

Fabrication and Characterization of Few Layered Graphene Sheet Decked with CeO₂ Nano Particles for Dye Sensitized solar cell Application

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Abstract— The present research work describes a simple and low cost process for the synthesis of Few Layered Graphene (FLG) sheet Decked by CeO₂ Nanoparticles (NPs) using Ultrasonic Assisted Synthesis (UAS) method. The synthesized sample is characterized by Field Emission Scanning Electron Microscope (FE-SEM), High Resolution Transmission Electron Microscope (HR-TEM), and X-ray Diffraction (XRD). The prepared FLG/CeO₂ nanocomposite is used as a photoanode in Dye-sensitized solar cell (DSSC) application. The current density-voltage (J-V) characteristics were measured with N719 dye under AM 1.5G, 100 m W/m² of the solar simulator. The efforts showed that the optimized Power Conversion Efficiency (PCE) is observed to be 2.17% in FLG/CeO₂ nanocomposite photoanode, compared to pure CeO₂ photoanode.

Keywords— Few-Layered Graphene, FLG/CeO₂ nanocomposite, photoanode, Dye-sensitized solar cells, power conversion efficiency.

I. INTRODUCTION

Dye-sensitized solar cells (DSSCs) have retained considerable attention during the last decade because of their prominent and promising solar energy conversion system and the potential of becoming a low cost alternative to silicon-based solar cells [1, 2]. In the configuration of DSSC, the dye plays an critical role in harvesting solar energy and converts it into electrical energy with the help of semiconducting photoanode materials. Therefore, the efficiency mainly depends on the type of the dye used in the solar cell and acts as sensitizers [3, 4]. Up to now the Numerous metal complexes and organic dyes utilized as sensitizers; the best study example is the Gratzel group reported that the ruthenium-bipyridyl dyes which show a high conversion efficiency of about 11% [5]. Buscaino et al. showed the remarkable power conversion efficiency of 11.2% by using ruthenium(II) dye [(C₄H₉N)₂ [Ru(4carboxy-4'-carboxylate-2,2'-bipyridine)₂ (NCS)₂ (n719) as sensitizer and the

photovoltaic data of the N719 sensitizer adsorbed on TiO₂ films in DSSC [6].

Graphene and metal oxides composites have attracted considerable attentions towards the researchers [7-9] due to their unique properties such as two dimensional structure, high chemical inertness, high electrical conductivity, and large specific surface and also many potential applications [10-13]. In such nanocomposites Graphene plays as an effective support. Moreover, in the case of a uniform metal oxide distribution in the plane of the graphene sheets makes charge transport phenomena possible, which may give rise to novel properties, different from those of the constituent components. This is demonstrated by recent studies of composited based on graphene and a number of metal oxides: ZnO, TiO₂, SnO₂ and others [14-16].

Among metal oxides, cerium oxide (CeO₂) were received considerable interest because of their high transparency electro-optical performance in the visible and near IR region [17, 18]. It is an n-type semiconductor whose band gap has been reported to vary from 2.7 to 3.4 eV depending on the method of synthesis and also have variable applications like fuel cells, solar cells, catalysis, and medical [19-22]. The controlled synthesis of CeO₂ nanoparticles less than 10 nm in size is of key importance because the catalytic activity of crystalline CeO₂ strongly depends on its surface structure. However, despite of their high catalytic activity, unsupported CeO₂ nanocrystallites have a tendency to form aggregates, in which the particles lose some of their properties. Thus, a new composite material consisting of graphene/CeO₂ NPs might allow one to create a high performance in DSSC application.

In this paper, we report a novel process for synthesis of FLG/CeO₂ nanocomposite through UAS method. In which, graphene oxide (GO) is varied with Cerium (III) nitrate hexahydrate as a precursor material and the resulting solution is ultrasonicated for getting fine dispersion. During the

process GO was simultaneously converted into FLG and nano size CeO₂ NPs decked on FLG sheet. The prepared FLG/CeO₂ nanocomposite used as a photoanode in DSSC.

