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# Silicon-Silver Dendritic Nanostructures Enabled Photoelectrochemical Solar Water Splitting for Energy Applications

*Uday Dadwal and Rajendra Singh*

## Abstract

Photoelectrochemical (PEC) splitting of natural water was studied using silicon nanowires decorated with silver dendrites (dendritic nanostructures) as working electrode. A metal assisted wet chemical etching method has been used for the synthesis of dendritic heteronanostructures. Measured photocurrent density  $1.7 \text{ mA/cm}^2$  under white light illumination exhibits the efficient decomposition of natural water. The decomposition of water is primarily ascribed to the enhancement in the working electrode surface and water effective interface and the decrease in the recombination of light induced (photoexcited) carriers in the existence of silver dendritic nanostructures. Enhancement in photoinduced charge carriers separation caused due to the existence of Schottky barrier between the silicon and silver dendritic nanostructures. The light induced carriers (holes) in silicon are transferred to the metal (Ag) dendritic nanostructures that work as a charge basin to effectively carry out the oxidation reaction of water during PEC measurement. The solar-to-hydrogen (STH) conversion efficiency of about 4.5% was reported, indicating the efficient PEC solar water (pH 7) splitting. A cost-effective and efficient method for the PEC solar water splitting is presented in order to enhance the STH efficiency for the production of clean and renewable fuel.

**Keywords:** photoelectrochemical, water splitting, dendritic nanostructures, metal-assisted wet chemical etching

## 1. Introduction

Water splitting is the chemical method which involves the decomposition or splitting of water molecules into hydrogen and oxygen gases [1, 2]. The splitting of water molecules in the presence of external bias (such as sunlight) and working electrode is called as photoelectrochemical (PEC) water splitting method [1–3]. In this method, suitable electrodes immersed in an aqueous solution which split water molecules under light [3, 5, 6]. A form of PEC water splitting occurs in nature is the photosynthesis process used by the plants and other organisms in order to convert the sunlight into chemical energy with the release of oxygen. The working electrode used for the PEC splitting of water can act as photoanode or photocathode depending upon the PEC reactions [1, 4–6]. If the PEC oxidation of water occurs at

the working electrode, then working electrode acts as photoanode (oxygen release at the working electrode). On the other hand, with the PEC reduction of water at the working electrode is referred to as photocathode (release of hydrogen). The requirement for the PEC water splitting process is that the band gap of the working electrode should be properly positioned with respect to the normal hydrogen electrode (NHE) in order to split the water under light illumination. This means that the top of the valence band must be more positive than the  $O_2/H_2O$  Redox potential (1.23 V) and the bottom of the conduction band must be more negative than the  $H^+/H_2$  Redox potential (0 V) [1, 6, 7].

In the presence of external light photon with energy more than the working electrode band gap, light is absorbed by the photogenerated electron. This excited electron jumps into the conduction band from the valence band of the working electrode. This leaves behind an oxidizing hole in the valence band. The excited electron goes to reduce the proton while the hole accepts electrons from the water [1, 6]. The presence of the noble metal nanomaterials such as silver or gold nanoparticles on the surface of the working electrode (silver dendrites on the surface of silicon nanowires in this case) can enhance the PEC reactions [1]. The metal nanoparticles act as a sink for photoexcited electrons from the working electrode. This increases the charge carrier density and improves the electronic conductivity near the surface region of the working electrode. It provides the efficient overall charge transfer process at the working electrode and water interface [1, 2, 6]. This eventually increases the water splitting process for the generation of alternate source of clean and renewable fuel using sunlight. The production of hydrogen using water splitting method provides a renewable and sustainable energy that presents a number of advantages including overcoming the global warming and greenhouse gases from fossil fuels [1–6]. Thus, the use of hydrogen in replacing conventional fossil fuels for renewable and sustainable energy applications presents a number of advantages [1–4].

Semiconductor nanostructures have shown an excellent photocatalytic activity for solar water splitting. These nanostructures act as nano-photocatalysts for achieving an optimum solar-to-hydrogen efficiency [6–8]. Hydrogen produced by the photoelectrochemical method is of specific attention to the case where photocatalyst decomposes water molecules in the existence of solar radiation without the association of any substance or external biasing. This makes the hydrogen production cost-effective and simple as compare with previously reported water splitting methods. There is an increase in concerns over rising global energy demand, environmental sustainability, and development of new energy solutions with minimal impact on the environment [1–4]. In the recent few years, significant attention has been given to hydrogen production via PEC water splitting which could be one of the prominent energy sources [1, 5, 6].

It has been shown that the solar water splitting uses both oxidization and reduction nature of semiconductor nanostructures as photocatalysts [8, 9]. Water splitting occurs spontaneously only when hydrogen and oxygen reactions lie between the conduction band minimum and a valence band maximum of the semiconductor. Investigations have been going on for the detail understanding, optimization and development of the photoelectrochemical method using various semiconductor nanostructures [10–12]. Semiconductor nanostructures have shown to be excellent nano-photocatalysts for the photoelectrochemical solar water splitting. Based on recent research work, various photocatalysts such as CdS,  $TiO_2$  and SiC for solar-to-hydrogen production has been investigated [13, 14]. A photocatalyst with non-destructive, environmentally pleasant, plentiful and cost effective in nature is promising for the photoelectrochemical solar water splitting. The nanostructures of additional semiconductors such as third-fifth nitrides, cobalt oxide (CoO) and

