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EXPERIMENTAL EVALUATION OF Ag/TiO2/rGO BASED HYBRID NANOCOMPOSITES AS AN EFFICIENT HER CATALYST VIA ARTIFICIAL PHOTOSYNTHESIS

Shahid Ashraf[*1], Amna Abrar[2], Muhammad Irshad Khan[3], Rabia Munir[4], Muhammad Baqar Hussain Shah[5], Abdul Qadeer Laghari[6], Shah Wali Ullah[7], Awais Ur Rehman[8]

[*1]*Department of Physics, University of Agriculture Faisalabad, 38000, Faisalabad, Pakistan*
[2]*Department of Chemistry, School of Science, Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University, Tianjin 300072, China*
[3,4,5]*Department of Physics, Allama Iqbal open university Islamabad, Pakistan*
[6]*Department of Basic Sciences and Related Studies, Benazir Bhutto Shaheed University of Technology and Skill Development, Khairpur Mir's - 66020, Sindh, Pakistan.*
[7]*Advanced Functional Materials (AFM) Laboratory, Engineering Physics Department, Institute Technology Bandung, Bandung 40132, Indonesia*
[8]*Department of Physics, Hazara University Mansehra, Pakistan*

[*1]shahid.ashraf97@yahoo.com, [2]abraramna@tju.edu.cn, [3]mikkohat95@gmail.com, [4]rabia.munir0043@gmail.com, [5]baqar.hussain@aiou.edu.pk, [6]leghariqadeer@bbsutsd.edu.pk, [7]33323751@mahasiswa.itb.ac.id, [8]awaisurrehmanphysicist@gmail.com

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Corresponding Author: *
Shahid Ashraf

Abstract
This research investigates the synthesis and evaluation of Ag/TiO2/r-GO to enhance the efficiency of solar cells. Ternary hybrid nanocomposite was prepared by the sol-gel method without any toxic agent. For the preparation of ternary nanocomposite, Ag and TiO_2 were prepared by sol-gel technique while graphene oxide (GO) was prepared by modified Hummer's method and reduced to reduce graphene by reduction of graphene oxide. Under the Sol-gel condition, deionized water was used as a green reducing agent. To compare the performance of ternary hybrid nanocomposite of Ag/TiO_2/rGO with pure TiO_2 and binary nanocomposite of TiO_2/rGO various techniques e.g. SEM, UV-Visible spectroscopy, and Raman Spectroscopy. Crystal size of Ag/TiO_2/rGO was decreased to 8nm compared to 12nm size of pure TiO_2. The combination of Silver over titanium-dioxide enhanced the photocatalytic activity of a solar cell. A hybrid nanocomposite of Ag/TiO_2/rGO showed the synergistic effect between Ag, TiO_2 and rGO and increases the wide photocatalytic spectrum of hydrogen evolution reaction (HER). For HER nanocomposites of Ag/TiO_2/rGO catalyst delivered high current density three times more than pure TiO_2 and two times more than silver nanoparticles. Photocatalytic activity and hydrogen generation was increased by charge transfer heterojunction and enhanced charge separation and degrading efficiency up to 98%. As water molecules absorbed on silver nanoparticles, HER

catalytic activity of $Ag/TiO_2/rGO$ was discussed that there was delayed in electron hole pair's recombination rate shown by visible light. Photo engendered electrons and holes move in reverse direction of reduce graphene oxide as well as Ag NPs has been enhanced the activity of photocatalytic H_2 generated from Water.

INTRODUCTION

Over a past few decades there's energy crisis in the world. To overcome this problem renewable energy is best option to meet this problem. Fossil fuels, wind energy and energy obtained from nuclear fuels, hydro power plants and energy obtained from sun known as solar energy are different sources of energy e.g., have been using to overcome the energy crisis [1].

