

Hybrid Effect of TiO₂/Reduced Graphene Oxide Based Composite for Photo-Catalytic Water Splitting & Strain Sensing

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Abstract. Solar Energy is an everlasting source of energy with minimal carbon footprint. However, due to lack of reliability and consistency it needs to be converted into more reliable and effective means that can be used to provide energy on demand. Hydrogen is a promising carrier and is thus an efficient mean of energy to be converted in, stored and transported. A more direct approach towards harnessing Solar Energy is by photo-aided generation of hydrogen via splitting of water using photolysis. Photo-catalytic water splitting is therefore a promising method for future energy security. On the other hand, strain sensing is a useful technique to measure medium range loads in trusses or tension rods & can easily replace the existing fragile & expensive semiconductor based sensors. This was done by using a composite of TiO₂ /Reduced Graphene Oxide (RGO); TiO₂ (anatase) was synthesized via sol-gel process and the main precursor was titanium tetrapropoxide (TTIP). Titania (anatase) characterized by XRD and photo spectrometry while Graphene oxide was synthesized via modified Hummer's Method. The obtained Reduce Graphene Oxide was dispersed using Sodium Dodecyl Benzene (SDB) and Hydrazine Hydrate. A drastic synergetic effect was found by simply mixing RGO with TiO₂ Solution. This not only broadened the photo-activity spectrum of TiO₂ from UV region to the more available visible light radiation but also exhibit strain sensing properties and considerable tunable gauge factor. The photocatalytic effect of our composite was tested by coating it over Polycarbonate & then analyzing emitted gas bubbles in a UV radiation chamber while strain sensing was done by coating it on an elastic substrate & applying loads against values of resistance which were measured. This study will also include the reduction of recombination and band gap of TiO₂ in order to synchronize it with the available Solar Spectrum thus maximizing solar-to-hydrogen efficiency.

Introduction

From the history first time in 1972 Fujishima done the splitting of water via photolysis and produce hydrogen [1]. They used Pt-TiO₂ electrodes in the presence of ultra-violet light. Titanium dioxide TiO₂ anatase nanomaterial is a fascinating topic of research. Due to the electron hole pair recombination the photo-catalytic property of TiO₂ must be highly affective. The intrinsic property or the band gap of titanium oxide anatase phase is (E_{bg} = 3.2 eV) [2]. So basically almost every research is going in the way to reduce the band gap of titanium oxide for the enhancement of photo catalytic ability of TiO₂ in visible spectrum. A number of different method is introduced by redesigning various titanium oxide based composite uncommonly major observation has been dedicated to allying photo-catalytic with carbonaceous substance so graphene is the interesting materials to coupling with TiO₂ to enhance its photo activity to reduced its band gap [3].

Initially we learnt that carbon exists in only two forms of allotropies graphite and diamond. The arrangement of atom is totally different in both allotropy, and some more discovered allotropies like fullerenes, buckyball and nanotubes [4]. But in 2004 Giems discovered new allotropy of carbon and first 2 dimensional material which contain single sheet of carbon atom is called graphene[5] due to its fascinating physical properties such as unique electronic properties, high transparency, supreme mechanical strength, high electrical and thermal conductivity to date, graphene single layer atomic

nanostructure has been focused to manufacturing advance functional material which have a great potential in many applications like displays, sensors, filtration, nano-electronics, energy conversion and catalysis [6-8]. So the graphene is used for the enhancement of photo activity with the intention to make advance photosynthesis system [9-11]. Graphene is highly suitable because of its large surface area, extendable single layer of carbon sp_2 hybridization which is great support to absorption of electron, graphene has zero band gap and highly conductive property that helps to in the electron transportation, graphene is also transparent to ultra-violet so it has also permit to absorb UV radiation for greater the photo-activity [12-13].