silicon are also shown to be important for photoelectrochemical solar water splitting [3, 12, 15]. Several methods have been reported for the synthesis of semiconductor nanostructures. Among these, metal assisted wet chemical etching method has been reported investigated for the synthesis of semiconductor nanostructures [16, 17]. Vertical standing silicon nanowires have been prepared using a standard aqueous solution of HF and AgNO<sub>3</sub> for different applications. It includes the fabrication of the solar cell and related devices [18–21]. Optical properties of a vertical standing array of silicon nanowires have been also explored for the fundamental understanding of various concepts. Due to the simple process flow of metal assisted chemical etching method, synthesis of metal assisted porous silicon has been investigated [20, 21]. Semiconductor nanostructures have been studied from the photoelectrochemical-induced solar water splitting. Other materials such as ruthenium polypyridyl complexes have been investigated as visible light-induced photo-sensitizers for water splitting applications [22]. Synthesis of carbon nanotube anode and tin oxide nanoribbons has been carried out for various applications [23]. In particular, such materials and others have been investigated for the hydrogen production by photocatalytic decomposition of solar water using a water splitting method.

In the context of the current status of the energy availability, energy sources should be clean and environmentally friendly. The renewable energy sources are of top priority in this context. One of the prominent alternate sources of renewable and clean energy emerged out to be hydrogen production by photoelectrolysis of water using solar energy. Hydrogen production by such a way is the promising fuel, which can be used in fuel cells for the generation of electricity with high efficiency. In addition, many chemical reactions and petroleum refining require hydrogen as a reactant. Therefore, in the recent past, a number of semiconductor nanostructures have been proposed for the development of solar water splitting methods. However, solar-to-hydrogen conversion energy efficiency is reportedly lower.

The aim of this report is to investigate the metal assisted wet chemical etching of semiconductor (silicon), and semiconductor nanostructures-induced solar water splitting for achieving the optimum solar-to-hydrogen efficiency. From the existing fundamental understanding, various parameters/conditions of the metal assisted wet chemical etching and photoelectrochemical solar water splitting will be optimized for the progress of hydrogen production as an alternate fuel in the context of the current status. It has been found that metal assisted chemical etching of silicon can result in the synthesis of tree branches-like silicon nanowires. Such nanostructures can be the promising nano-photocatalysts for the hydrogen generation as an alternate fuel using photoelectrochemical solar water splitting. The solar water splitting using photoelectrochemical method has been explored by reviewing the current density and impedance measurement of the dendritic nanostructures (working electrode) and water interface using electrochemical method. The electrical properties of the dendritic nanostructures as working electrode have been studied using Mott-Schottky (M-S) measurements. The oxygen gas evolution is also considered during the PEC process.

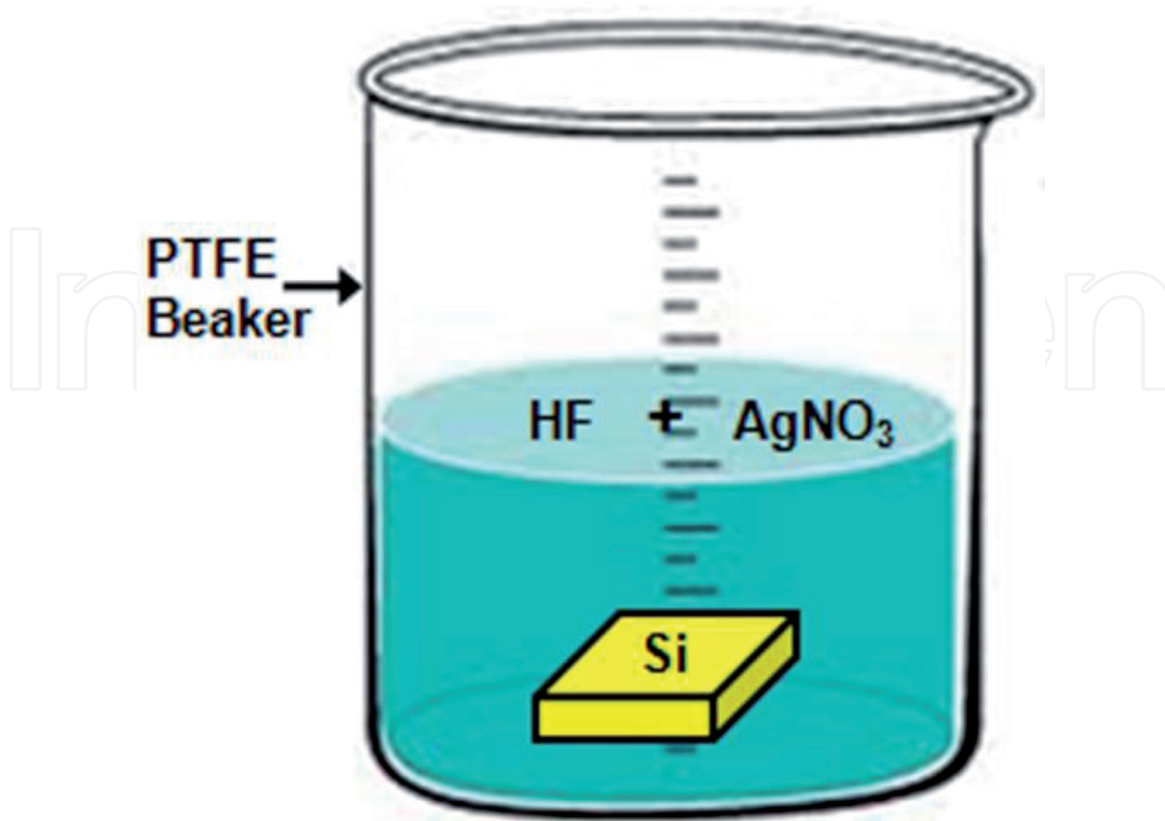
This study reports that the PEC solar water splitting using silicon silver dendrites nanostructures as working electrode can provide effective way for lower cost collection of sunlight for the renewable fuel development.

