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Lignocelluloses Modified TiO_2 Nanomaterials as Renewable Photocatalyst for Water Splitting

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Abstract: Photocatalytic water splitting process is a hopeful means to solve depletion and environmental pollution problems caused by fossil fuels as well as for sustainable hydrogen production using renewable natural resources like sunlight and biomass (cotton stalk). In this study the aim was to fabricate cotton stalk extracted Lignocellulose (LGO) Titanium oxide (TiO_2) nanoparticles via sol-gel in ethanol and to investigate their photocatalytic water splitting activities under Visible light irradiation. Hence, in this study the opportunity for structural development of lignocellulose (LGO) modified TiO_2 nanomaterial towards highly efficient and realistic photocatalysis applications are evidently abundant after improved light absorption, charge-carrier dynamics, and improved particle size porosity that benefits photocatalysis functionalities. LGO-TiO_2 nanoparticle, (≈19.57 nm) for photocatalysis was prepared via sol-gel method. The fabricated nanomaterial photoelectrochemical characterization was operated using three electrode system with a photoanode as a working electrode, coiled Pt wire as a counter electrode and Hg/Hg_2Cl_2 as a reference electrode, and 0.5 M Na_2SO_4 (with pH buffered at 6.75) purged with N_2, solution was applied as a supporting electrolyte. The structural and morphological characterizations of the fabricated nanomaterial are carried out using FTIR, XRD, SEM, and EDX techniques, based upon which the mechanistic insights are discussed. SEM analysis suggests that an average size of particle grain size is found to be in the range of 0.5-4 μm. The photocurrent densities of regular TiO_2 and LGO-TiO_2 towards water splitting reaction under light illumination from xenon lamp were compared and found in reasonable agreement. The work also studied the application of visible light illuminated LGO-TiO_2 photoanode photocatalyst to the overall water splitting with a photoconversion efficiency of 18.91% higher than that of bare TiO_2 nanoparticles and this suggests that surface functionality, surface topography, porosity and particle size, as well as purity and chemical composition of the prepared sample was successfully functionalized..

Keywords: Biomass, Water-Splitting, Lignocellulose, Photocatalyst

1. Introduction

In the 21st century Lignocellulose biomass industry has become green, possible alternative of fossil resources in order to compensate the increasing trend of world's demand for petroleum usage in the chemical world. Fossil fuel based sources of energy, such as coal, oil, and natural gas, have been used to meet the world's energy demands for a centuries. Due to this severe increasing energy demand of the modern society and limited supply of current fossil fuels, grasping alternative renewable energy sources has become one urgent and central mission for scientists. So that finding renewable, clean and pollution free alternative energy sources is thus urgently needed [1]. This has made a precious green alternative material in the areas of renewable fuel production when its surface treated electrochemically with other active constituents as a photocatalyst [2, 3].

Ecological concerns have resulted in a renewed interest in natural, renewable and compostable materials, and therefore issues such as materials elimination and environmental safety are becoming an important event [4, 5]. Thus to keep the universe to be safe, functionalizing new fashion design within a perspective of sustainable growth has been applied to more and more materials [6]. Among the various materials, maximum attention has been given to TiO_2 because of its unique characteristics such as: high photocatalytic activity,

resistance to photo-corrosion, photo-stability, low cost, nontoxicity, and due to its redox capability under ultraviolet (UV) irradiation, i.e., usually the wavelength < 385 nm [7, 8]. Additionally, such characteristics extends to extensive applications in the area of photovoltaic, sensors, optics, in dye-sensitized and solar cells, for hydrogen gas evolution, self-cleaning surfaces and environmental purification applications [9, 10].