There are number of method to make tiO_2 and graphene composite like hydrothermal, solvothermal and sol gel method [14]. The above listed technique is very time consuming, not simple and need special equipment and through these techniques the look after the ratio or balancing of chemical are not controllable to so we use different method which consume low cost and also allow to fabricate in bulk quantity. The method we used is called aqueous processing.

Additionally, the started material for the synthesis and fabricated of TiO_2 -graphene composite is graphene and graphene oxide. Graphene is directly exfoliated from graphite and with some other material or synthesis via CVD, but graphene have not fully dispersed in water due to strong Vander Waal force of attraction they act as hydrophobic, so the fabrication of tiO_2 -graphene composite is difficult due to the hydrophobic nature of graphene, so oxidation of graphene make its graphene oxide and due to oxygen functional group it is make hydrophilic and easily soluble in water but the problem is the graphene oxide is insulator and useless in electronic application, so further more treatment make graphene oxide conductive and useful in electronic application [15].

TiO_2 is a promising material for photo-catalysis but its behavior in combination with graphene is ignored yet it holds amazing hybrid properties that are helpful in various applications, which we have ultimately tried to unfold in our research. One of the basic secondary applications of a titania/graphene film also includes strain sensing activity [16, 17] that proves the composite viable as a multi-functional composite, which are now main interest for commercial products. Strain sensors are minute devices to accurately measure tiny mechanical movements or determine tensile loads; this further has applications in structural analysis, fatigue study and tiny actuators. This is done by precisely calculating change in resistance which then corresponds to applied mechanical strain as a result of conversion of mechanical deformation into an electrical shift. A progressive direction of research is in the incorporation of materials with different properties to achieve enhanced properties in a single composite. The integration of TiO_2 & rGO results in hopeful photoactive & strain-sensitive activity with potential uses in various industries. We have worked to prepare a low-cost, fast & simple spray based composite that can be easily coated equally on plain and intricate surfaces and dries out swiftly on the surface leaving equally distributed composite granules due to the presence pre-addition of a surfactant i.e. SDS[18]. The process involves zero post treatment which renders low damage to the synthesized composite film. The involved properties were analytically examined and thus expand innovative arenas for future study of multi-functional composites.

Experimental Work

The raw materials that were used in the present study were obtained from various sources placed in the country and abroad. Primary equipment used were ball mill, Weight balance, magnetic stirrer, ultra-sonicator, centrifuge machine, thermometer and oven

Methods.

Synthesis of Reduced Graphene Oxide. Chemical synthesis and green reduction in the context of top down route will be pursued for the synthesis of Reduced Graphene Oxide (rGO), as top down synthesis is the way to produce large quantities of Graphene inexpensively. Through the in-depth research about the synthesis methods of Graphene, modified Hummer's Method is selected for the formation of Graphene Oxide which will be preceded by Chemical reduction method.

Preparation of Graphene Oxide. Graphene oxide was synthesis via modified hummer's method. 1 gm of graphite powder and 0.5 gm of sodium nitride was added into 23 ml of sulphuric

acid after 30 min stirring in magnetic stirrer and then gradually added 3 gm of potassium permanganate below 20 °C and stirring for 30 min then ice bath removed and stirring at 30 °C for 30 min after that gradually added 50 ml of distilled water and stirring for 2 hours at 98 °C then make a solution of hydrogen peroxide and distilled water then added into the mixture at room temp then make 5% concentrated hydrochloric acid for washing purpose and distilled water to for washing the graphene oxide.

Reduction of Graphene Oxide. After the washing and drying of graphene oxide. Graphene oxide was dispersed in 40 ml of DMF using ultrasonicator and then added 10ml hydrazine hydrate and then stirring the solution at 98 °C for 5 hours after then washing was done through centrifuge machine.

Synthesis of Titania Nano Particle. Preparation of nano powder

TiO₂ was obtain from Titanium tertaisopro-oxide was dissolve in abs ethanol and distilled water to the solution in term of molar ratio of Titanium tertaisopro-oxide, H₂O 1:4 Hydrochloric acid was used to adjust the pH change between 2 to 4 pH and the solution was stir for 1 hour precipitated TiO₂ was filter and dry at 50 °C for 2 hour after ball milling the dry powder obtain were calcinated at 390 °C for 3 hour.