There are a lot of sources of renewable energy which can be endured until the civilization of human including sun light, geothermal heat, tides and air. Till 2016 around the world, Renewable sources Subsidize the 19.5% consumption of energy [2].In which 9% energy obtained by source of biomass and 4% by hydropower plant and 4.8% by using geothermal energy and 2.2% by using wind energy. Solar panels are significant components in solar power plants, solar cells are integrated side by side and solar cells series form a solar panel, solar panels are strong, smooth and long life in its finishing mood [3]. Some impurities are added to produce a semiconductor in silicon wafers to convert sun light energy into electrical energy. Solar cells relate to each other electrically and solar panels are coated with antireflective substantial normally titanium dioxide and silicon dioxide. Initially coated the solar cell with stainless steel, plastic, coated glass, metal contact and thin layer of flexible solute. Then deposited a thin layer of oxide to generate an electric contact on panel in series of cell. Afterwards packed the cell with resistance rapper [4].

Various method used to study the effect of TiO_2-rGO, designed ternary hybrid nanocomposite of $Ag/TiO_2/rGO$ enhances the spectrum of light adsorption by hydrogen evolution to study the effect of reduce graphene oxide and titanium dioxide and structure of ternary hybrid nanocomposite. Currently researchers showing their attention in formation of nanomaterials and in development of their applications [5]. Researchers reduces the recombination of electron and holes by reducing the band gap by using TiO_2. Silver has an outstanding capability to enhance the plasmonic character. The Schottky barrier is designed by the combination of Ag with titanium dioxide and the adaptation of hot electron depends upon the elevation of the barrier which is because of photocatalytic reaction. Advance the structure of silver titania also advance efficiency of a solar cell. Graphene has different compensations to transference electrons and good interaction with light captivating material [6]. Graphene with bulky surface area, sustained pairing structure, and due to its maximum mobility of charge decrease the rate of recombination of holes and electron, Ag metal used to improve photocatalytic properties which activated because of titania reduce graphene oxide nanocomposites. Electron hole pair rate of recombination decrease due to motion of photo generated electrons over nanoparticles. By moving photogene rated electrons onto nanoparticles has the advantage of nanoparticles to reduce electron hole pair's recombination rate. Furthermore, due to precise surface plasmonic resonance visible light captivate on silver nanoparticle and upsurges titania attraction to observable range of light [7].Lately numerous scientists have been specified about nanocomposite of $Ag/TiO_2/GO$ on poisonous and corrective reducing agents. Although associated with graphene oxide, rGO is substantial to increase the motion of charges and conceivable catalytic position [8].

Executing the silver nanoparticles on titanium dioxide and reduce graphene oxide nanocomposites behave as an efficient appreciation to enhance its photo-electro catalytic properties. On another side, between silver nanoparticles and titanium dioxide Schottky barrier is intended, limiting the reverse of electrons inserted from titanium dioxide to silver and so incapacitating the

control electron hole pair recombination. Ag nanoparticles produce LSPR which is congested under light, and hot electrons are frequently deposited on TiO_2 surface [9].
Moreover, graphene and silver nanoparticles have a helpful effect in informative photographic possessions. Consequently, the performance of titania reduce graphene oxide and silver titania is less than as equated to composite of Ag/TiO_2/rGO. Performance of silver nanoparticles as electron receptors, transporting electron onto titania whereas reduce graphene oxide permits the separation and transference of electrons by minor movement "as a bridge" in a position to a function, silver nanoparticles enhance the photocatalytic activity because of maximum activity of titania, inside the use of nanocomposites Ag/TiO_2/rGO numerous studies have been deliberated on damage to dyes like azo dye, methylthionine chloride, water cracking and this research deliberate the morphological image of ternary nanocomposite Ag/TiO_2/rGO and property collaboration [10].Photo degradation results of titanium dioxide exposed that silver encumbered content have 9 mol% of titania and discus the mechanism of photocatalysis which represent the response rate of ternary nanocomposite 22.3% higher that of pure TiO_2. Titanium dioxide with maximum density also works with decent metal nanoparticles like silver, which execute tests for synthesis of Ag/TiO_2 nanoparticles retaining a chemical reduction method [11]. Over the past few decades, the global energy crisis has intensified the search for efficient and sustainable renewable energy sources. Solar energy, due to its abundance and eco-friendly nature, has gained significant attention, particularly in the field of artificial photosynthesis for hydrogen production. Titanium dioxide (TiO_2) is a widely used photocatalyst, but its large band gap limits its activity under visible light. To address this, researchers have explored combining TiO_2 with silver nanoparticles (Ag) and reduced graphene oxide (rGO), forming ternary nanocomposites like Ag/TiO_2/rGO. These composites show promise due to their enhanced light absorption, improved charge separation, and reduced recombination rates, mainly attributed to the surface plasmon resonance of Ag and the high conductivity of rGO. Despite these advantages, key research gaps remain. There is limited experimental work specifically evaluating Ag/TiO_2/rGO for hydrogen evolution reactions (HER) under artificial photosynthesis. Mechanistic understanding of the interactions among the three components is still unclear, and structural optimization of the composite is underexplored. Furthermore, issues related to the long-term stability, green synthesis methods, and comparative analysis with binary systems need more focused investigation. Addressing these gaps is essential to develop cost-effective and efficient HER catalysts for real-world renewable energy applications.

