Effect of Nanotube Diameter on Photo-Electro-Chemical Properties of Carbon Quantum Dot Functionalized TiO_2 Nanotubes

Sanju Rani and N. Rajalakshmi

***Abstract*—We report the photo-electro-chemical properties of Carbon Quantum Dots (CQD) functionalised TiO_2 nanotube arrays (TNA). The TNA formed by electrochemical anodization of a Ti foil offer highly aligned, vertically oriented nanostructures suitable for photo-catalytic application. These nanostructures are functionalised with CQDs synthesized by the electrochemical etching of graphite and the resultant samples are characterized by high resolution transmission electron microscopy, photo-current and photon-charge conversion efficiency measurements, Mott-Schottky and impedance spectroscopy. The results indicate that the nanotubes with larger diameter can support a higher density of CQDs and hence shows better values for photo-current and light conversion efficiency. Furthermore, these samples offer a lower charge transfer resistance across the semiconductor-electrolyte interface. The CQD functionalised TiO_2 nanotubesarrays with suitable diameter can therefore be used for efficient hydrogen generation by water splitting under the illumination of solar radiation.**

***Index Terms*—TiO_2, carbon quantum dot (CQD), photo-electro-chemical, clean energy.**

I. Introduction

Although the fossil or hydrocarbon fuels have so far been dominated our energy infrastructure for a couple of centuries, the awareness and realization about global warming caused by the greenhouse gases emitted by the combustion of these fuels, has forced the scientists and engineers to look for alternative sources of energy that reduces overall green-house emissions. Hydrogen offers the prospects of a clean fuel having high energy content [1] without carbon emissions. The combustion of hydrogen with oxygen produces heat energy and water as a byproduct. In this scenario, hydrogen as a fuel appears to be an attractive option; however, it has to be produced by processes that do not involve carbon emissions.

At present, the majority of the industrial hydrogen production depends on fossil fuels in which thermal reduction process is used extract hydrogen from hydrocarbons. Although efficient, such a technique is not environment friendly because it causes a massive emission of the CO_2. It is therefore important to look for sources of hydrogen that do not contain carbon and water is the most abundant material containing hydrogen. Water is also a stable molecule and therefore energy is required to split it to release hydrogen. [2] However, the required energy to split water should come from a carbon free source to justify the production of hydrogen from water. Although, the electrochemical reduction of water (commonly known as electrolysis) is an established technique, the requirement of electrical energy is again a matter of concern if it is not produced from renewable sources. In this context, the photo-electro-chemical (PEC) splitting of water, in which part of the required energy can be drawn from sunlight, is an attractive option because it reduces our dependence on the electrical energy to split water for producing hydrogen [3].

The PEC system of water splitting requires a light active electrode material as anode (photo-anode), a noble metal cathode and a reference electrode. The photo-anodes are semiconductor materials that can generate electron-hole pairs when light of suitable energy (frequency) equal to its band gap is used for illumination. The photo-generated charge carriers help for reduction water according to the following reaction: [4]

$$2H_2O \rightarrow \underline{\text{Visible Light and Catalyst}} \rightarrow 2H_2 + O_2$$

An appropriate band-gap energy (suitable for the absorption of the solar spectra), suitable band-edge positions (compared to the electrochemical reduction/oxidation energy levels of water), corrosion resistance are some of the most important properties required from an efficient photo-anode material. Metal oxides offer superior thermal and chemical stability over other materials such as sulfides and tellurides; however, these materials usually posses higher band-gap energies suitable for the absorption of only the UV part of the solar spectra. In particular, titanium dioxide (TiO_2) is a very well-known photo-catalyst with efficient charge carrier generation, long hole diffusion length and corrosion resistance properties; However, the with a band-gap energy of about 3.2 eV, it can work efficiently only under UV radiation [5].