Preparation of Titania/Reduced Graphene Oxide Composite. We have titania and graphene oxide we mix it together through magnetic stirring by ratio of 70 % titania and 30% reduce graphene oxide, then coated on 3 different substrate rubber, polycarbonate and glass.

For photo-catalytic effect we need rGO in powder form. For strain sensing application we need dispersed rGO solution with help of sodium dodecyl sulphate.

Testing and Characterization.

UV Spectroscopy. The photo-degradation of methyl orange was tested by using UV-visible spectroscopy. Firstly, original methyl orange was placed in a crucible along with buffer solution of 100% transmittance, it showed maximum absorbance peak at 456nm with absorbance value of 3.

In order to check photo-activity of rGO/ TiO₂ composite, methyl orange was dipped with this composite and 1.5 and 2.10 minutes of UV exposure was given to methyl orange which showed significant decrease in absorbance values i.e. 2.75 and 2.25 respectively, which is the actual proof that rGO/ TiO₂ composite has degraded the absorbance of methyl orange and hence it is photo-active. Calculation of absorbance can be done by using following formula: $A=abc$, where a is absorbance, b is molar absorptivity and c is molar concentration

Scanning Electron Microscope. Scanning electron microscopy was performed for confirmation of nano-sized structure of TiO₂ /rGo. Scanning electron microscopy of rGO/ TiO₂ sample was done using field emission SEM. SEM was obtained on JSM-6380A. Particles were found as nano-sized along with uniform distribution. rGO was dispersed and have significant adhesion with substrate. Two micrographs of SEM were obtained having scale of 2 and 5 microns respectively. Applied voltage was 15KVolts. SEM images were obtained at 3500X and 4000X respectively. The sample was coated with gold.

XRD. Compound analysis was done using XRD. XRD of both titania and reduced graphene oxide were done on XRD Panalytical. Strong Diffraction peaks of titania were obtained at 25 and 44 degree and graph was plotted between intensity against 2 theta. The obtained peaks were match with previous data and results were similar which proved the existence of titania in sample. XRD of reduced graphene oxide was carried out using XRD Panalytical as well. One peak was observed at 26 degree and other peak, which was comparatively broader, was obtained at 20 degrees which actually shows the existence of graphene oxide, while the former one is the prove of rGO existence. The graph was plotted between intensity versus 2 theta.

Strain Sensing. In order to calculate strain-sensing property of a material, a term known as gauge factor (GF) is use. It is basically the ratio of relative change in electrical resistance R to the mechanical strain. GF value defines the maximum limit of a substance a material can sense. For example, if the graph of strain sensing is studied, it can be clearly seen that the values of resistance increase to a certain extent then they begin to decrease, this maximum point is actually the gauge factor of that particular material. Experimentally the GF of TiO₂ /rGO was found to be 15 in our experiment.

$GF = (\Delta R/R)/\epsilon$, where ΔR = change in resistance and R = initial resistance, ϵ = strain

Band Gap Study. The whole theme of project evolves around the band-gap study of TiO_2 that how to reduce the band gap of titania in order to split water in visible spectrum. The initial band gap energy of water is 1.4eV but it cannot be split directly as it is transparent to UV, IR and visible light. For this purpose, titania is used but it also has band gap energy of 3.2eV falling just above from visible spectrum so for the purpose of minimizing titania band gap energy, reduced graphene oxide was used. It helps in reducing recombination of electron-hole pairs and provide the metastable energy state to photo-catalytic titania and hence the overall band-gap energy of titania is reduced. Experimentally band gap of titania was reduced to 2.7eV by making its composite with rGO, which falls in the visible range. Several other chemicals can be added to reduce band gap energy of titania. For example, black phosphorous, red phosphorous, $Ni(OH)_2$ etc.

