Techniques for investigation: Semiconductor/electrolyte interface processes in photoelectrochemical cell for solar water splitting

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Abstract: Photoelectrochemical water splitting process for solar hydrogen production has attained great consideration due to acceptance of hydrogen as a sustainable and environmentally friendly energy carrier. The key functional components of a PEC cell are the semiconductor electrode and semiconductor-electrolyte interfacial junction. The semiconductor-electrolyte interface, the other crucial functional unit of PEC cell is rarely investigated. The nature of the charge carrier's movement at the semiconductor/electrolyte interface is fundamental for the optimization of semiconductor electrode performance for efficient hydrogen generation. To understand the above processes at the interface, various techniques are being used to investigate the electrochemical reactions and photocatalytic response of a stable photoelectrode. In this review, the charge transfer kinetics and various methods used to investigate the e^-/h^+ transfer processes at the semiconductor/electrolyte interface are reviewed and discussed.

Key words: Techniques for investigating the processes occur at Semiconductor-Electrolyte Interface.

INTRODUCTION

In the search for a sustainable society which uses energy based on renewable solar energy, an efficient approach is needed to convert solar light into chemical fuel. Hydrogen is being considered as a favorable future fuel carrier on account of its high potential in terms of diversified supply and negligible emission of carbon and greenhouse gases. Photoelectrochemical water splitting reaction using solar light is the most convenient route for hydrogen production to fulfil the future energy requirements[1-8].The main functional units of PEC cell are the semiconducting materials and semiconductor-electrolyte interface junction shown in Fig.1.
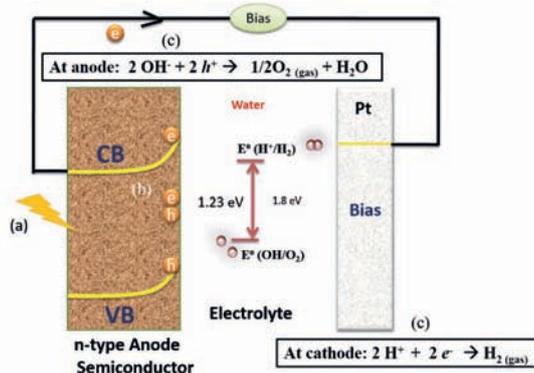

Fig. 1   Schematic illustration of PECwater splitting process with n-type semiconductor as photoanode under applied bias. The main processes involved are (a) light absorption (b) electron-hole pair separation and movement and (c) redox reactions on the corresponding surfaces.

A huge wealth of data is available in the development of efficient semiconducting materials by various modification strategies to improve the PEC response. The role of semiconductor/electrolyte interfacial junction in photoelectrochemical behavior of semiconducting materials is rarely analyzed. The nature of e^-/h^+ transferal processes at the semiconductor/electrolyte junction is fundamental to optimize the semiconductor electrode performance for efficient hydrogen generation.

TECHNIQUES / EXPERIMENTAL METHOD FOR INVESTIGATING THE INTERFACIAL PROCESSES OCCUR AT SEMICONDUCTOR/ELECTROLYTE JUNCTION

There is a wide number of experimental techniques have been used to analyze the interfacial process of semiconductor-electrolyte interface. Some of these methods are described below and summarized in Table 1.

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Table. 1. Experimental techniques to understand the interfacial processes of Semiconductor/Electrolyte junction:

Technique	Used for
Current-Voltage Curves	*provide anodic and cathodic behavior of semiconductor with band edges position estimation*
Electrochemical Impedance Spectroscopy : Bode plot/ Nyquist plot	*To study the kinetics of interfacial processes of photoelectrochemical cell such as charge transfer resistance.*
Mott- Schottky Analysis	*To study the interfacial properties such as flatband potential, donor density and space charge region width.*
Photocurrent Transients	*To study the rate of photogenerated charge transfer at semiconductor/electrolyte junction*

Optical Techniques:
  a) Photoluminescence
  b) Electroluminescence
  c) Transient and Time-Resolved Measurements
	Recombination processes and presence of surface state

Scanning Probe Methods:
  a) Scanning Electrochemical Microscopy
  b) Scanning Tunneling Microscopy
  c) Conducting Atomic forcemicroscopy (CAFM).
	To study the surface phenomena that affect the charge diffusion at the electrode surface and structural imperfections.