Several approaches have been attempted to sensitize TiO_2 towards visible light absorption, which include doping with other materials, composite formation, dye sensitization and quantum dots functionalization. Doping and composite formation, although are effective techniques, but produces a lot of defect states which, in turn, act as traps for photo-generated charges. Dye sensitization method, though works well for solar cell application, does not suit the water splitting purpose because of the proximity to water which

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tend to dissolve the dye. In this context, quantum dot functionalization offers the most feasible option; however, the materials for quantum dots should be stable and non-toxic. [6]-[8] In the recent times, the carbon quantum dots have emerged as efficient alternative to the chalcogenides (sufides, tellurides) because of ease of synthesis and non-toxicity compared to the materials containing heavy metals. Lot of work have been reported on the functionalization of bulk/powder TiO_2 and other photo-catalyst materials with CQDs, but the field of CQD functionalized TiO_2nano-structures not explore. [9], [10] Among the various nano-structures, nanotubes offer a better catalytic performance because of the availability of both inner and outer surfaces which, along with the property of directional charge transport, yield higher contact area for water and easy separation of the photo-generated charges. In particular, the vertically oriented TiO_2nanotube arrays (TNA) formed by electrochemical anodization of Ti foil have shown potential for efficient water splitting because of the presence of ordered porosity and alignment with respect to the electrode substrate. The electrochemical anodization is an industrially established technique and therefore the fabrication of such nanotube arrays can easily be scaled up [11].

This work reports the fabrication of TNAs with different diameters (for the individual tubes) and functionalization by CQDssynthesized by the electrochemical etching of graphite rods. The resultant CQD-TNA samples have been characterized by X-ray diffraction, scanning electron microscopy, optical absorption spectroscopy, photo-current measurements, IPCE, Mott-Schottky and the electrochemical impedance spectroscopy. The performance of the samples as a function of nanotube diameter has been analyzed and results are discussed.

II. Experiments

The TiO_2 nanotubes arrays were synthesized with two different pore sizes with same length by an electro chemical anodization process using ethylene glycol bath with Ti foil as anode and Pt foil as cathode. The Ti foil with 0.25 mm thickness and 99.9% was used in all experiments, which were cleaned by using ultra-sonicating in acid and alcohol solvents. Constant DC voltage of 60 V were applied for 1 hr to get 10 micron TiO_2 nanotubes the pore size of 80 nm and 120 nm was obtained by variying EG bath water composition from 1% to 4%. The samples prepared with 1% and 4% of water are marked as AG0 and CG0 respectively. Carbon quantum dots were prepared with electrochemical etching of graphene rods by applied constant DC current of 40 V in alkali solutions with alcohal. After this electrochemical process, 5 gm of $MgSO_4$ was added to remove the water from quantum dots and these quantum dot suspensions were separated by centrifugation. TNT nanotubes samples with two different pore size were functionalized with carbon quantum dot (CQD) by dipping the TNT in quantum dot solution for 10 min and followed by oven dry at 60^{o}C for about 1 hr. The CQD functionalized samples are marked as AG2 and CG2 (corresponding to AG0 and CG0 samples without functionalization). Morphology of the samples were analysed by SEM and HRTEM/TEM images. The SEM was done using FEI quanta 400 system while HRTEM were performed on Philips CM-12 machine operating at 200 kV.

Photo-electro-chemical measurements were carried out using CH Instruments electrochemical workstation model 5000E. A three-electrode configuration was used for all the measurements and 1 molar NaOH solution was used as electrolyte. TiO_2 nanotubes sample, and Pt foil were used as anode and cathode respectively, while Ag/AgCl electrode was used as reference. Photo-current measured were done by a 500 W Hg arc lamp applying voltage -1 to 0. Mott-schottky measurements for flat band potential and impedance for interfacial charge transfer were also done using same setup.

III. Results and Discussion

Fig. 1 shows the XRD patterns of the TNA samples with similar nanotube lengths but different pore diameters and wall thickness. From XRD pattern is very clear that anatase phase has been formed. (Matched with JCPDS file no. 89-4921). It was also observed that crystallinity of the samples remains same for both the pores size as can be seen. The different geometrical parameters for the two types of samples (prepared with different percentage of water contents in the electrolyte) are presented in Table I.