Results and Discussion

XRD of titania sample was performed on XRD Panalytical. Fig. 1 shows peaks of titania at 25 degrees and 44 degrees which were tested at 2theta confirms strong diffraction peaks in contrast with those found in titanium oxide. The XRD of rGO was also performed on XRD PANalytical. Fig. 2 shows Single peak of rGO was observed at 26 degrees while a fairly broad peak was observed around 46 degrees which is of GO, results were plotted against 2theta. Fig. 3 shows

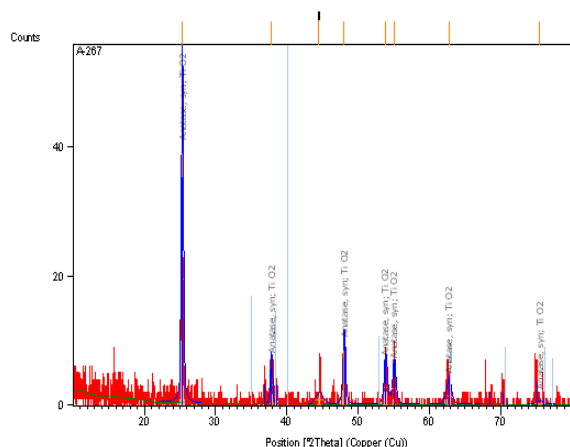


Fig. 1. XRD spectra of Reduced Graphene oxide.

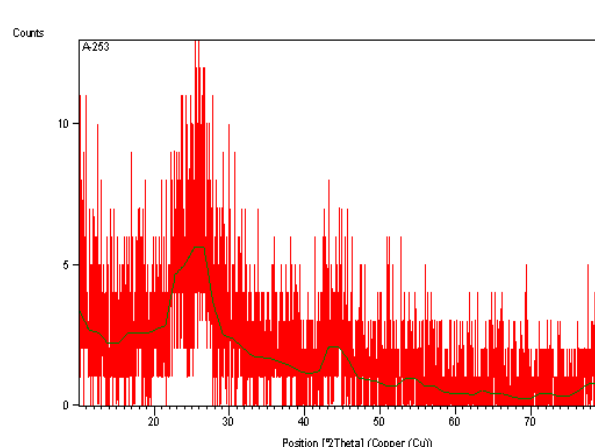


Fig. 2. XRD spectra of titania nano particle.

the spectroscopy of original methyl orange solution which shows maximum absorbance which is set at 465nm. Fig. 4 & Fig. 5 plot the systematic decrease in absorbance of methyl orange when it is exposed to UV light with dipped composited coated photo electrode for 1.5 & 2.10 min, respectively.

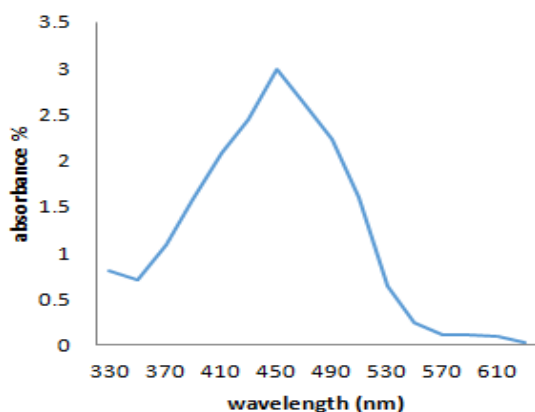


Fig. 3. Absorbance of methyl orange.