## 2. Experimental

N-type Czochralski (CZ) grown (100) silicon wafers of diameter 2-inch were cut into small size samples ( $3 \times 3 \text{ cm}^2$ ). The samples were then exposed to a typical silicon cleaning procedure [24, 25]. The cleaning was carried out using isopropanol



(IPA), de-ionized wafer (DI) and boiling in a piranha solution of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  (1: 1 by volume) for 15 minutes [24, 25]. This follows the DI wafer rinse and 5% HF dip for 30 seconds in order to take away the native oxide from the Si substrate. The schematic of galvanic cell for the metal assisted chemical etching of semiconductor is shown in **Figure 1**. The cleaned silicon wafer pieces were then etched by a metal assisted wet chemical etching method for the synthesis of nanostructures. Metal assisted wet chemical etching was carried out using an optimized process consisting of an aqueous solution of 5 M HF (49%): 0.02 M  $\text{AgNO}_3$  (1: 1 by volume) (see **Figure 1**) [1]. The metal assisted chemical etching of the silicon sample was carried out for 30 min at room temperature (RT). The details of the metal assisted wet chemical etching method can be found from the earlier reports [26–28]. Topological study of the etched silicon has been done using (FEI QUAN TA 3D FEG) field emission scanning electron microscope (FE-SEM). The structural quality of the dendritic nanostructures has been evaluated using X-ray diffraction method (XRD) in bulk mode in the range between 40 and 80 degree using Rigaku Ultima IV thin film X-ray diffractometer. A  $\text{Cu K}\alpha_1$  radiation source of wavelength  $1.54 \text{ \AA}$  was used in the XRD measurements. The band gap of the nanostructures was studied at room temperature using ultraviolet–visible–near infrared spectrometer [1]. The PEC work station from Zahner Instruments has been employed for studying the natural water splitting [1]. PEC work station consists of a high power light emitting diode as a white light irradiation source (430–730 nm) and a three electrode assembly photoelectrochemical cell. The heteronanostructures were submerged in water filled within the PEC cell. Natural water (pH 7) was taken as an electrolyte for all PEC water splitting experiment. Thus, a photoelectrochemical cell was consisting of dendritic heteronanostructures as photoanodes (working electrodes), a platinum wire as counter electrode and a double junction  $\text{Ag}/\text{AgCl}$  that acted as a reference electrode.



**Figure 1.**

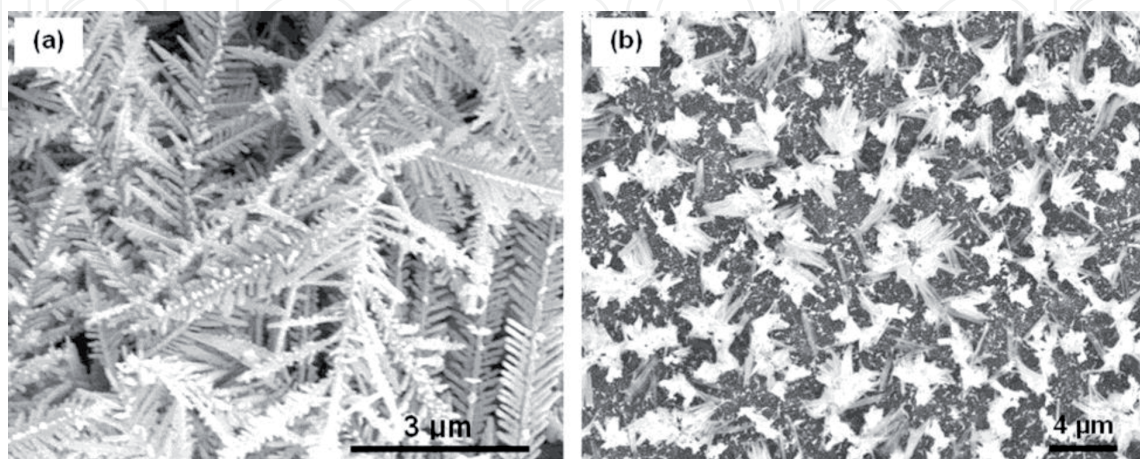
*Schematic of the galvanic cell consisting of Si immersed in HF and  $\text{AgNO}_3$  solution. A polytetrafluoroethylene (PTFE) beaker was used for the wet chemical etching of the silicon wafer.*

The external bias ( $V_{\text{ext}}$ ) of voltage  $\pm 1$  V with a slew rate of  $5 \text{ mV s}^{-1}$  was applied between the working photoelectrode and a reference electrode. The current range was set to  $\pm 20$  mA during the measurements. The study was carried out both in dark and under white light illumination of intensity ( $I_0$ )  $50 \text{ mW cm}^{-2}$ . The electrochemical impedance spectra (EIS) were carried out in a frequency range of 10 mHz to 25 kHz at a potential of 1 V under illumination. Electrical properties measurement of the working electrodes was carried out using the M-S investigation at a frequency of 1 kHz in the dark condition.