One of the most recent nanomaterials that has been attracted a great attention due to its unique properties is titanium dioxide. It is a very useful semiconducting transition metal oxide material and exhibits a versatile material that appears in three crystalline polymorphic phases: rutile, anatase and brookite. However, since titanium oxide is cheap, non-toxic has excellent material properties, suitable energetics (band edge positions) to drive both proton reduction and water oxidation, and stability in an aqueous environment and in the area of electrochemistry [11]. In the last three decades to an engineer titania (TiO_2) is a suitable photo-catalyst material for water splitting in an electrochemical cell as well for degradation of organic contaminants [12-14]. Hydrogen that is formed by the solar splitting of water is clearly considered to be the cleanest energy fuel or solar fuel to meet future demand for energy, and various attempts have been made in order to develop advanced processes to produce hydrogen. Among those techniques, photoelectrochemical cell (PEC) water splitting has attracted significant attention in the past decades as a promising renewable energy source due to their low production cost and their simplicity. Since the early 1970s, Fujishima and Honda reported a single-crystalline TiO_2 semiconductor photoanode for photoelectrocatalytic decomposition of water under UV-excitation and an external bias for the first time, great efforts have been devoted to the development of photocatalytic hydrogen production technologies [15].

Heterogeneous catalysis has a fundamental role in the development of sustainable industrial processes, as it potentially possesses the ability to achieve the objectives of industrial catalysis, while paying attention to the principles of sustainable and green chemistry [16]. There have been significant approaches to fabricate various nanocatalysts, including high-voltage acceleration technique, sol-gel method, coprecipitation-peptization, and template-assisted synthesis [18]. Recently, several porous media photocatalytic activity of immobilized TiO_2 particles on macroporous ceramic alumina foams, zeolite, carbon nanotube, aerogel, and active carbon, which as far as possible provide pore structures for dispersing TiO_2 photocatalysts have been reported [17, 19].

Biomass is the term used to describe all the organic matter produced by photosynthesis that exists on the earth's surface and is available in varying quantities throughout the developing world [20]. The dry matter biomass, so called lignocellulose biomass is the most abundantly available raw material for the production of bio-fuels like bio-ethanol. It is composed of carbohydrate polymers (cellulose, hemicellulose), and an aromatic polymer (lignin) [4, 21]. Hydrogen production by photocatalytic reforming of lignocellulosic biomass may also be more feasible and practical as compared to photocatalytic water splitting due to its potentially higher efficiency. The thermodynamics of photochemical water splitting were reported to store a maximum of only 12% of the incident light energy [22]. Therefore, any semiconductor photocatalyst should possess band gap energy (1.23 eV< Eg <3.0 eV) and band positions [23].

In this work, it should be effectively fabricated cotton stalk extracted Lignocellulose (LGO) Titanium oxide (TiO_2) nanoparticles via sol-gel in ethanol and investigated their photocatalytic water splitting activities under Visible light irradiation as compared with bare/pure TiO_2 with in the phtotoelectrochemical cell (PEC).

2. Experimental

All chemicals and reagents used in this study were analytical grade. Raw cotton stalk dry biomass was chopped and reduced into smaller pieces followed by washing with cold distilled water. 35 g dried raw biomass was loaded into the cellulose thimble in Soxhlet extractor set up, and 1000 mL of acetone was used as solvent for extraction. The boiling temperature was carefully adjusted to 45°C and 25 min respectively on the heating mantle for a 4 hour run period. After extraction, the sample was air dried at room temperature and 1.5 g of extracted dried biomass was transferred into a 250 mL Erlenmeyer flask then 150 mL of 500 mol/m^3 NaOH was added. The mixture was boiled for 3.5 hour with distilled water. It was filtered after cooling through vacuum filtration and washed until neutral pH. The residue was dried and~6% wt was collected [24].

20 g air dried material was extracted with water at 80°C for 1 hour using a dry biomass ratio of 1:10. The mixture was vacuum filtered in a Buchner funnel and then washed with 500 ml water. The water extracted material was further extracted with 20 wt% sodium hydroxide (NaOH) solution at 80°C for 1 hour to dissolve the lignin and to obtain lignocellulose. After the mixture was filtered the alkali extract was collected, and the residue was washed with water until the pH was neutral [25]. Finally, the extract was dried and around 38% wt yield was collected.