I-V Curves

Current-voltage plots obtained in three electrode photoelectrochemical cell are the basic characterization method of semiconductor/electrolyte interface, used to understand the interfacial e^-/h^+ transport. These curves provide a rough estimation of anodic and cathodic behavior of semiconductor with band-edge alignment positions and other processes such as stability, photo corrosion at the surface of semiconductor. Under illumination, higher current value than dark indicating the photogeneration of minority charge carriers under the illumination of the interface. I-V curves under illumination also give an idea of the kinetics of charge transfer and nature of the interface [9-10]. The current-potential curve also provides valuable information about open circuit potential. However, when no detailed models are accessible, I-V curves alone provide the qualitative information of the SE interface.

Electrochemical Impedance Spectroscopy (EIS): Bode plot/ Nyquist plot:

Electrochemical Impedance Spectroscopy (EIS) is responsive to charge accumulation and charge passage kinetics at the interface of semiconductor and electrolyte. EIS measurements of a sample are conducted for a large range of frequencies and the obtained spectrum is evaluated in the complex plane [11]. The real and imaginary parts of impedance are measured at different angular frequencies, and an equivalent circuit is suggested to investigate the physical nature of the elements on the basis of their dependence on external parameters such as voltage, temperature, and electrolytic solution. The frequency dependence of the EIS measurements is often attributed to the capacitance of the surface state present and space charge layer capacitance to measure the combined space charge/surface state/semiconducting material capacitance [12].

Diez-Garcia et al. (2016) developed a theoretical model based on the kinetic mechanism for thin calcium ferrite electrodes involved in water splitting. They concluded that direct transfer was taking place of the electrons from the conduction band to electrolytic solution and majority of the carrier recombination took place in the bulk of

the material. EIS helps us study the behaviour of photoelectrodes and find methods for improvements in their properties [13].

Bertoluzzi et al. (2012) discussed a model that explains the kinetics of charge carriers in a thin semiconductor film which is undergoing photoelectrochemical water splitting in order to differentiate between charge transfer processes and trap-assisted recombination. This could be used to understand the current potential curve during photogeneration. It is possible to identify the physical processes that contribute to limiting the current density at a low value of potential, lower e^-/h^+ pair separation and effective charge movement from the traps [14].

Impedance spectroscopy can be used to provide important parameters influencing photoelectrodes with a comparatively simple measurement. Klahr et al. (2012) performed impedance spectroscopy to figure out the mechanism of photocurrent production by varying the light intensity, potential bias and electrolyte pH for hematite photoelectrodes [15].

Trinh et al. (2014) conducted the study of the presence of adsorbate intermediates at the interface of semiconductor/ electrolytic solution. The complex differential capacitance was calculated by the synchronized measurement of the electrochemical impedance of competing absorbates. By assuming that the electrochemical mechanism observes Tafel kinetics and by applying the linearized currents, the impedance response can be calculated [16]. Wijayantha et al. (2011) characterized the electron transfer kinetics and recombination at the time of oxygen evolution at illuminated polycrystalline alpha-Fe_2O_3 electrodes. The rate constant for electron transfer has been observed to increase with the increase in potential. Therefore, the change in potential of the Helmholtz layer has an impact on the activation energy for the oxygen evolution reaction (OER). This complex potential dependence demonstrates the non-ideal nature of the alpha-Fe_2O_3 electrolyte interface due to the photogenerated surface species [17]. There are many reports that discuss the EIS in more detail [18-21].

Mott Schottky Analysis:

Semiconductor/electrolyte interface is electrically charged and has an associated interfacial capacitance due to the presence of ions on the liquid side and e-/h+ towards semiconductor. The width of the space charge region is more towards semiconducting material than that of electrolyte resulting in the difference or generation of the electrostatic potential at the semiconductor/electrolyte interface. Presence of any surface states at the semiconductor surface also leads to the difference in the applied potential and interfacial capacitance across the space-charge region. The difference in the electric potential between electrode surface (flatband) and electrode bulk resulting into the band bending and capacitance of space charge region. The magnitude of band bending tells about the electronic properties of surfaces and provide the estimations about the energy levels of the semiconductor/electrolyte junction. The interface capacitance and potential variation across the space charge region follows the Mott-Schottky equation given below [22-23]:

$$\frac{1}{C2} = \left(\frac{2}{q \in_s \in_o NA^2} \right) \left(V_{app} - V_{fb} - \frac{kT}{q} \right)$$