2 MATERIALS AND METHODS

2.1 Preparation of Graphene Oxide (GO)

Graphene oxide was synthesized by modified hummer's technique. In this method, I poured H_2SO_4 into H_3PO_4 in a 9:1 by volume. For consistent integration of both acids, I utilized magnetic agitator along with hot plate, and then I assorted graphite powder into exceeding prepared solution. Moreover, I integrated $KMnO_4$ moreover in above solution, incorporation conditions preceded for 8 hours until the postponement shade turned light green, followed by 2.025 ml H_2O_2 efficiently dripped into suspension and stimulated for 14 min. There was an exothermic response and then the solution was cooled to room temperature, DI water and HCl were introduced into the solution. It was efficiently centrifuged with a centrifuge for 15 min at approximately 4000 rpm, the supernatants were drained and the product was washed with HCl and DI water in small amounts, the final product was dehydrated in an oven for 40h at 80°C graphene oxide powder was obtained, namely GO.

2.2 Synthesis of TiO_2

Preparation of Titanium dioxide was done with technique of sol-gel. Titanium isoperoxide was used as predecessor and 80 ml of ethanol was added into 20ml of titanium isoperoxide and stirred the mixed solution for 30 minutes. In this way we obtained solution A. After that, solution B was prepared by mixing 15ml of H_2SO_4 into 75ml of DI water and put it on stirrer for mixing. Solution B was mixed for 30 minutes. Then we added both solutions A and solution B and obtained a solution C. Solution C was kept on stirrer for 6 hours at constant temperature of 80℃ and finally a milky gel was obtained which was cooled at room temperature and kept in an oven at temperature of 100℃ for 1 hour. After this we dried the titanium gel in furnace at 350℃ and after grinding with pestle final powdered form titanium was obtained. Synthesis of $Ag/TiO_2/rGO$ ternary nanocomposites

Synthesis of Sliver was done by Sol-gel method. 0.69 gram of $AgNO_3$ poured into the beaker and mixed with 20 ml of ethyl alcohol and stirred for 40 hours. Solution of silver was mixed with various concentration of 0.1 M, 0.2M, 0.3M powdered of TiO2and 0.9 mg of reduced graphene oxide. In this way ternary nanocomposite of $Ag/TiO_2/rGO$ was kept in oven for 2 hours at temperature of 100℃ and then for drying nanocomposite was kept in heated furnace for 30 minutes at temperature of 350℃. Finally, pure form of $Ag/TiO_2/rGO$ nanocomposite was obtained.