II. EXPERIMENTAL

A. Synthesis of FLG/CeO₂ nanocomposite

The GO was prepared according to modified hummer's method in the presence of the ultrasonic process [23]. The FLG/CeO₂ nanocomposite synthesized by using an Ultrasonic Qsonica sonicator (Model no: Q500, 20 KHz Frequency, 500 W) at 45% amplitude. In this process, 0.5 g of GO was dispersed in 200 ml ethanol to get a dark brown color solution by stirring for 30 min, then 2 ml of hydrazine monohydrate solution was added to the resulting dispersion solution. Then the mixture was stirred for 60 min at 95°C. Finally, an appropriate amount of Cerium (III) nitrate hexahydrate was added into the above GO solution, resulted solution was transferred into 500 ml vessel and placed in an ultrasonic chamber for 2 hrs sonication at room temperature. Finally, the solution was filtered and washed 3 times with distilled water and dried in hot air over at 90°C for 5 hours to evaporate the solvents. The subsequent powder was calcination at 600°C for 2 hours in a muffle furnace. The obtained FLG/CeO₂ nanocomposite with different weight percentages (FLG1.0, 2.0 and 3.0 wt %) by changing the amount of the FLG. For evaluation, Pure CeO₂ NPs was synthesized by the same way using above method except that GO was not added.

B. Fabrication of FLG/CeO₂ photoanode

In the primary part, 2.0 g of CeO₂ nanopowder was dispersed in 20 ml of ethanol and subjected to Ultrasonication bath for 30 min. After that the solution was pulverized in a porcelain motor and pestle to get a stable colloidal dispersion. In which Ethanol acts as a dispersing agent because it prevents the coagulation of CeO₂ NPs which affects the porosity of the film. Furtherly, the paste was diluted by the slow addition of 1 ml PEG (MW 10000) to maintain viscosity and concentration of the paste. Finally, a few drops of a detergent (Triton X-100) were added to overcome the surface tension property of the paste, to facilitate even spreading and to avoid subsiding the formation of surface cracks. In the finishing part, to obtain a FLG/CeO₂ nanocomposite paste at a different weight percentage of FLG (1.0,2.0 and 3.0 wt %), the method of Sacco et al. [24] is followed. Briefly, FLG/CeO₂ nanocomposite powder is also dissolved in ethanol and subjected to Ultrasonication bath for 30 min, to get a stable colloidal dispersion the same above process is used. FTO conductive glass with a sheet resistance of (sheet resistance =9 Ohms/sq, and >80% transmittance in the visible region) were first cleaned with a detergent solution using an ultrasonic bath for 15 min, rinsed with water and ethanol, and then dried. CeO₂ and FLG/CeO₂ nanocomposite pastes were deposited on the FTO conductive glass by doctor blade technique in order to obtain CeO₂ and FLG/CeO₂ film. The film on the substrate was annealed at 450°C for 30 min.

III. CHARACTERIZATIONS

The surface morphology analyzed by field emission scanning electron microscopy (FESEM, Model no. Carl Zeiss Merlin Compact 6027), particle size and decoration of the CeO₂ NPs on the FLG is performed by High resolution transmission electron microscopy (HRTEM, Model no: JEOLJEM 200CX). The crystal phase and composition of FLG/CeO₂ nanocomposite investigated by XRD (XRD, Model no: Bruker D8 advanced) with CuK α radiation ($k=1.540\text{\AA}$). The current density-voltage (J-V) parameters of the DSSCs were measured by under the illumination of a simulated AM1.5G solar light from the 450-W Xenon lamp (model no: Oriel Class 3 A) using a solar simulator with Keithley 2440 source meter.

IV. RESULTS AND DISCUSSION

Fig 1 shows FESEM image of the CeO₂ NPs and FLG (1.0, 2.0 and 3.0 wt %) CeO₂ nanocomposite. The surface morphology of the CeO₂ NPs (Fig. 1(a)) is observed as onion resembles the texture which reflects its layer structure. After ultrasonic treatment, the morphology is retained and the surface area covered with CeO₂ NPs decked on FLG sheet which is confirmed by FESEM as shown in Fig 1(b-d). The Vander walls, tent the FLG to aggregate back to the graphite structure, decked with NPs and functional groups helpful to overcome these interactions.