Here q is the charge, Vapp is the applied potential and Vfb is the flat band potential, N is the donor density, s is the dielectric constant of material, q is electronic charge, k is Boltzmann constant, is the permittivity of free space, and k is Boltzmann constant. According to the Mott-Schottky relation, the measurement of interface differential capacitance and it's linear plot vs applied potential offer the determination of (i) donor and acceptor concentrations in semiconductor from the slope of this linear plot (ii) valuation of flat-band potential from extrapolation of the linear plot of $1/C^2$ vs applied potential, the extensively used analysis in the presence both dark and light conditions. These plots of capacitance and potential have been obtained by different models of electrochemical impedance spectroscopy by Mantia et al (2010), Hankin et al (2019), Gelderman et al 2007 [24-26].

In addition to this Mott Schottkyanalysis is useful in many other applications. Albery et al. (1996) [27] showed that the curved part analysis of Mott-Schottky plots can provide the potential distribution at the semiconductor/electrolyte interface. Adan-Mas et. al. 2017 [28] suggested that the Mott-Schottky model also useful in the correct selection of potential values to carry out the EIS measurements. In Gelderman et al. 2007 [26], used polycrystalline ZnO electrode, exposed the many crystal planes and suggesting that different Vfb values were obtained on account of different conductivity values along different crystallographic planes.

There have been found some deviations in the linear Mott-Schottky behaviour due to the complex nature of the nanostructured semiconductor and water interface.

Pareek et. al. 2014[29] observed the deviation in the flat-band potential with applied frequency and electrolytic pH values. An increase in applied frequency reduces the flat band potential showing the dependence of the frequency of capacitance at higher frequencies. The pH of the solution affects the redox potential and thus the flat band potential. Mantia et al. 2010 explained the frequency dependence of the capacitance. This is seen in Mott–Schottky plots which affect donor density and flat band potential. In the low band bending region, the slope is constant for all frequencies but the effect of frequency increases with increasing potential [24].

Cen et. al. 2016 showed a non-linear Mott-Schottky plot for non-uniform donor density distribution with decreasing slope towards higher potential[30].

Transient photocurrent spectroscopy

Transient photocurrent measurements are performed by passing a current through a sample illuminated by white light. At the electrode, pulses of coloured light perturbations are passed. The light source is modulated periodically while the current through the system is observed. The transient delays are fitted to models and time constants determined. Dumortier et al. developed a model for transient current measurements in TiO_2 photoanode and Pt cathode [31]. They found two different pathways for the cell reaction by numerical modelling and transient phenomena. There was the charging of surface states and the transfer process of H+ ions at the TiO_2/Na ion interface.

Using transient photocurrent measurements, possible decay mechanisms of the photoelectrode can be determined by observing the recombination rate of photogenerated e^-/h^+ in the semiconductor. Thus, photoelectrodes cab be characterised, especially the charge accumulation at the SEI. This was done by Le Formal et al. in their investigation of photocurrent transient behaviour of α-Fe_2O_3 photoanodes [32]. Ngami et al. investigated the charge transfer process at the semiconductor electrolyte interface of TiO_2 electrodes. They found that the oxidation of specifically absorbed OH^- ions is causing the transients. This can give insights into electrode kinetics [33].

Laskowski et. al. studied catalysed photoanodes and concluded that the photocurrent transients are influenced by the presence of surface state and their formation or other presence other catalytic activity [34].

Optical Techniques Specific to Semiconductors

The generation of charge carriers at the semiconductor under illumination condition and their effect and movement towards the semiconductor/electrolyte interface has led to the formation of new techniques to study the photo effects at semiconductors. Some of the more relevant techniques are: a) Photoluminescence b) Electroluminescence c) Time resolved and transient measurements, and d) Transient absorption spectroscopy

Photoluminescence:

"Photoluminescence is the emission of light which is caused by the irradiation of a substance with external light. In particular, PL spectra and their intensity dependencies can be used":

- "to determine the band gap energy and/or the wavelength of maximum gain

- to determine the composition of ternary or quaternary layers
- to determine impurity levels (which can e.g. lead to the emission of light with longer wavelengths than otherwise possible)
- to investigate recombination mechanisms"

Photogenerated charge carriers at semiconductor/electrolyte interface yield photoluminescence (PL) by radiative recombination. It is a competitive process with the photocurrent generation and allows us to study the photo effects at semiconductor surface. Several researchers have studied the photoluminescence of the energy research materials on their surface modifications in accord with the "dead-layer" model given by Smandek et al. 1989 [35].