Commercial available anatase titanium dioxide shows an acidic reaction. So, the investigated material was washed with ammonia solution to neutralize the acidic solution. The solution was washed with distilled water to remove the excess ammonia and the final pH was recorded as (7.17-7.19). Subsequently, TiO_2 was dried at 80°C for a few hours and grounded with a mortar then after it was kept ready for further analysis [26].

Lignocellulose (LGO) modified TiO_2 material was synthesized as follows: 6 g of amorphous TiO_2 and 5 g of LGO were mixed with 25 mL of distilled water for 6 hours at 90°C using water bath and then air-cooled at room temperature. The resulting product was collected and washed

thoroughly with distilled water, and finally dried at 60°C in an oven. The obtained powders (pH = 6.94-6.97) were dried for 24 hours at the temperature of 80°C and calcinated in a muffle furnace at 400°C for 2 hours [27].

Fourier transform infrared Spectrum 65 FT-IR (Bruker IFS120 M, PerkinElmer) were recorded in the range 4000-400 cm^{-1} using KBr pellets under standard conditions. The crystal structure of the powders was analyzed using Scanning Electron Microscopy (ZEISS EVO 18), Energy Dispersive X-ray Spectroscopy (EDAX) with INCA software for quantitative analysis and XRD (SHIMADZU, XRD-7000 X-RAY DIFFRACTOMETER), and the XRD patterns were collected in 2θ range from 10 to 80 in degrees with a Cu target and an x-ray tube at 40 kV and 30 mA.

Photoelectrochemical cell (PEC) was operated on an electrochemical workstation (CHI 660E, CH instruments) using three electrode system with a photoanode as a working electrode, coiled Pt wire as a counter electrode and Hg/Hg_2Cl_2 as a reference electrode, and 0.5 M Na_2SO_4 (with pH buffered at 6.75) purged with N_2, solution was applied as a supporting electrolyte. The working electrode was fabricated by securing a copper wire on the exposed electric conductive part of fluorine-doped tin oxide (FTO) with transparent glass paint. TiO_2 and LGO-TiO_2 nanoparticles were used as a photoanode (working electrode, with an area of 3 cm^2). The water splitting photoelectrode was illuminated at100 mW/cm^2 with a power density from 150W xenon lamp within the entire solar spectrum.

3. Results and Discussions

FT-IR spectroscopy was used to analyze the prepared photocatalyst in the range of 4000-400 cm^{-1}. Thus, (Figure 1) showed that the FTIR spectrum of bulk and LGO modified TiO_2 nanoparticls. The peaks at around 2922 $cm^{-1}$and 2850 cm^{-1} shows C-H asymmetric and symmetric vibration mode of alkyl (-CH_2) groups, respectively. The peaks around at 630 cm^{-1} assigned to the characterstics vibration of Ti-O-Ti network in the titanium dioxide [11]. The broad peak observed at 3433 cm^{-1} corresponds to the stretching vibration of hydroxyl groups in the lignocellulosic material. The broad peak observed in the fingerprint region at about 490 cm^{-1} found in Ti-O is due to out of plane bending [11] and in the range observed from 950-1100 cm^{-1} corresponds to the interaction between the Ti-O network and the carbonyl, C=O in the hemicellulose polymer. More intense peak at around 1100-1150 cm^{-1} is the characteristics of C-O stretching due to the presence of ether or ester bond in the lignocellulose polymer matrix [28].

The XRD spectrum of LGO, TiO_2, and LGO-TiO_2 nanoparticles are shown in Figure 2. The consecutive and being peaks in lignocellulose doped TiO_2 shows the characteristic appearance of the modified material treated at 400°C for 2 hours. The major diffraction peaks (2θ values) were found at 19.06, 25.32 and 32.14. Thus, the crystallite size can be calculated from the classical Debye-Scherrer equation, D = Kλ/βcosθ, where, D is the crystallite size, λ= 0.1541 nm, is the wavelength of the X-ray CuKα radiation, K is Scherrer constant (usually taken as 0.9 for spherical like nanoparticles), β is the Bragg's diffraction angle or full-width half-maximum (FWHM) value. Therefore, from Table 1 the average crystallite size of lignocellulose modified TiO_2 nanomaterial is in the range between 17-20 nm [11]. In addition the observed peaks are sharp indicates the prepared sample was pure.