### 3. Results and discussion

In the metal assisted wet chemical etching method, Si substrate is immersed into the HF/AgNO<sub>3</sub>. It results in faster etching of Si from the Si-metal interface in the presence of HF solution. This results in the dissolution of Si underneath the metal ions resulting in the fabrication of semiconductor nanostructures in the form Si nanowires, which were found to be decorated with the tree branches-like Ag nanowires (dendrites) having branches, sub-branches and leaves like structures (**Figure 2**) [1]. The potential advantage of such type of nanostructures is that the surface-to-volume ratio of the nanostructures increases significantly as compared to the vertical standing nanostructures over the substrate. This facilitates the nucleation site for the hydrogen production and hence photocurrent (as can be seen in this study). These nanostructures have been used in the photoelectrochemical method for the water splitting applications. Thus, water splitting using photoelectrolysis can be used for the production of hydrogen, which is an alternate source of renewable and sustainable solar energy.

The prepared dendritic heteronanostructures were utilized for the PEC splitting of the natural water. In the water splitting, PEC cell was considered with a three electrode gathering where the dendritic heteronanostructures were utilized as working electrode (photoanode). During PEC measurement, potential has been recorded versus the Ag/AgCl reference electrode. Here, it is to be noted that the  $E_g$  of the Si nanostructures is of the order so as to cause both the PEC oxidation  $2\text{H}_2\text{O} + 4 \text{ h}^+ \rightarrow \text{O}_2 + 4\text{H}^+$  (working electrode and water interface) and reduction  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  (counter electrode and water interface) reactions during the water

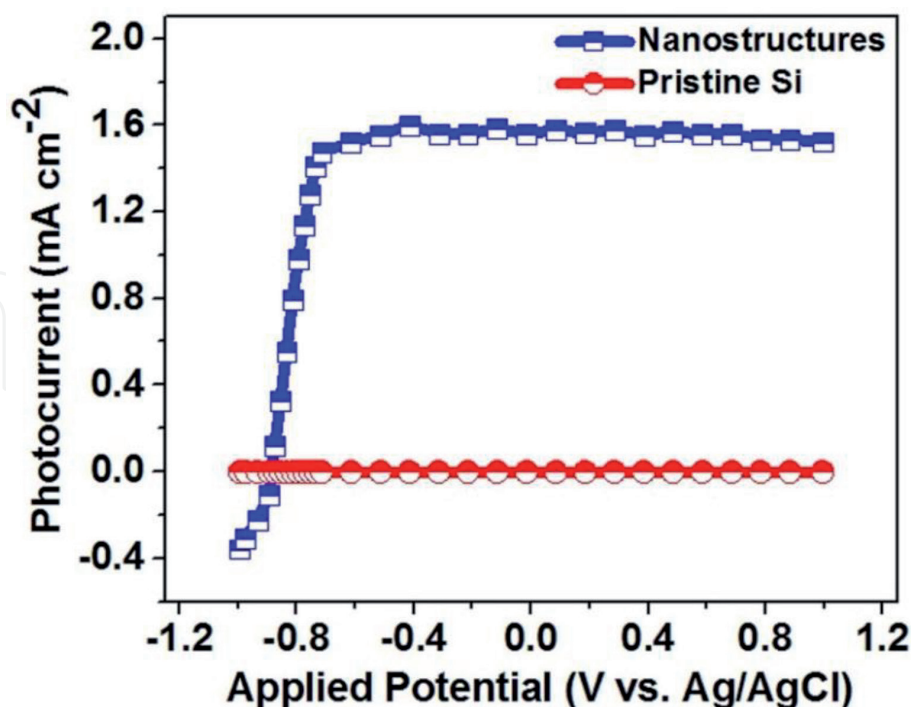


**Figure 2.** Field-emission scanning electron microscopy (FE-SEM) images of the tree branches-like silicon dendritic nanowires. The nanostructures are synthesized using the method metal assisted wet chemical etching of silicon wafer in an aqueous solution consisting of 5 molar (M) HF (49%): 0.02 M AgNO<sub>3</sub> (1:1 by volume). The etching is carried out for 30 minutes at room temperature. (Dadwal et al., DOI: 10.1016/j.ijhydene.2018.10.163) [1]. Reprinted with permission from Dadwal et al., (2018), Elsevier.

splitting [1, 3, 8]. When the  $V_{\text{ext}}$  is applied between the photoanode and the reference electrode, photogenerated holes from the silicon nanowires oxidize the water, which result in photocurrent as can be seen from **Figure 3** [1].

It has been observed that the onset voltage at which the working electrode (dendritic nanostructures) reveals sharp rise in the measured photocurrent density ( $J_p$ ) under illumination is about  $-1$  V. From the onset voltage,  $J_p$  rises to  $1.7 \text{ mA cm}^{-2}$  with the increase in  $V_{\text{ext}}$ . It has been further observed that the rise in  $J_p$  beyond these values is negligibly small and gets saturated with  $V_{\text{ext}}$ . The saturation photocurrent density ( $J_p^{\text{sat}}$ ) approximately  $1.7 \text{ mA cm}^{-2}$  for the dendritic heteronanostructures is quite large as compared to the pristine silicon sample (**Figure 3**). This measured difference in  $J_p$  and saturation photocurrent density can be ascribed to the statement that under enlightenment by the energy of the incident light greater than the band gap, photogenerated electrons are excited more to the conduction band from the valence band of Si nanowires [1]. Consequently, the overall water splitting rate depends more upon the experimental arrangements of the PEC work station and on the behavior of dendritic heteronanostructures as photoanodes in determining the optimum photocurrent density.