Ellis et al. 1983 studied the energetics of n, p type GaAs/electrolyte interface to calculate the width of space charge layer and capture velocity of surface minority charge carriers [36]. Po-Yen Kunget al. 2015 [37] utilized the organic pigments photo-sensitizersand produce down-conversion photoluminescence spectra to excite Surface plasma response of silver nanoparticles.

Electroluminescence

"Electroluminescence (EL) is an optical phenomenon and electrical phenomenon in which a material emits light in response to the passage of an electric current or to a strong electric field". In this phenomena e^-/h^+ pair recombine from semiconductor and donor and acceptor present in the electrolyte under externally applied potential and release energy in the form of photons. This technique is more complex and specific to materials or systems than photoluminescence. Electroluminescence (EL) spectrum are more often recovered in conjunction with photoluminescence. Ouyang, J. et al. 1989 observed the identical PL and EL peaks for Mn-doped ZnS indicating the same luminescent center and shift in EL peaks with other dopants indicating the specificity for each material [38]. A Krier et. al. 2000 shown the In As electroluminescence spectra of InAsSbP/InAs interface, results indicated the staggered type alignment at the interface [39].

Time-resolved and transient measurements

Pulsed/chopped illumination and transient measurements of photocurrent and luminescence spectra is an advanced technique to understand in depth the interfacial charge transport. Willig et al. recorded the transients photoluminescence spectra of n-SnS_2 modified with Dye and investigate the transfer rate of electron towards the conduction band [40].

Transient absorption spectroscopy

TAS is the advanced technique based on pump-probe in which transient absorption in visible/or near IR region using pulsed laser source are measured to study the basic processes of photoelectrochemical water splitting reaction such as trapping, transport, and lifetime of photogenerated electron/holes (charge carriers) pairs in semiconductors [41-42]. The change in intensity of the transient absorption signal provides the kinetics of charge carriers under light condition. Moreover, this technique can also use to study the position of trapped electron and holes at surface and or bulk. In situ TAS measurement during photoelectrochemical water splitting reaction allows the direct determination of photoexcited charge carrier kinetics in the semiconductor. At Microsecond scale TAS transient measurements are carried out using a laser flash photolysis (LFP)spectrometer and nanosecond laser pump and flash lamp probe [43-44]. Charge transfer process and their kinetics study at the n-type semiconductor/electrolyte interface for water oxidation process has been investigated using µs –TAS by R. Qian et al. 2019 and M. Lorenc et al. 2002 [45-46]. M. Barroso et al. 2013 recorded the µs –TAS spectra of Fe_2O_3 and indicated the presence of potential dependency irrespective the fabrication technique [47]. Furthermore, pico and femtoseconds transient absorption spectroscopy measurements can be used to study ultrafast kinetics of interfacial charges of semiconductor/electrolyte junction. I. Grigioni et al 2018 demonstrated that direct detection of photogenerated electrons in the semiconductor by using mid-infrared (IR) probes is possible. They have also

demonstrated the lifetime for photo-excited electron in pristine WO_3 and $BiVO_4$ semiconductor and observed longer lifetime for photoexcited electrons in WO_3 than in $BiVO_4$[48].

Scanning Probe Methods

The emergence of scanning probe techniques such as scanning tunnelling microscopy (STM), Scanning Electrochemical Microscopy and atomic force microscopy (AFM) in the recent years received attention on account of their capability of exploring the atomic structure of the semiconductor surface and presence of other redox species. A large number of surface states can drastically modify the behaviour of the semiconductor/electrolyte interface by pinning the Fermi level. Moreover, the band bending which takes place at a semiconductor-electrolyte interface makes it sensitive to the presence of light. These scanning probe techniques can be used to explore the atomic structure of the semiconductor surface and adsorbed layers at the interface.