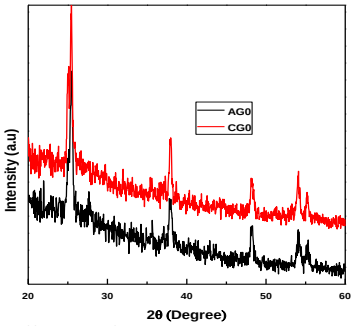

Fig. 1. X-ray diffractions for AG0 and CGo TNT nanotubes arrays.

TABLE I: Pore Volune, Wall Thickness and Surface Area of TNT Arrays

Sample	Inner pore diameter (nm)	Wall thickness (nm)	Surface area (μm^2)
1 vol % of water **(AG0)**	120-130	10-15	13.96
4 vol % of water **(CG0)**	70-80	8-12	10.04

Surface area for both type of samples were estimated by using formula [12].

$$A=2\pi\ (D_0^2 - D_i^2) + 2\pi L(D_o - D_o)$$

where

D_0 = Outer diameter of pores

D_i = Inner diameter of pores

L= Length of nanotubes

A= Surface area

The scanning electron micrographs of the TNA samples are presented in Fig. 2. The difference in pore diameter is clearly observed from the top view images, whereas the cross sectional images show the length of the nanotubes (thickness of the TNA samples). The pores are near circular

in shape and regularly spaced which offer advantage in terms of the available surface area in contact with water/electrolyte for the PEC measurements. Furthermore, this also helps in uniform sensitization by the quantum dots (as has been explained in the later sections).

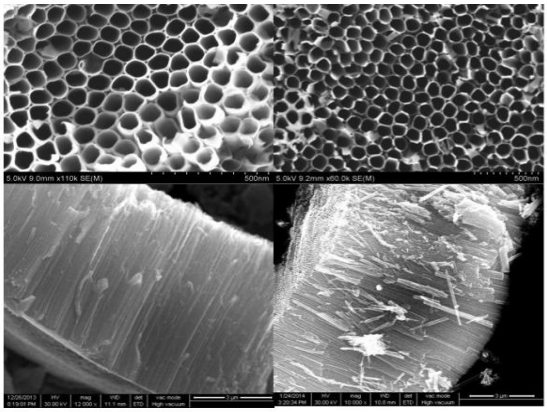

Fig. 2. FE-SEM images (a) top view TNT 1% water (b) top view TNT 4% water (c) cross-sectional view TNT 1% water (d) cross-sectional view TNT 4% water.

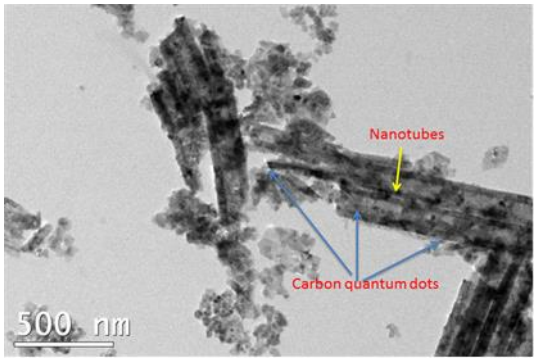

Fig. 3. HRTEM image of TiO2-CQD.

The CQDs were attached to the nanotube arrays by immersion method. The crystallized nanotubes were immersed in a colloidal suspension of the CQDs for overnight and then dried in a jet of pure nitrogen. A representative HRTEM image of one of the CQD-TNA samples is shown in Fig. 3. The tubular microstructure with smaller particles is clearly evident from the image indicating the attachment of CQDs onto the surface of the nanotubes.