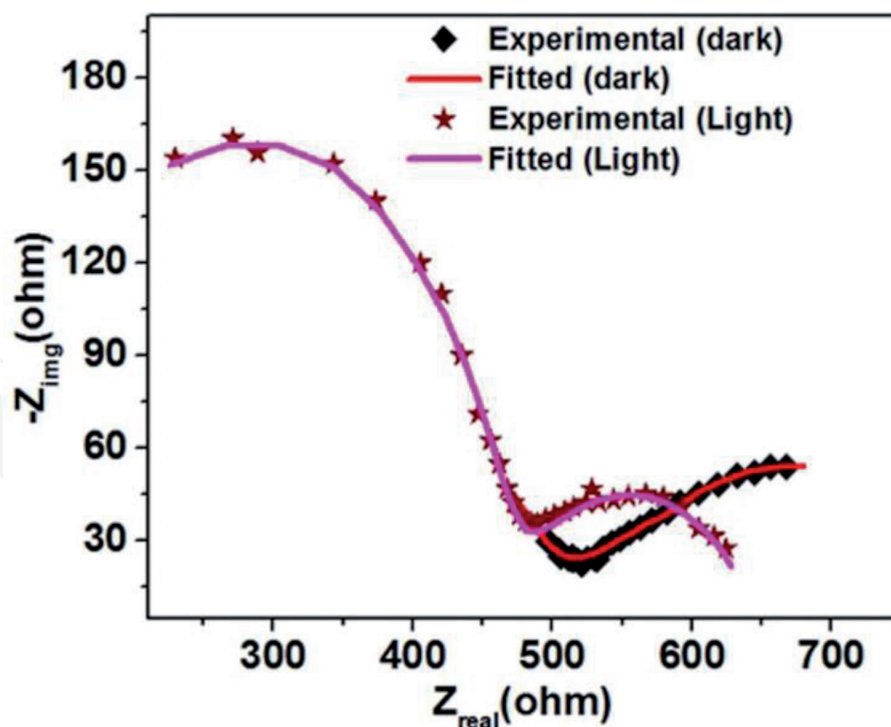
The dendritic heteronanostructures and water interface impedance was explored using the electrochemical impedance spectroscopy, which shows the impedance ( $Z$ ) of a PEC system through the frequency spectrum ( $Z_{\text{real}}$  versus  $Z_{\text{imag}}$ ) (see **Figure 4**) [1, 29, 30]. The potential of the photoanode (working electrode) with respect to the reference electrode Ag/AgCl has been fluctuating at 5 mV. A DC bias of 1 V was applied between the working electrode and counter electrode. The impedance spectra have been noted in the frequency choice from 10 mHz to 25 kHz under dark and illumination conditions. **Figure 4** shows that the Nyquist plot in the low frequency region is assigned to the charge transfer resistance ( $R_{\text{ct}}$ ) between the working electrode and water interface in the PEC water splitting [1, 31, 32].



**Figure 3.**

Photocurrent density as a function of applied potential under a white light enlightenment  $50 \text{ mW cm}^{-2}$ . The photocurrent was produced by the PEC solar water splitting using natural water as an electrolyte and dendritic heteronanostructures as working electrodes (photoanode). The experiment was performed using a PEC cell in a three electrode arrangement (Dadwal et al., DOI: 10.1016/j.ijhydene.2018.10.163) [1]. Reprinted with permission from Dadwal et al., (2018), Elsevier.





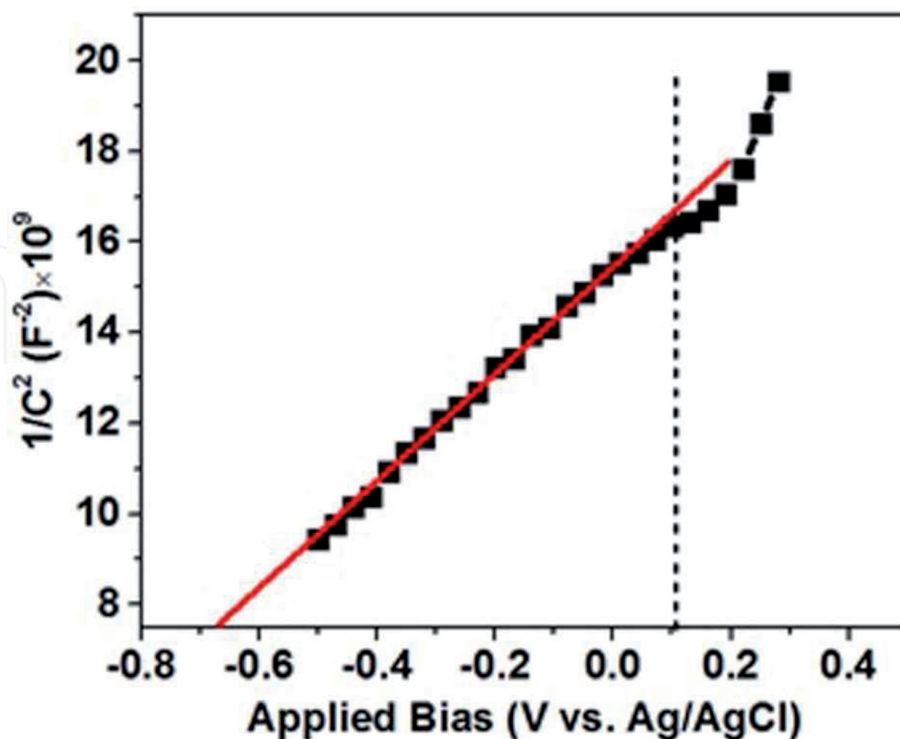
**Figure 4.** Impedance measurement of the dendritic heteronanostructures as working electrodes obtained by the electrochemical impedance spectroscopy. The measurement was performed together in the light absence and under the white light enlightenment using a PEC cell in a three electrode assembly (Dadwal et al., DOI: 10.1016/j.ijhydene.2018.10.163) [1]. Reprinted with permission from Dadwal et al., (2018), Elsevier.