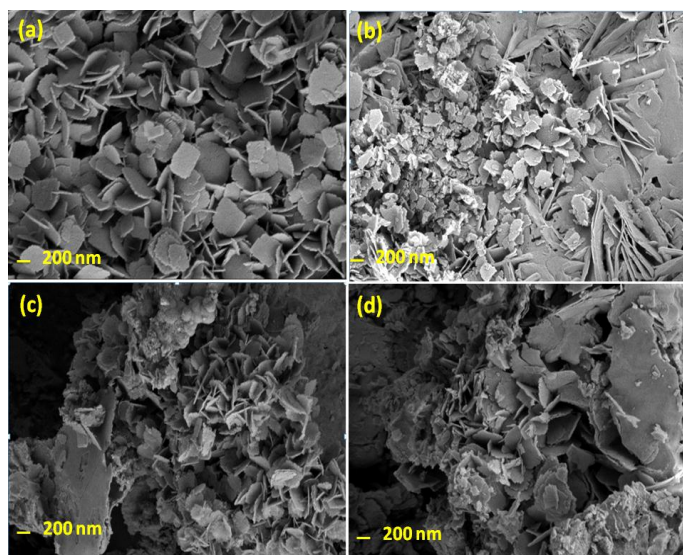


Fig.1. FESEM images of (a) CeO₂ NPs (b) FLG (1.0 wt %)/CeO₂ nanocomposite (c) FLG (2.0 wt %)/CeO₂ nanocomposite (d) FLG (3.0 wt %)/CeO₂ nanocomposite.

The further morphology, particle size and microstructure of FLG (1.0, 2.0 and 3.0 wt %)/CeO₂ nanocomposite were studied by conventional TEM and high resolution transmission electron microscopy (HRTEM). Fig 2 shows electron microscopic images of CeO₂ NPs (Fig 2 (a)), FLG (1.0, 2.0 and 3.0 wt %) / CeO₂ nanocomposite, the size distribution of the CeO₂ NPs (Fig 2 (b)) and selected area diffraction angle pattern of CeO₂ NPs as shown in (Fig 2 (c)). It is seen from the image of CeO₂ NPs are uniformly decked on the FLG sheet (Fig 2 (d-f)).

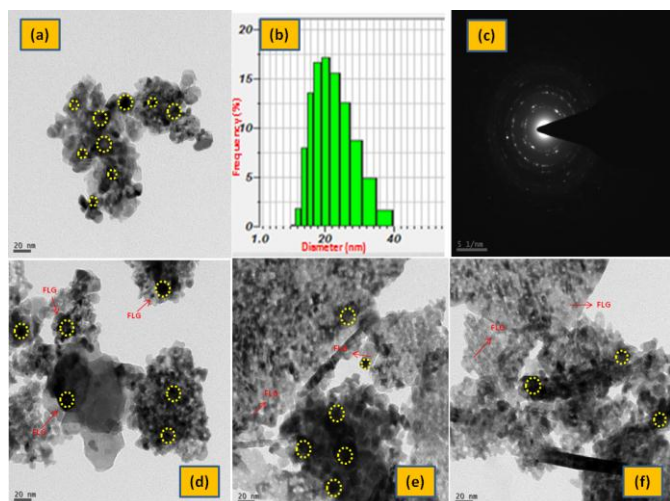


Fig.2. TEM, HRTEM images of (a) CeO₂ NPs, (b) size distribution of CeO₂ NPs, (c) SAED pattern of CeO₂ NPs, (d) FLG (1.0 wt %) /CeO₂ nanocomposite, (e) FLG (2.0 wt %) /CeO₂ nanocomposite, (f) FLG (3.0 wt %) /CeO₂ nanocomposite.

The phase and composition of CeO₂ NPs and FLG (1.0, 2.0 and 3.0 wt %) / CeO₂ nanocomposite was determined by X-ray diffraction (Fig 3). The CeO₂ NPs characteristic peaks are observed at 28.5°, 33°, 47.7°, 56.3°, 69.4°, 77° and 79° corresponding to the (111), (200), (220), (311), (400), (331) and (420) planes, respectively. The CeO₂ phase (cubic structure) the results are well matched with standard JCPDS database (JCPDS no. 34-0394). A small peak is observed at (2θ =25.3°) which represents the (002) plane FLG sheet. These results indicated that the formation of FLG/CeO₂ nanocomposite.