Photo-Electro-Chemical Measurements

The photo-electrochemical measurements (photo-current vs. voltage) were performed after soaking all the samples (CQD-TNA) in the electrolyte for 15 min for stabilization. Fig. 4 shows linear sweep voltammetry data (with respect of Ag/AgCl as reference electrode and Pt as cathode) of AG2 and CG2 under dark and illumination condition in the -1 to 0 volts range. A significant increase in the current is observed under illumination as compared to dark current (without illumination). Moreover, in the sample AG2, the photo-current values are about 3 times higher than that in CG2, and the saturation is also observed at a lower potential. The higher photo-current and early saturation indicates larger surface area and good fucntionalization of AG2 sample which early shown in FE-SEM micrographs [13].

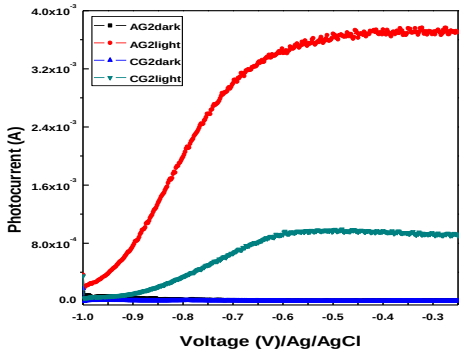

Fig. 4. Photo-current voltage characteristics for AG2 and CG2 TNT nanotubes arrays under dark and illumination.

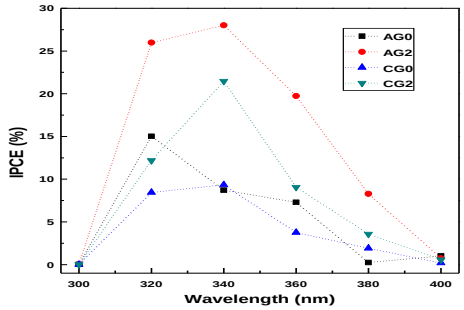

Fig. 5. IPCE plots for AG0,AG2, CG0 abd CG2 TNT nanotubes arrays.

Fig. 5 shows the incident photon to charge conversion efficiency (IPCE) of the samples with two different pore sizes. Both the bare samples and with CQD functionalized subjected to IPCE measurements. In concurrence with the photo-current data, the sample AG2 shows highest IPCE values compared to the bare samples and also the sample CG2, indicating higher charge generation efficiency under the illumination.

Electro-chemical impedance spectroscopy is a very useful technique for analyzing the internal resistance of the working electrode material and the resistance between working electrode and solution or electrolyte. The interaction of electrolyte with surface of working electrode can be understood from Nyquist plots. In this plot the 'semicircle' characteristics at high frequencies shows the charge transfer resistance between the working electrode and electrolyte. The diameter of this semicircle revels electrode resistance.

Fig. 6(a) shows the Nyquist plot of AG and CG (without functionalization) samples and Fig. 6(b) shows Nyquist plots of AG2 and CG2 (with functionalization) under dark and illumination conditions. It is observed from Fig. 6(a) that the diameter of semicircular arc in the case of sample CG0 is larger as compared to that in sample AG0, which clearly indicates that the charge transfer resistance is higher for sample CG0. In the case of functionalized samples, a very large charge transfer resistance occurs as evident by the absence of a clear semicircular region at the high frequencies. Under the illumination, however, a finite charge transfer resistance arises in the form of distinct semicircular regions as observed in Fig. 6(b). Furthermore, the radius of semicircular arc is smaller for AG2 sample. It reveals that in case of AG2 charge transfer resistance is lower for AG2 as compare to CG2. These results are also supported by photo-current measurements [14].

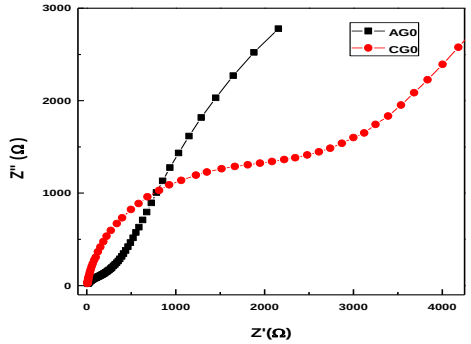

Fig. 6(a). Nyqist curves for AG0 and CG0 Nanotubes arrays.