Here,  $R_{ct}$  is the difference between the high frequency and low frequency intercepts with the  $x$ -axis on a Nyquist plot. The  $R_{ct}$  value of  $150\ \Omega$  was found to be decreased drastically under illumination [1]. As a consequence, the total impedance ( $|Z|$ ) of the system gets reduced. It is to be noted that the importance of  $|Z|$  is considerable lower as compared to the previously reported results for the case of substances for instance Au-TiO<sub>2</sub> nanocomposite and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [33]. This means that  $R_{ct}$  of the dendritic heteronanostructures surface is sufficiently low to boost the charge carrier allocation at the dendritic heteronanostructures surface in the presence of  $V_{ext}$ . Low  $R_{ct}$  value can be accredited to the Ag dendrites role in the charge carrier allocation at the Si nanowires (photoanode) and water interface. Ag dendritic nanostructures can sweep away the photoexcited carriers from the Si nanowires/water interface which thereby decrease the photogenerated electron hole recombination. It thus made available carrier electrons from the external circuit to reach the photocathode (counter electrode). This effectively carries out PEC reduction of the water at the counter electrode [1]. That is why, a major rise in the eventual photocurrent has been observed during the present PEC solar water splitting experiment.

Further insight to the dendritic heteronanostructures assisted PEC water splitting reaction can be obtained through Mott-Schottky analysis at a frequency of 1 kHz in the dark condition. Mott-Schottky allows determining the internal electrical properties of the photoanode together with the flat-band potential ( $V_{fb}$ ) and charge carrier concentration ( $N_D$ ). The investigation has been carried out by computing the space charge section capacitance ( $C_{SC}$ ) with external bias  $V_{ext}$ .  $C_{SC}$  procedures in the semiconductor near the photoanode and the water interface owing to equilibration of the chemical potential. Near the working electrode surface, for the  $n$ -type semiconductor, holes, locally come to be the majority carrier. In the presence of sufficient applied bias, deep depletion layer forms where the holes can counter with the hydroxyl ions in the water [36, 38]. Thus, at the onset



voltage, efficient hole reaction (PEC oxidization) enables resulting a major rise in  $J_p$ , as observed [1]. For the semiconductor and water interface,  $C_{SC}$  is determined by on the  $V_{fb}$  according to the equation as  $\frac{1}{C_{SC}^2} = \frac{2}{\epsilon\epsilon_0 N_D e A^2} \left( V_{ext} - V_{fb} - \frac{k_B T}{e} \right)$  [31–33]. Here,  $\epsilon$  is the dielectric constant of the silicon (11.7),  $\epsilon_0$  the permittivity of the free space,  $N_D$  represents semiconductor carrier or donor density,  $e$  denotes the fundamental charge,  $A$  denotes the effective surface area of the dendritic nanostructures for the PEC water splitting and  $k_B T$  is the thermal energy. Using the Mott-Schottky expression, a plot between the  $1/C_{SC}^2$  as a function of applied potential is shown in **Figure 5**. It showed that the slope of the graph is positive, indicating working electrode is  $n$ -type with electrons as the majority carriers. Further, from the slope of the straight line,  $N_D$  was calculated  $\sim 1 \times 10^{20} \text{ cm}^{-3}$  [1]. The existence of such a large carrier concentration endorses the role of metal (Ag nanostructures) which can reportedly act as a sink for the photogenerated carriers as well as donor dopants to subsequently increase the electron concentration. Ag dendrites donor dopants nature is due to the existence of Schottky barrier ( $\phi_b$ ) of  $\sim 0.2 \text{ eV}$  (Mott-Schottky rule) between the Ag dendrites/Si junction. This consequence in the realization of satisfactory band alignment for the photogenerated carrier separation and their transferal from the Si nanowires to Ag dendrites heterostructures. Owing to this, a large value of the  $N_D$  has been found from the Mott-Schottky measurement. Since the charge carrier density is governed by linearly with the conductance, hence, improvement in the charge carrier concentration resulted in lowering of the charge transfer resistance among the working electrode and water boundary. Furthermore, for a large carrier concentration, it has been described that the metal atoms sweep away the photo-generated carriers from the working electrode and electrolyte interface [1]. Thus, there exists a definite possibility to enhance the lifetime of charge carriers resulting reduction in the electron and hole recombination process. Thus, the increase in charge carrier concentration and reduction in the electron and hole recombination



**Figure 5.**

Mott-Schottky plot of the dendritic heteronanostructures as working electrode at the frequency of 1 kHz. Solid red colored line corresponds to the linear fit to the data. The measurement was carried out in the dark using a PEC cell in a three electrode configuration (Dadwal et al., DOI: 10.1016/j.ijhydene.2018.10.163) [1]. Reprinted with permission from Dadwal et al., (2018), Elsevier.