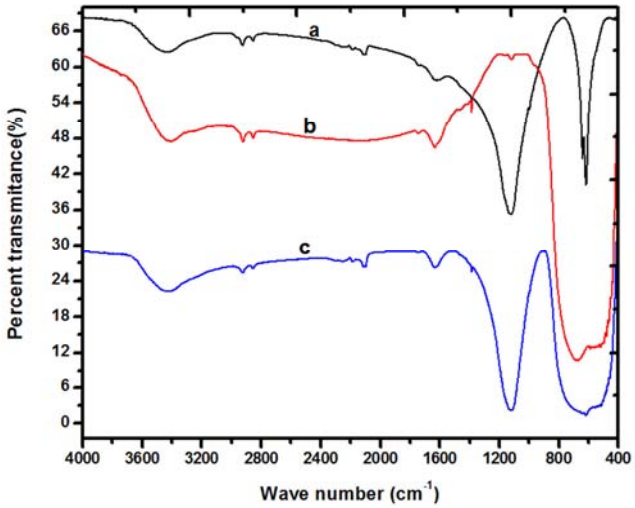


Figure 1. *(A) FT-IR spectrum of LGO (a) black), (b) TiO_2 (red) and (c) LG-TiO_2 (blue).*

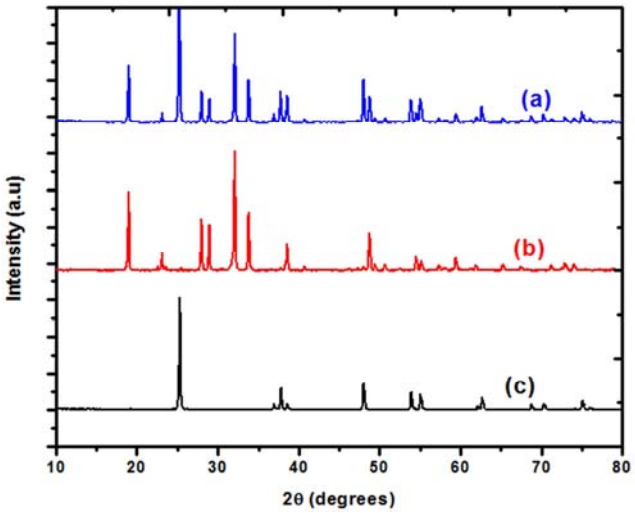


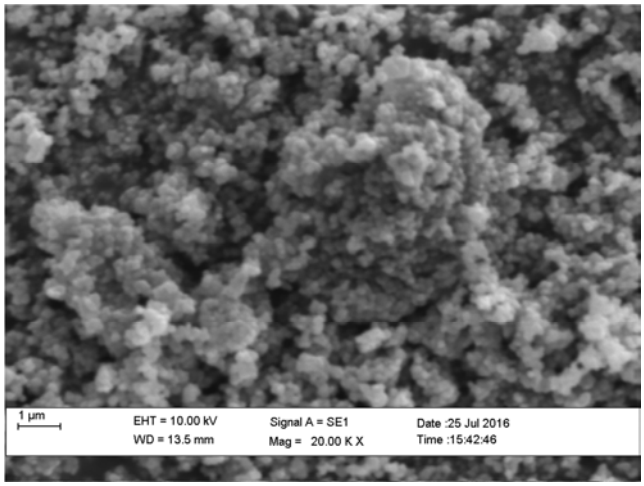
Figure 2. *XRD patterns of (a) LGO-TiO_2 (blue), (b) LGO (red) and (c) TiO_2 (black) nanoparticles.*