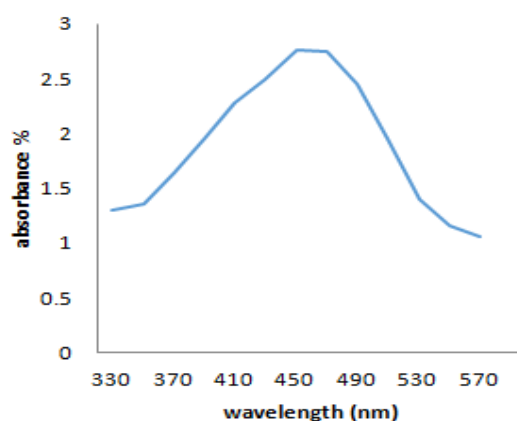


Fig. 4. Absorbance of degrade methyl orange.

The presence of graphene not only provides better surface adhesion for our composite but also provides increased surface area due to its greater theoretical specific surface area. The final and the most important function of rGO particles is to prevent the excessive recombination of electron-hole pairs in TiO_2 and increases charge density thereby increasing photoactive efficiency [26-27].

Fig. 6 shows the relation of resistance and time. Applied stress proceeds at a constant rate of 5mm/min with time and hence resistance is shown to increase with respect to time and hence increasing stress. The linearity of the graph shows good application for strain detection devices and is in the usable elasticity range of 5% which makes it even specific for our desired application. Fig. 7 and Fig. 8 plot strains and relative and actual resistance simultaneously to give a picture about the trend of resistance when mechanical strain is applied. Gauge Factor is found to be 15 for our sample which is the ratio of electrical resistance to mechanical deformation.

Fig.10 SEM results were obtained on JSM-6380A. Particles were found to be nano-sized range and are uniformly distributed with little dispersion of rGO. Particles were also found to have firm adhesion with the substrate.

Practically, Fig. 11 hydrogen evolution was tested in an enclosed UV chamber which contained quartz glass tube, quartz being transparent to UV radiation helped greater transmission of UV irradiation into the tube which contained distilled water along with composite coated photo electrode. The top of the quartz glass was sealed but left with a single outlet that led to a Stainless Steel tank. Fig. 12 shows the setup for strain sensing.

Water has an initial band-gap of 1.4eV but it cannot be split directly as water is transparent to infrared, visible and UV radiations. For water splitting, therefore, titanium oxide with a band gap 3.2 eV is added to water directly which will break down water under UV radiation. The photo catalytic activity of titanium oxide is further increased by the addition of rGO particles, which as mentioned above, prevent recombination and lead to more photo activity. As soon as the UV light is turned on in the UV chamber, bubbles start to appear [19].

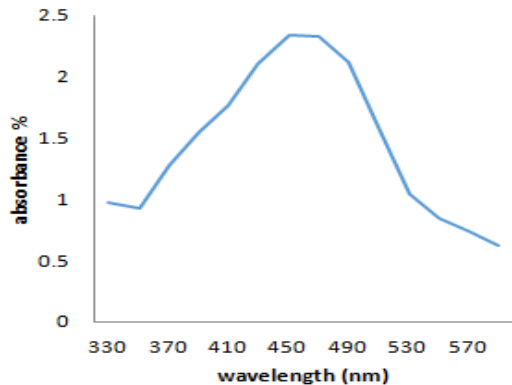


Fig. 5. Absorbance of degrade methyl orange.

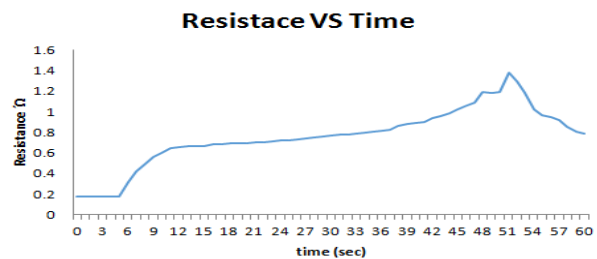


Fig. 6. Resistance vs time.

