when added the graphene sheets with changing in the properties of titanium dioxide nanoparticle. It can be noticed the peak in (002) which attributes to the graphene in TiO₂/G. The new peaks that appeared in FTIR, and the bandgap reduced to be about 2.9 eV. Thus, the introduction of graphene sheets to the thin film of TiO₂ photo-anode electrode via the solvo-electrochemical route is an effective method to improve the performance of the ITO/TiO₂ thin film DSSC, which increases the short current density and increases the conversion efficiency of dye-sensitized solar cell from the 2.14 to 2.53 % after employed the thin-film titanium dioxide modified photo-anode.

Keywords: photo-anode, DRS, Raman, Pt electrode, TiO₂

Introduction
Titanium dioxide (TiO₂) is one of the primary inorganic semiconductor oxides which typically used today due to its have optical and electronic properties[1]. TiO₂ at the nanoscale has been generally studied in the photochemical and electrochemical fields in contemporary years[2–5]. Relevant topics include sensor, photocatalysis, perovskite solar cell, and other solar cells. O'Regan and Grätzel in 1999 have reported the dye-sensitized solar cell (DSSC)[6], Titanium dioxide used as the primary material for the photo-anode electrode thin film of the DSSC[7,8]. The dye-sensitized solar cell is an electronic device covert the sunlight to electrical current. It consists from photo-anode semiconductors nanoparticles such as (TiO₂, ZnO, SnO₂), dye (N719, N3), liquid electrolyte, and the counter electrode as the
Platinum electrode or carbon nanostructure (graphene, MWCNT, SWCNT and the active carbon)[9,10]. Some of the studies have been used the conductive polymers such as the poly(3,4-ethylene dioxythiophene (PEDOT)[11], and Polythiophene (PTH). The interaction between (3D) nanoparticles with (2D) graphene, which leads to an increase in the transport of electron from the valence to conductance bands[12–14]. Graphene is one layer of graphite has hybridization sp² and excellent chemical and physical properties[15–17]. Electrophoretic deposition method that used today is an effective electrochemical technique, and the collide solution in an electrochemical cell has enhanced the binder attached to the conductive glass[17–19]. Moreover, it can be controlled the morphology of electrode and thickness via a control on time and applied voltage. The aim of the present study focused on prepared titanium oxide nanoparticles (TiO₂) and (TiO₂/graphene) nanocomposite in a facial method in one step. It used these thin films as the photo-anode electrode in DSSC with the Platinum electrode. The all photovoltaic parameters are estimated from the current-voltage curves under one sunlight irradiation.

Experimental part

**Materials**: The all materials were used in this research used without further purification. Titanium tetra-isopropoxide (TTIP) and Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (N719) were supplied from the Aldrich company. The acetylacetone, isopropanol, and acetone were purchased from the Merck company. The graphene powder was supplied from the supermarket company.

**Instrumentation**: The instrumentals were used in the present work, (X-Ray diffraction (6000 XRD), FT.I.R Spectrophotometer (Bruker 8400), Field-Emission Scanning electron, AFM (Atomic force microscope, AA4000) USA), DRS Spectroscopy (Quantachrome Instruments, USA), BET-BJH Surface Area Analyzer (Quantachrome Instruments, USA). DC power supply (Phywe, Germany), 3465B digital multimeter, USA). and Keithley analyzer was employed to estimate the I-V parameters.

**Preparation TiO₂/Graphene thin film nanocomposite and Fabrication of DSSC**

The TiO₂/Graphene thin film nanocomposite was prepared by follows the steps; the mixture of the solution was prepared from the TTIP, absolute ethanol, and deionized water at the volume ratio 17:34:70 mL. After that, the solution was ultrasonicated for the three hours to get a clear solution. The yield product was collected after the separated it by the ultracentrifuge. The participate was placed in the oven for ten hours at 700 °C after calcination by 450 °C for one hour. After the TiO₂ nanoparticles were synthesized in the
previous step, weighted 0.1 g of Titanium dioxide nanoparticles and 0.03 g graphene nanopowder. It suspended mixture solvents from the isopropanol and absolute ethanol. The supporting electrolyte was prepared from the 0.05 g iodine that dissolved in 5mL acetone and 2mL acetyl acetone and added to the mixture. Thus, the solution was ultrasonicated for 3h. The electrolyte solution was transferred into the electrophoretic container to fabricate the thin film nanocomposite on the ITO conductive glass[17,20,21]. Finally, ITO/TiO2/Graphene thin film was immersed in 1×10⁻⁴ M of N719 dye solution at room temperature for 24 h, which prepared in an acetonitrile solvent. Pt counter electrode was used as prepared in the previous work. Both two electrodes were collected and filled up by the electrolyte that contains on the 0.5 M N-methyl-N-butyl-imidazolium iodide (BMI), 0.1 M LiI, 0.05 M I₂, and 0.5 M 4-tert-butyl pyridine (TBP) that dissolved in acetonitrile solvents. The performance ITO/TiO₂/Graphene / Pt dye-sensitized solar cell was checked under irradiated with the light source at 100 mW/cm².