Table 1. *Average nano-crystallite sizes for TiO_2, LGO and LGO-TiO_2.*

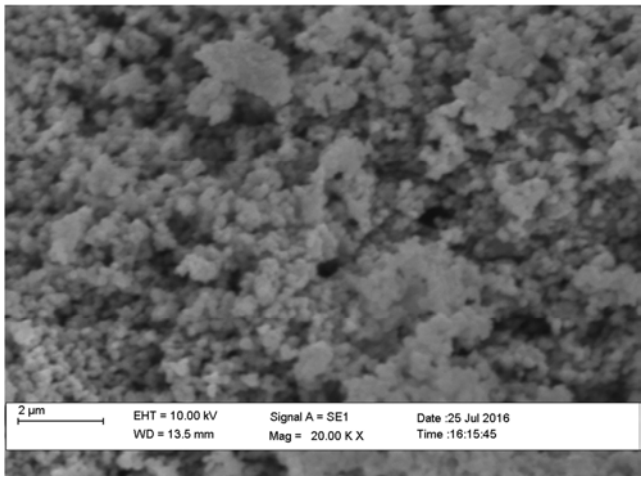
Nano-crystals	(FWHM)/degree	(Crystallite size)/nm
TiO_2	0.16000	19.81
LGO	0.16010	21.44
LGO-TiO_2	0.14915	19.57

Measurements from SEM provide information about the surface topography on the prepared crystal surface of the sample. In Figure 3 (B) crystals has a very small size which investigated from XRD results and LGO is clearly and well

spread across the crystal surface of TiO_2 after 400°C calcination. This could be caused by the presence of solvent trapped in the crystal structure of TiO_2 could be explained from the emergence of carbonyl functional group after previously obtained from FTIR spectra. The morphology of titania powders calcined at the same temperature in Figure 3 (A) exhibited irregular morphology due to the agglomeration of main particles. In all cases the average size is found to be nearly spherical and its grain size is going to be in the range of 0.5-4 μm. From the images a homogeneous type of coating and the adhesive interaction between inter-particle interactions was clearly observed over wide areas that shown from Figure 3(B).



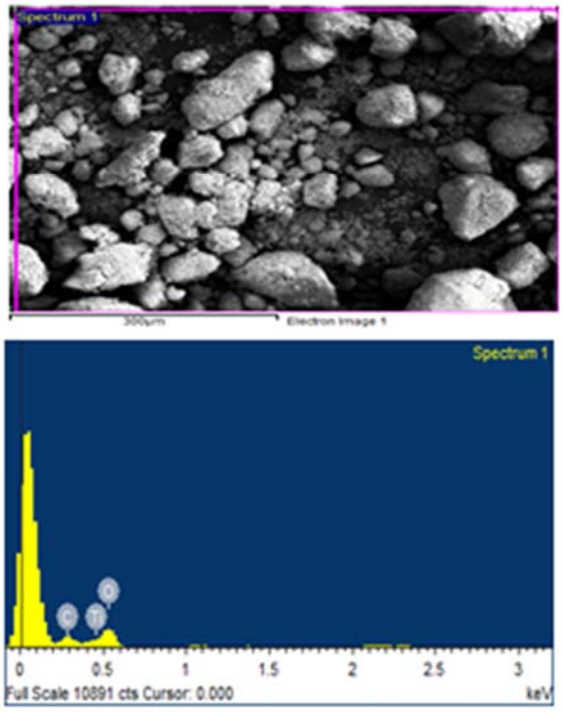
(A)