2.3 Synthesis of $Ag/TiO_2/rGO$ Ternary Hybrid Nanocomposites

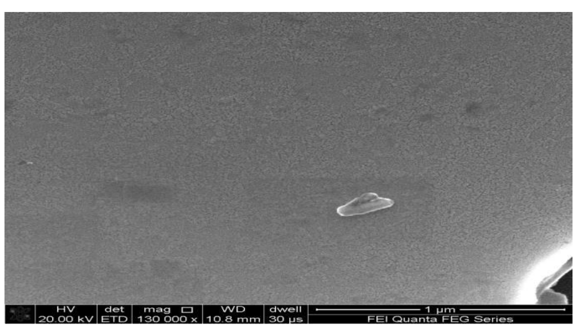
Synthesis of Sliver was done by Sol-gel method. 0.69 gram of $AgNO_3$ poured into the beaker and mixed with 20 ml of ethyl alcohol and stirred for 40 hours. Solution of silver was mixed with various concentration of 0.1 M, 0.2M, 0.3M powdered of TiO_2 and 0.9 mg of reduced graphene oxide. In this way ternary nanocomposite of $Ag/TiO_2/rGO$ was kept in oven for 2 hours at temperature of 100℃ and then for drying nanocomposite was kept in heated furnace for 30 minutes at temperature of 350℃. Finally, pure form of $Ag/TiO_2/rGO$ nanocomposite obtained.

RESULTS AND DISCUSSIONS

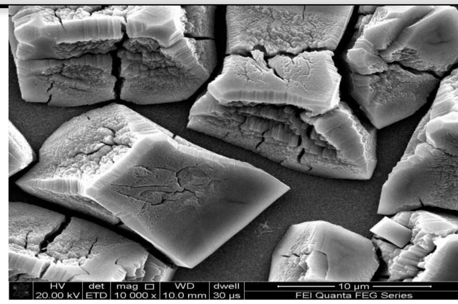
Afterward the preparations of samples, various techniques used to determine the structure, morphology, and properties ternary hybrid nanocomposites. Images of prepared samples were obtained by SEM; XRD determines structural analysis of samples while UV/Visible gives as the numerical data in form of graphs.

3.1 SEM characterization of $Ag/TiO_2/rGO$ Ternary Hybrid Nanocomposite

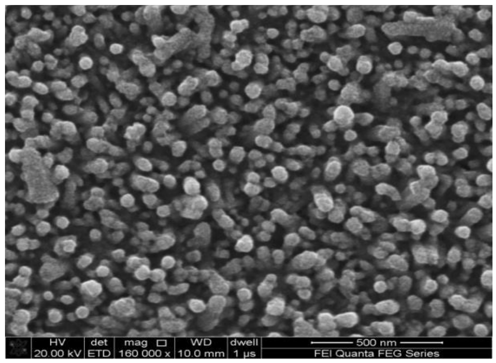
SEM images show the surface morphology of the $Ag/TiO_2/rGO$ ternary nanocomposite with various resolutions and shows that Ag/TiO2/rGO has uniform spherical morphology. It can be seen that silver and titanium dioxide are stuck together, and no changes occur with addition of reduced graphene oxide. With surface morphology via SEM, it was confirmed that $Ag/TiO_2/rGO$ shows a good composition between titanium dioxide and reduced graphene oxide. Further observation confirmed that synthesis of ternary hybrid nanocomposite of $Ag/TiO_2/rGO$ favorable effectively light harvesting.