RESULTS AND DISCUSSION

The X-ray patterns were shown in Fig.1 for the TiO₂ nanoparticles thin film and its nanocomposite. It can be seen the peak intensity of TiO₂ nanoparticles thin film anatase increases with width at 2θ = 25.3° that corresponding with (1 0 1) plane of anatase phase. Others peaks at (37.7°, 48.3°, 55.8°, 65.7°, 27.1°, 76.5°) are identical to Miller indexes (004, 200, 105, 204, 220, 215), respectively. TiO₂/graphene thin film nanocomposite appeared in the same diffraction peaks of TiO₂ nanoparticle thin film. In contrast, the diffraction peaks of graphene were not clear due to that diffraction peaks of graphene appear in 24.5°; therefore, they were shielded by sharp diffraction peak in (2θ = 25.3°) for the TiO₂, and graphene was added in a minimal amount. It is essential to apply Debye-Scherer[19,22] and to determine the particles sizes hence, the average of particles size is 10 nm.
By the field emission electron spectroscopy (FE-SEM), as shown in Fig. 2. It can be cleared the TiO$_2$ nanoparticles the particles have a spherical shape and aggregations with high order due to the high temperature of the calcination process is effected to a uniform of the nanoparticles and the average crystal size of 89 nm. The FE-SEM image of TiO$_2$/G nanocomposite was illustrated as the graphene adhered to titanium dioxide particles to reduce the crystal size to be about 63 nm. Furthermore, the mapping spectra's results displayed the high dispersion of elements in the TiO$_2$ thin film with its nanocomposite. For that, the composition of elements for the TiO2 included the titanium, oxygen, and sodium at the K energy levels. In contrast, in TiO$_2$/G, thin-film papered the carbon elements also with other elements in the TiO$_2$ thin film. Moreover, these data have been confirmed with the atomic force spectroscopy (AFM), the surface morphology of the TiO$_2$ is a difference from their thin-film nanocomposite. It seems the surface papered more smoothly with fewer valleys owing to add the graphene sheets that incorporate with the titanium dioxide nanoparticles.
Fig. 2: FE-SEM and AFM images of TiO$_2$ and TiO$_2$/G thin film with the EDS mapping spectrum.

Raman spectroscopy of TiO$_2$ nanoparticles appears six modes[23] active at the anatase phase (142, 198, 396, 516, 519, 640) cm$^{-1}$ without any peak due to rutile and brookite phases. The peak in 640 cm$^{-1}$ Eg due to Ti-O stretching mode while two peak $A_{1g}$ and $B_{1g}$ in 516, 519, attributed to O-Ti-O stretching mode, and the peak is located in 396 cm$^{-1}$ assigned to O-Ti-O bending mode, as shown in Fig. 3.
Nitrogen adsorption-desorption results (Fig. 4) showed the IV type\cite{24}. The H1 hysteresis loop has a high relative pressure region (0.47-0.97) indicates to sharp capillary condensation due to TiO$_2$ nanoparticle has a mesoporous spherical shape. Moreover, BET and BJH results have given the information for the surface area 53.32 m$^2$/g and pore volume 7.12 cm$^3$/g, mean pore diameter 6.61 nm.

Diffuse reflectance spectroscopy (DRS) used to estimate the band gap energy of TiO$_2$ nanoparticles as prepared compared with TiO$_2$/G. The band gap of TiO$_2$ nanoparticles was equal to 3.1 eV with a wavelength of 390 nm Fig. 5. While the band gap value became 2.9 eV in the TiO$_2$/graphene, which consists of wavelength 420 nm. Due to the chemical bonding formation of Ti-O-C; this is because the a thin film nanocomposite can absorb the visible light
and enhanced electron generated of a thin film for the TiO2 nanocomposite, as shown in Fig. 5.

Fig. 5: DRS data of the TiO2 nanoparticles and TiO2/G nanocomposite.

FTIR spectrum of TiO2 nanoparticle appears broadband concentrated at 547 cm\(^{-1}\) attributed to Ti-O-Ti in the organic crystal lattice. In contrast, the other two bands at 1629 cm\(^{-1}\) due to the OH bending. The broadband in 3400 cm\(^{-1}\) indicates OH stretching that results from the interaction between the surface of TiO2 nanoparticles and adsorbed the water molecules (OH-group)[25] on surface TiO2 nanoparticles. FTIR of TiO2/G nanocomposite appeared a new weak band 1145 cm\(^{-1}\) due to the-O-C, as displayed in Fig. 6.

Fig. 6: FTIR charts of TiO2 and TiO2/G nanocomposite.

TiO2 nanoparticles thin film with its composites used as photo-anode electrode and the platinum electrode as a counter electrode of the DSSC. The results were collected in Table 1 and showed in the I-V plot in Fig. 7.

Table 2: Full parameters of photovoltaic for the TiO2 and its nanocomposite of dye sensitized solar cell (DSSC)
It can be seen that the efficiency of conversion energy increased from 2.14 to 2.53, corresponding to the increase in the output of current. When added the graphene sheets with the titanium dioxide nanoparticles, the role of it enhanced the recombination of charge transfer in the operation of the dye-sensitized solar cell. The results agreed with other studies in elsewhere[7,26].

CONCLUSION

Titanium dioxide and its nanocomposite successfully were prepared as a thin film on the ITO conductive glass. The XRD results confirmed the formation anatase phase at high purity. The peak of graphene sheets has appeared in (002) Miller index refers to formation nanocomposite. FE-SM and AFM results have used to study the surface of thin films. The graphene sheets changed the titanium dioxide properties, that be cleared from the performance of the dye-sensitized solar cell to give the conversion energy of 2.53.
Furthermore, the Raman, FTIR, and BET-BJH result also enhanced the information of XRD. DRS method illustrated the bandgap of the TiO$_2$/G of 2.9 eV.

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