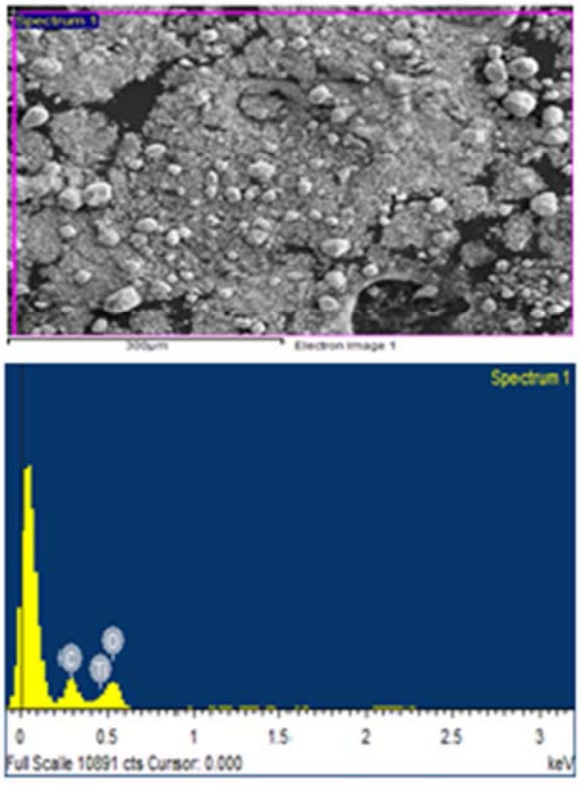
(B)

Figure 3. *(A) SEM images of 6 wt% LGO modified TiO_2 and (B) 50 wt% LGO modified TiO_2 calcined at 400°C.*

The surface elemental compositions of the as prepared photoanodes were further identified by Energy Dispersive X-ray Spectroscopy (EDAX) measurement, and the atomic ratios were calculated from the EDX spectrum. The result shown in Figure 4 (A) and (B) SEM image investigations followed by chemical compositions peaks (atomic and weight %, table 2) with elements; titanium (Ti), oxygen and carbon could be clearly seen in the survey and it clearly showed no trace of any other impurities could be seen within the detection limit of the spectrum.



(A)



(B)

Figure 4. *(A) SEM micrographs coupled EDAX spectrum result of 6 wt% and (B) 50 wt% LGO-doped TiO_2 nanoparticles.*

Table 2. *Elemental composition (atomic %) of 6 wt% LGO and 50 wt% LGO doped nanomaterial films, treated at 400°C.*

	6 wt% LGO-TiO_2			50 wt% LGO-TiO_2			Total
	Elements			Elements			
	Ti	O	C	Ti	O	C	
Atomic %	25.31	59.52	15.17	18.91	50.50	30.59	100
Weight %	51.65	40.58	7.77	43.52	38.82	17.66	

Plots of Photocurrent density (j_p, Acm^{-2}) as a function of measured potential, E_{meas} (V/SCE) for TiO_2 and LGO-TiO_2 calcined at 400°C were shown in Figure 5. Curve (a), i.e., unmodified TiO_2 shows the lower photocurrent density of 9.95 mA cm^{-2} with respective potential at -0.88 V/SCE. The observed low photocurrent density was due to low surface functionality and slow electron transfer across its crystalline structure while Curve (b), i.e., LGO-TiO_2 displayed the higher photocurrent density when it compared with bare TiO_2 sample and its maximum photocurrent density value, 16.51 $mAcm^{-2}$ was recorded at a potential of -0.76 V/SCE within the same environment. This indicates that LGO-TiO_2 is a good photo-response nano-conducting material for the transfer and deterioration of the photo-induced electrons. The surface modification of TiO_2 using LGO was successful and increased the effective surface area of an oxide layer causes generation in higher photocurrent density, i.e., fast electron transfer could exist across the whole surface of the functionalized nanomaterial. Such increment allows the material could absorb more light to generate more electron-hole pairs (excitation) for the targeted application.