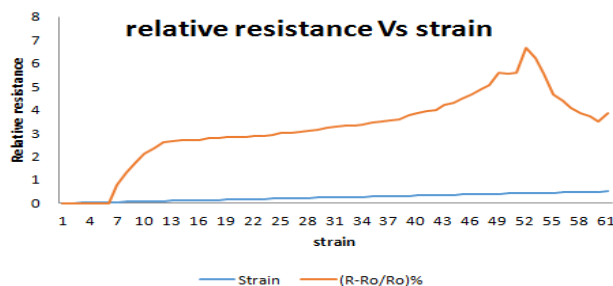


Fig. 7. Relative resistance vs strain.

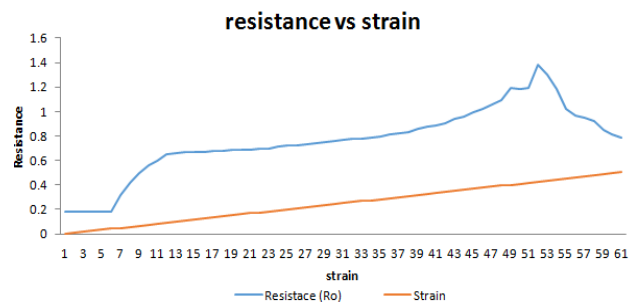


Fig. 8. Resistance vs strain.

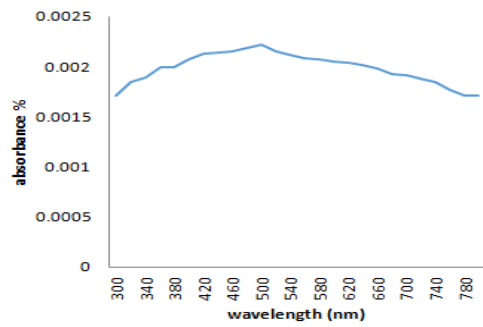


Fig. 9. Absorbance of composite for band gap study.

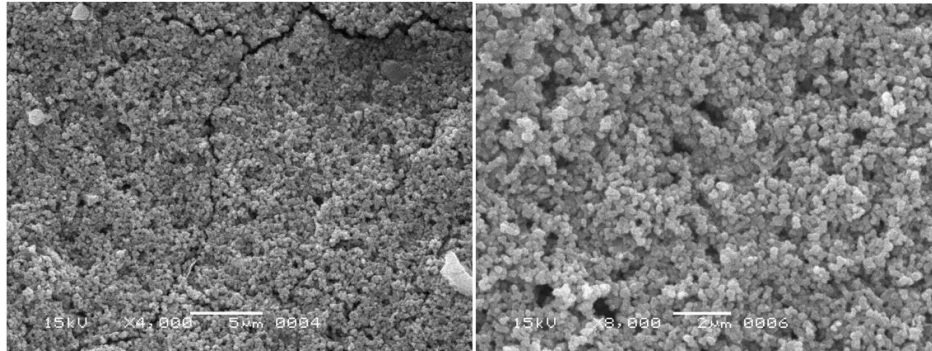


Fig. 10. SEM images of TiO_2 /rGO composite at different magnification.



Fig. 11. Practical Setup for photo-hydrogen generation.



Fig. 12. Tensile loading of the specimens with relevant resistance reading.

Conclusions

Currently we have successfully achieved considerable photocatalytic activity for water splitting as well as strain sensing properties in order to use our synthesized functional composite for various applications. This multifunctional composite can be used in a wide range of applications can be easily coated on various substrates as per application. The multi-functional composite used titania as base catalyst while hydrazine hydrate, and SDS (Sodium Dodecyl Sulphonate) were added for better dispersion of reduced Graphene Oxide which acted as co-catalyst to pull down over all band gap activation energy of photo catalytic composite. This multi-functional was found to have enhanced photocatalytic activity than that of regular titania. The synthesized composite methodology was in compliance with sustainability as the catalyst is completely recoverable and can be easily recycled posing minimum damage to environment. Thus the combined properties have impending uses for not only water splitting but miniature strain sensors as well. Over all, the research provides the most basic insights for TiO_2 /rGO based composites as a future research prospect as well as their applications in a wider range.

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