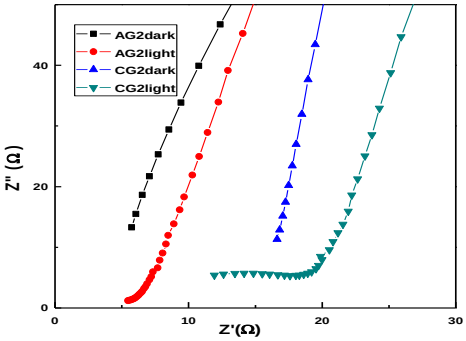

Fig. 6(b). Nyqist curves for AG2 and CG2 Nanotubes arrays under dark and illumination.

When an electrolyte and a semiconductor come in the contact with each other, there is an initial flow of charge and a capacitive layer is formed at equilibrium at thesolid/liquidinterface. This kind of equilibrium defined by using three layer model such as space charge layer with 10-100 nm thickness, diffusion or Gouy layer with 1-10 nm and Helmholtz layer with 0.4- 0.6 nm. The total capacitance of all three layers can be obtained by considering them in series. Capacitance of Helmholtz layer and Gouy layer is very small as compared to space charge layer. Impedance spectroscopy can be provide total capacitance of the solid/electrolyte interface from which Mott-Schottky plots can be derived by using Mott-schottky equation.

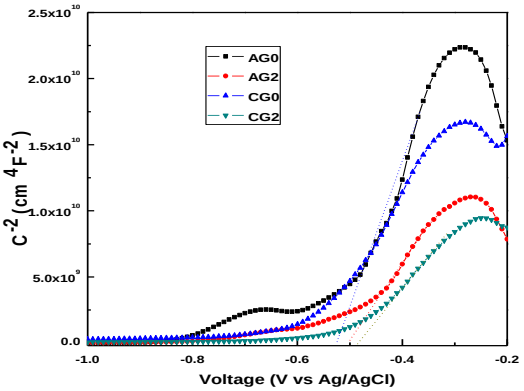

Fig. 7. Mott-Schottky plots of AG2 and CG2 TNT nanotubes under dark and illumination.

TABLE II: FLAT BAND POTENTIAL AND DONOR DENSITY

Sample	Flat band potential	Donor density
AG2 dark	-0.54	$2.02X10^{17}$
AG2 light	-0.51	$3.62x10^{17}$
CG2 dark	-0.54	$2.40x10^{17}$
CG2light	-0.47	$3.25x10^{17}$

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 q N_d}(V - V_{Fb} - \frac{KT}{q})$$

where q= electronic charge

K = Boltzmann constant

KT/q can be neglected, as it is very small to other values (25 mV) at room temperature.

Fig. 7 shows the Mott-Schottky plots for both samples in dark and under illumination. The flat band potentials and donor densities are calculated from these plots and these are presented in Table II. The sample AG2 under illumination shows largest donor density caused by the photo-generated charge carriers. This supports the earlier observation of higher photo-current and photo-conversion efficiency obtained from the AG2 sample. It is also interesting to note that the flat-band potential of the sample CG2 is most positive (right shifted) among all and has a value of -0.47 V. However, in spite of having the lowest flat-band potential the corresponding photo-current does not show improvement which may be attributed to the shifting of the conduction band below the hydrogen reduction level. The flat-band potential of the samples AG2 therefore appears to be optimum for the photo-electro-chemical hydrogen generation (as observed from the photo-current measurements) [15], [16].

IV. CONCLUSIONS

The TiO_2 nanotube arrays formed by electro-chemical anodization offer an excellent platform for the functionalization of carbon quantum dot by immersion method. We have studied the TNA with two different diameters (for individual nanotubes) and found that the TNA with 120 nm (larger diameter) yield better functionalization and higher values for photo-current density and light conversion efficiency. Samples also show lower interfacial resistance at the semiconductor-electrolyte junction that establishes the suitability for use as a photo-anode for photo-electro-chemical hydrogen generation under solar radiation.

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