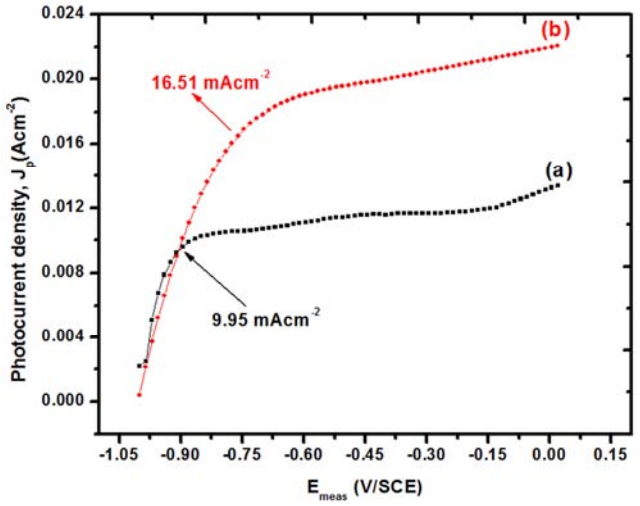


Figure 5. *Photocurrent density, j_p as a function of measured potential, E_{meas} (V/SCE).*

The corresponding visible spectrum efficiencies from figure 6 were found to be 11.24% and 18.91% for bare TiO_2 and LGO-TiO_2, respectively, under illumination intensity of 100 mW cm^{-2} from a 150 watt Xenon lamp. The increase in anodic film photocurrent efficiency near to the electrode surface corresponds to an increase in grain size particle to volume ratio that results higher PEC water splitting efficiency. Therefore, the overall schematic degradation efficiency shown from this figure and the respective numerical calculation of total percent photoconversion efficiency (%ε_{photo} (total)) of light energy was carried out using the equation [29].

$$\%\ \varepsilon_{photo}\ (\text{total}) = \frac{j_p\left[E^o_{rev} - \left|E_{app}\right|\right]}{P_o} \times 100$$

where j_p is the photocurrent density (mW cm^{-2}), E^o_{rev} is the standard reversible potential (which is 1.23 V for water splitting reaction), P_o is the power density of incident light (mW cm^{-2}), $\left|E_{app}\right|$ is the absolute value of the applied potential.

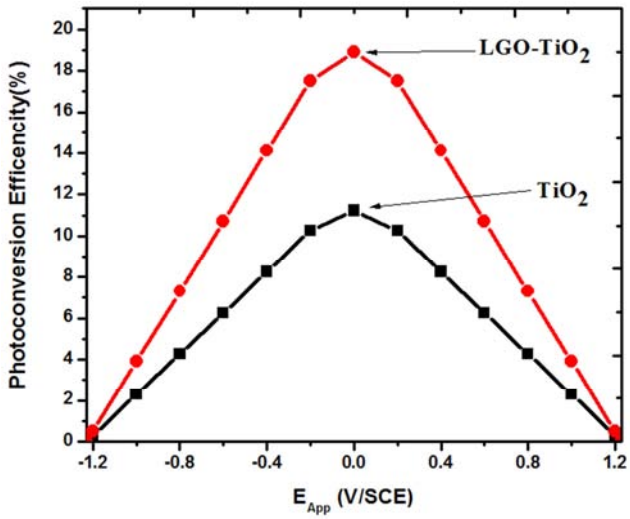


Figure 6. *Dependence of photoconversion efficiency, % ε_{photo} (total), on applied potential E_{app} (V) for TiO_2 (black) and LGO-TiO_2 (red).*

4. Conclusion

Solar water splitting accompanied with photocatalytic organic pollutant degradation is recognized as a potential science and technology advancement for solving fast depletion of fossil fuel and serious environmental problems. Pure/bare TiO_2 and lignocellulose (LGO) modified photocatalysts were successfully fabricated through sol-gel method followed by calcination temperature treated at 400°C. The catalytic performances of LGO-TiO_2 sample was also investigated as a good photocatalytic active nanomaterial towards water splitting for renewable hydrogen energy production. The results showed that LGO-TiO_2 nanostructures annealed at 400°C was better for PEC water splitting for hydrogen renewable solar fuel evolution; i.e., photo-conversion efficiency ≈ 18.91% than that of pure TiO_2 and this suggests that surface functionality (FTIR), surface topography (SEM), porosity and particle size (XRD), as well as purity and chemical composition (EDX) of prepared sample was successfully functionalized. Therefore, the electronic property of the fabricated and modified nanomaterials thrugh LGO incorporation in TiO_2 reduce the band gap and allows more solar light absorption.

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