in the company of Ag dendrites at the near surface region of Si nanowires, are believed to be the main subsidizing factor for enhancing the photocurrent density. On the other hand, the value of  $V_{fb}$  was found about  $-0.7$  V and was acquired by extrapolating the interception of the straight line with the axis of the applied potential (**Figure 5**). It is to be noted that the  $V_{fb}$  is close to the onset potential which means that the photogenerated charge carrier separation efficiency is improved in the absence of band bending [1]. Such types of result have been also reported in the case of zinc oxide nanowire photoanodes with ultrathin Titania shells for the study of water splitting [34]. Thus, in this case, an improvement in the charge carrier separation can give a positive effect of increasing the carrier diffusion length and the eventual enhancement of the PEC water splitting.

In the PEC solar water splitting, the hydrogen gas evolution rate depends largely on the photocurrent density  $J_p$  and external bias  $V_{ext}$  between the photoanode with respect to the reference electrode. Thus, hydrogen gas evolution can be clearly observed from the Pt counter electrode. As the photogenerated current is given by the rate of change of the total charge ( $q$ ) per second, the total number of carrier electrons ( $n$ ) corresponding to the generated photocurrent, are calculated from the expression  $n_e = \frac{J_p t}{q}$  per unit area per second. Where,  $t$  is the illumination time in

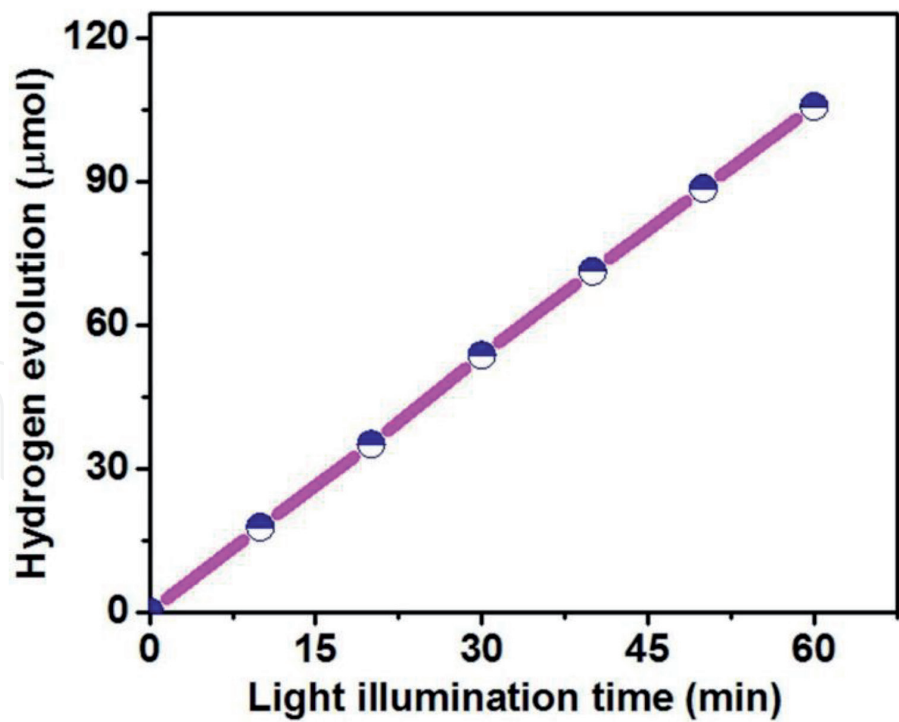
the PEC water splitting. Since in the PEC water reduction reaction ( $2H^+ + 2e^- \rightarrow H_2$ ), two electrons correspond to the one hydrogen gas molecule. Thus, the total number of the evolved hydrogen gas molecules ( $n_{H_2}$ ) can be found by dividing the above expression by two, that is,  $n_{H_2} = \frac{J_p t}{2q}$ . Results showed that at the onset

voltage  $J_p \sim 1.7 \text{ mA cm}^{-2}$ ,  $n_{H_2}$  value was found to be  $5.3 \times 10^{15}$  per unit area per second. The value of  $n_{H_2}$  increased to  $6.5 \times 10^{15}$  per unit area per second for the saturation photocurrent density  $J_p^{sat} \sim 1.7 \text{ mA cm}^{-2}$  under the illumination. In order to justify these results, hydrogen gas evolution as a function of illumination time has been analytically studied using the measured  $J_p$  (see **Figure 6**). The mole of the evolved hydrogen gas ( $N_{H_2}$ ) during the PEC solar water splitting was calculated from the Faraday's laws of electrolysis  $N_{H_2} = \frac{A}{2F} \int_0^t J_p dt$  [35]. Here,  $A = 3 \text{ cm}^2$  is the