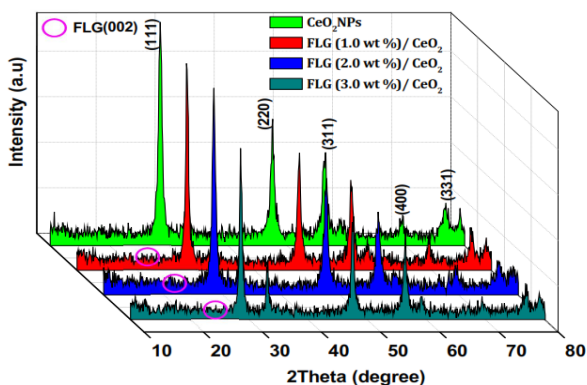


Fig.3. The XRD pattern of CeO₂ NPs FLG (1.0, 2.0 and 3.0 wt %) /CeO₂ nanocomposite

The current density-voltage (J-V) curves of CeO₂NPs and FLG (1.0,2.0 and 3.0 wt %) /CeO₂ nanocomposite photoanode as shown in Fig 4. The DSSCs characteristics of V_{oc}, J_{sc}, FF, PCE values are described in Table1. There is a clear enhancement current density (J_{sc}) from 6.90 to 8.62 mA/cm² and an increase of open circuit voltage (V_{oc}) from 0.51 to 0.53V. The PEC enhancement from 1.75 to 2.17 % respectively. The appropriate amount of FLG (1.0 wt%) introduces in CeO₂ NPs the increase in the number of photo generated electrons, for making CeO₂ NPs conductive and the

electrons are easily moved through the FLG sheet further leading to reduction of recombination rate. Finally, the highest efficiency was achieved in the FLG (1.0wt%)/CeO₂ photoanode.

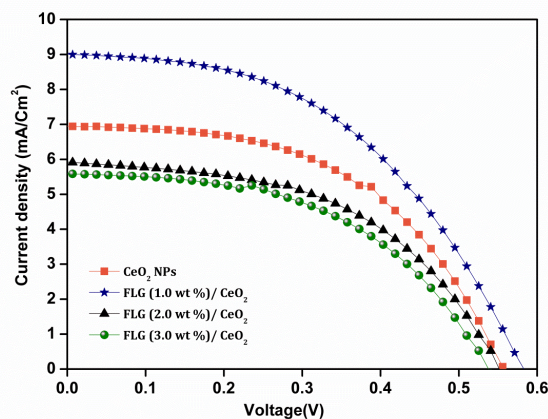


Fig.4. J-V curves of CeO₂ and FLG(1.0, 2.0 and 3.0 wt %)/CeO₂ photoanode based DSSC.

Table-1: Photovoltaic (parameters) of the DSSCs based on CeO₂ and

Photoanode	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PEC (%)
CeO ₂ NPs	0.51	6.90	49.6	1.75
FLG (1.0 wt %) / CeO ₂	0.53	8.62	45.3	2.17
FLG (2.0 wt %) / CeO ₂	0.50	5.84	48.5	1.43
FLG (3.0 wt %) / CeO ₂	0.49	5.53	48.1	1.31

FLG(1.0, 2.0 and 3.0 wt %)/CeO₂ photoanode .

V. CONCLUSION

Successfully prepared FLG/CeO₂ nanocomposite by simple and low cost technique, Ultrasonic assisted synthesis (UAS) method. The characteristic features obtained FLG/CeO₂ nanocomposite were explored by various characterization techniques such as surface morphology, structural properties were investigated. The fabrication of FLG (1.0, 2.0 and 3.0 wt %) /CeO₂ nanocomposite used photoanode in DSSC. A noteworthy enhancement of (2.17%) in the power conversion efficiency (PCE) was achieved in DSSC in FLG (1.0%) /CeO₂ nanocomposite to compare CeO₂ NPs under A.M 1.5G solar simulated.

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