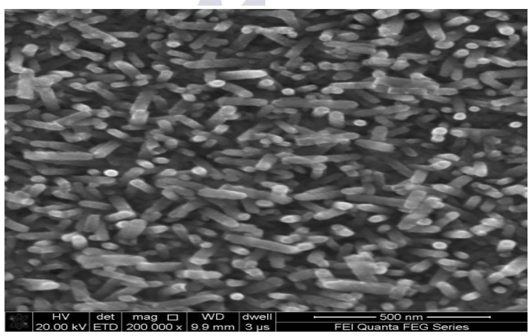
a) SEM Image of reduced graphene Oxide



b) SEM image of Titanium Dioxide TiO_2



C) SEM images of 0.1M Ag/TiO2/rGO



d) SEM images of 0.2M Ag/TiO2/rGO

e) SEM images of 0.3M Ag/TiO2/rGO

Figure 1: SEM Analysis of TiO_2, Ag/TiO_2/rGO and rGO

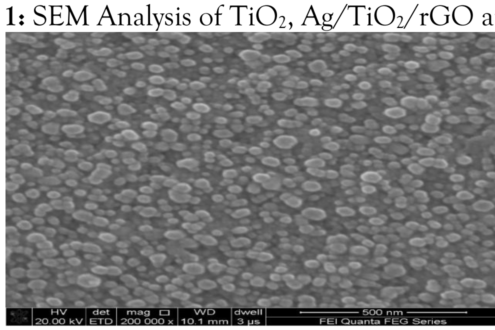


Figure.1 (a) the far-right panel presents a relatively smooth surface with a sparse particle distribution, representing a thin sheet of reduced graphene oxide (rGO). This smooth morphology, along with the presence of a small visible particle, demonstrates rGO's role as a conductive platform facilitating charge transfer. Moving to the Fig.1 (b), large, well-defined crystalline structures are visible, which correspond to the bulk form of TiO_2 and its precursor material. These block-like particles indicate a less reactive, low surface area morphology typically found in unmodified materials. a dense array of rod-like nanostructures appears, suggesting the successful synthesis of TiO_2 nanorods, which offer increased surface area and more active sites for photocatalytic reactions. The provided SEM image in Figure 1 (C), (d), (e) showcases the morphological transformation and structural characteristics of synthesized nanomaterials, likely representing the progression in the formation of Ag/TiO_2/rGO ternary nanocomposites with 0.1M, O.2M, 0.3M concentration of Ag with TiO_2/rGO. The third image reveals a field of finer, nearly spherical nanoparticles, likely indicating the deposition of silver (Ag) nanoparticles across the TiO_2 or TiO_2-rGO surface. These Ag particles enhance the photocatalytic activity by improving light absorption through localized surface plasmon resonance and suppressing electron-hole recombination. Overall, the sequence of images illustrates the successful stepwise assembly of the Ag/TiO_2/rGO hybrid nanocomposite, emphasizing the morphological features essential for enhanced photocatalytic hydrogen evolution.

3.2 UV-Visible Analysis

UV/Visible spectroscopy is dominant non-destructive technique. By using this technique light will be pass through the prepared specimens and measure the absorption and determined the scattering of light. Light absorption. properties of ternary hybrid nanocomposite of Ag/TiO2/rGO confirmed by using this technique of UV/Visible.

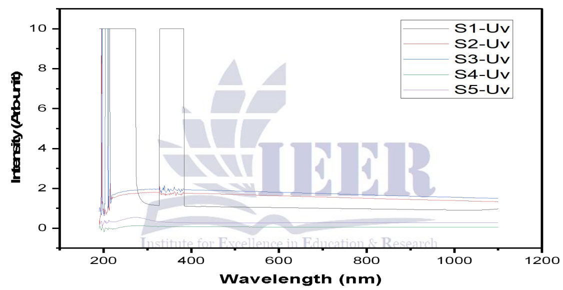


Figure 2: UV-visible characterizations of Ag/TiO_2/rGO

The UV-Visible absorption spectra shown in the graph illustrate the optical behavior of five different samples, labeled S1 to S5, over a wavelength range of 200 to 1200 nm. All samples exhibit strong absorption in the ultraviolet region, particularly between 200 and 250 nm, which is characteristic of the intrinsic band gap absorption of titanium dioxide (TiO_2). This strong UV absorption is attributed to the charge transfer transition from oxygen 2p orbitals to titanium 3d orbitals. Among the samples, S1 and S2 show the highest absorbance intensity in the UV range, indicating a potentially higher concentration of photoactive material or improved structural properties that enhance light harvesting. In contrast, S3, S4, and S5 display relatively lower absorption, which may be due to differences in composition or a reduction in active surface area. Beyond 400 nm, in the visible region, all samples show a rapid decrease in absorption; however, a slight tailing effect suggests the possible presence of silver nanoparticles (Ag) and reduced graphene oxide (rGO), which contribute to extended light absorption through plasmonic resonance and improved charge transfer. Overall, the spectra confirm that the synthesized nanocomposites are primarily active in the UV range, with S1 and S2 demonstrating the most promising optical properties for photocatalytic applications such as hydrogen evolution.