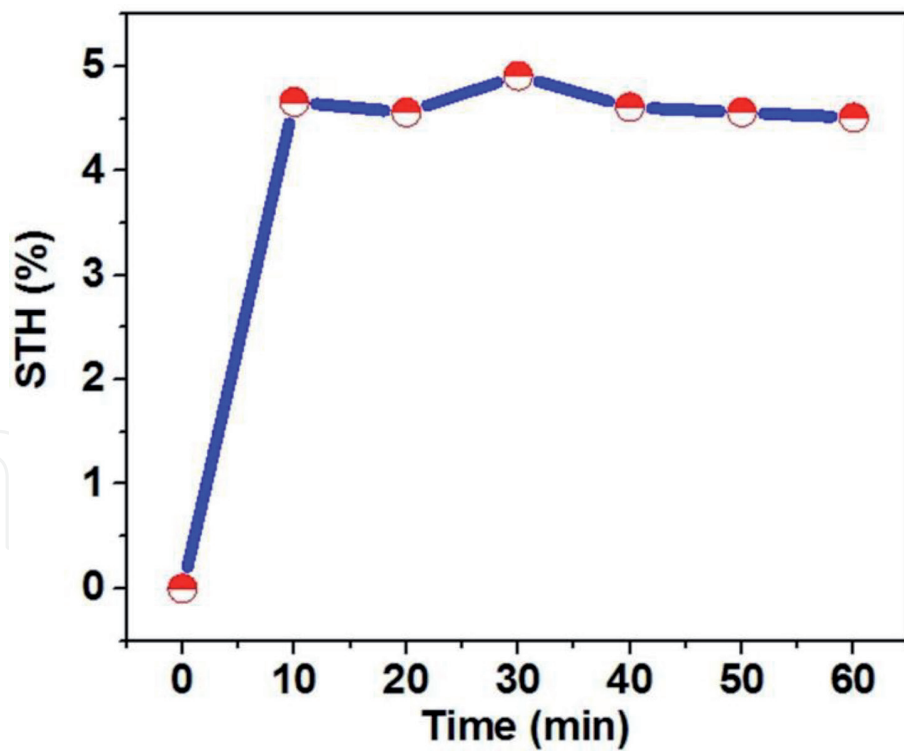
light receiving area and  $F = 96485 \text{ C/mole}$  represents the Faraday constant (charge in coulomb carried by one mole of electrons). The evolved hydrogen gas during the PEC solar water splitting was calculated for 1 h. It is noted that the calculated amount of the hydrogen gas shows nearly a linear behavior over the illumination time indicating the good constancy of the dendritic heteronanostructures as working electrodes in the water. An average evolution rate of the hydrogen gas was found to about  $1.7 \mu \text{ mol min}^{-1}$ . This generation rate is comparatively higher than the other semiconductor nanostructures that had been reportedly used as photoelectrodes for water splitting [14, 35–37].

The working electrode (photoanode) requires a  $V_{ext}$  versus the reference Ag/AgCl electrode in the presence of light illumination so as to derive the overall PEC solar water splitting reaction. The solar-to-hydrogen conversion efficiency (STH), defined as the quantity of the hydrogen gas evolved at the counter electrode under the light illumination with regard to the quantity of incident light photons and can be expressed as  $STH(\%) = \Delta G^\circ \left[ \frac{\{Hydrogen\ generation\ rate(moles^{-1})\}}{I_o \times Light\ receiving\ area(m^2)} \right] \times 100$  [36]. Here,

$\Delta G^\circ = 237 \text{ kJ mole}^{-1}$  is the Gibbs free energy stored in the hydrogen molecules. The value of STH was derived for the dendritic heteronanostructures using water as electrolyte under the white light enlightenment of  $I_o = 50 \text{ mW cm}^{-2}$  (**Figure 7**).



**Figure 6.** Hydrogen gas evolution as a function of the white light illumination time. The evolution was calculated from the measured photocurrent current density under a white light illumination of intensity  $50 \text{ mW cm}^{-2}$ .



**Figure 7.** Solar-to-hydrogen conversion efficiency (STH) of the dendritic heteronanostructures photoanodes as a function of applied bias. PEC solar water splitting was performed under a white light enlightenment of intensity  $50 \text{ mW cm}^{-2}$  using a PEC cell in a three electrode arrangement.

The maximum value of the STH  $\sim 4.5\%$  near the  $J_p^{sat} \sim 1.7 \text{ mA cm}^{-2}$  at  $V_{ext} = 0.4 \text{ V}$  was found to be quite higher as compared to the earlier reports [36, 38]. This indicates the vibrant impact of the dendritic heteronanostructures on the PEC

natural water splitting where the enhancement in STH is resulted from the rise in  $J_p$  owing to the lower value of  $R_{ct}$  between the photoanode and water boundary.

Thus, with the usage of silicon and lower cost metal assisted wet chemical etching method semiconductor dendritic nanostructures have been synthesized. The synthesized photoanode nanostructures are found to be suitable for the effective PEC splitting of natural water.

#### 4. Conclusion

Metal assisted wet chemical etching of silicon resulted in the synthesis of semiconductor dendritic heteronanostructures. In the PEC water splitting, these dendritic heteronanostructures as working electrode showed reasonably good solar-to-hydrogen conversion efficiency of 4.5%. Photocurrent density was found to be enhanced due to the availability of (a) additionally large surface area of such type of nanostructures for the light absorption and (b) the presence of silver dendrites which increase the charge carrier transfer by minimizing the carrier recombination process. Low charge transfer resistance of the working electrode and water boundary and the higher carrier concentration resulted in efficient PEC water splitting. Hydrogen gas evolution showed a negligible decrease with an average rate of  $\sim 1.7 \mu \text{ mol min}^{-1}$  over the light illumination time. This indicates the good stability of the dendritic heteronanostructures as working electrodes in natural water. The solar-to-hydrogen conversion efficiency was found to be about 4.5% indicating that synthesized dendrites nanostructures was working as an efficient working electrode for water splitting.

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