3.2 Raman Spectroscopy

Raman spectroscopy is nondestructive technique which provides detailed information chemical structure, molecular interactions, and crystallinity. Most of the light have same wavelength as source of laser and does not indicate useful information and this technique also known as Raleigh scatter. High intensity ratio of D/G is said to the presence of some defects, together with amorphous carbon, vacancies and grain boundaries 37. Therefore, the rise in D/G suggests a rise of sp^2 domain in $Ag/TiO_2/rGO$ nanocomposite, reconfirming the effective reduction of GO.

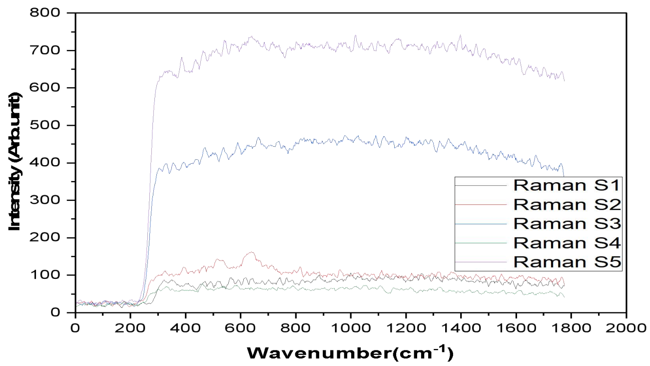


Figure 3: Raman scattering characterizations of $Ag/TiO_2/rGO$

The Raman spectra presented in the graph illustrate the vibrational characteristics of five different samples, labeled Raman S1 to Raman S5, within a wavenumber range of 0 to 2000 cm^{-1}. The spectral intensity varies significantly among the samples, with Raman S1 exhibiting the highest intensity, followed by S2, indicating a strong Raman-active phase likely due to better crystallinity or a higher concentration of active materials such as silver nanoparticles and reduced graphene oxide (rGO). The moderate intensity observed in S3 and S4 suggests a lesser degree of structural order or lower content of these active components, while the lowest intensity in S5 may be attributed to minimal incorporation of Raman-active species or weaker interactions with the excitation source. Distinct peaks typically associated with TiO_2 phases are observed in the lower wavenumber region (100–800 cm^{-1}), corresponding to vibrational modes of anatase or rutile structures. Additionally, broad features around 1300–1600 cm^{-1} are more prominent in the higher intensity samples (S1 and S2), which can be linked to the D and G bands of rGO, indicating the presence of structural defects and graphitic carbon, respectively. These spectral features collectively suggest that S1 and S2 possess better compositional integration and structural properties, enhancing their potential performance in photocatalytic or photoelectrochemical applications.

4 Conclusions:

The experimental evaluation of $Ag/TiO_2/rGO$-based hybrid nanocomposites as an efficient catalyst for the hydrogen evolution reaction (HER) via artificial photosynthesis demonstrates significant potential for clean energy production. The hybrid nanocomposites exhibit enhanced catalytic performance due to the synergistic effects between silver (Ag), titanium dioxide (TiO_2), and reduced graphene oxide (rGO). Ag, as a noble metal, provides excellent electron transfer properties, while TiO2 contributes to photocatalytic activity, and rGO acts as an efficient electron conduit, enhancing charge carrier separation and transport.

The $Ag/TiO_2/rGO$ hybrid nanocomposites show remarkable stability and high HER efficiency under visible light irradiation. This is attributed to the improved light absorption and effective charge transfer dynamics facilitated by the hybrid structure. The results suggest that the combination of these materials can offer a cost-effective, sustainable approach to hydrogen production, which is crucial for the development of renewable energy technologies.

Furthermore, the stability tests confirm that the nanocomposites maintain their catalytic activity over multiple cycles, highlighting their long-term viability for real-world applications. These findings underscore the promising role of $Ag/TiO_2/rGO$ hybrid nanocomposites as an efficient HER catalyst for artificial photosynthesis, contributing to the advancement of clean hydrogen production technologies.

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