Scanning Tunneling Microscopy (STM)

Scanning tunneling microscopy (STM) by Binnig and Rohrer is an emerging technique for investigating the semiconductor/electrolyte interface properties. In this probe tip scanned across the surface, which generates a small current between tip and surface through "tunneling" process and imaging surface at the atomic level. Besides the imaging at the atomic level, this technique has the potential to investigate the electrochemistry of the semiconductor/electrolyte interface. STM applications for investigating the semiconductor/electrolyte interfaces are mainly of two types a) in situ monitoring of changes occur at the material surface due to in contact with the electrolyte and b) determination of the kinetics of interfacial energetics at semiconductor/electrolyte interface. Bard et al. 1987 etched the nanometer scale features of GaAs surface immersed in solution under illumination condition by moving the tip across the surface [49]. Thundat et al. 1990 demonstrated topographical changes at the surfaces occurred due to electrochemical reactions by scanning tunnelling microscopy under uniform potential. Combining STM topographs with other probe techniques provide useful information. The STM tip was used to make localized structures by utilizing photoelectrodeposition and photocorrosion. These results suggest promising applications in lithography [50].

Scanning Electrochemical Microscopy (SECM)

Scanning electrochemical microscopy was developed by Bard and his co-workers. It is a high- resolution electrochemical scanning probe technique [51]. The probe is a pipette with two channels for the electrodes in electrolytic solutions. A meniscus is formed at the tip of the pipette due to the electrolyte. The probe undergoes small oscillations perpendicular to the substrate, creating an ac current caused by the change in the dimensions of the electrolyte contact and dc current. The pipette geometry significantly controls the dc conductance current, measured by microscopy.

In SECM, mass transport to the substrate surface occurs through diffusion. If the analyte is charged, changing the potential difference between the electrodes is used to manipulate the ion migration. The movement of the analytes to the semiconductor electrolyte interface can be controlled precisely. Therefore, SECM can be used to study fast heterogeneous electron transfer kinetics. Bard's group used this microscopy technique to study the SEI energetics of GaAs. They investigated the differences between n-type GaAs and p-type GaAs and looked at the valence band energy closely. Zhang et al. (2016) also investigated the interfacial charge kinetics while in feedback mode to be able to develop a simulation for oxygen evolution in photoelectrochemical cells [52]. Snowden et al. (2012) used FEM modelling to quantitatively study surface kinetics and mass transport using SECM by measuring the conductance and working electrode current simultaneously [53]. Kinetic measurements in the scale of interface dimensions and high-resolution voltammetric imaging can be performed as well. The simulations helped to understand the role of migration and diffusion.

Ma et al. (2019) used a scanning electrochemical microscope to study water oxidation of Au-modified hematite. The probe used was made up of optical fibre to radiate the photoanode with visible light. Characterisation techniques, X-ray photoelectron spectroscopy and scanning electron microscopy, were used to study Au-modified and unaltered hematite samples. In the Au modified hematite, Au metallic nanoparticles were embedded in the hematite structure [54]. Zhang et al. (2018) reviewed the development of SECM and the principles it worked on. He discussed recent advances such as interfacial reaction kinetics and screening of photoelectrodes and photocatalysts. The quantisation of intermediates during the reaction was used to judge the effectiveness of catalysts and develop novel composite photoanodes and high-efficiency devices. [55].

Atomic force microscopy (AFM)

Photoconductive atomic force microscopy (pc-AFM) is used for characterisation of structural and optoelectronic properties with nanoscale resolution. Photocurrent maps of pc-AFM provide information about properties across the film and give insight into the charge transport mechanism. Eichhorn et al. 2018 applied pc-AFM for optoelectronic properties in nanostructured $BiVO_4$ thin-film and analysed its charge-transport limitations. The current distribution was observed to be non-uniform across the film with a higher photocurrent at facet boundaries and planes and lower photocurrent at the grain boundaries. The understanding of interaction at nanoscale dimensions is essential to know the charge carriers transfer from heterogeneous photoelectrode [56].

Potential-sensing electrochemical atomic force microscopy (PS-EC-AFM) is utilised to probe the electronic and interface properties of electrochemical systems. Contact-based PS-EC-AFM directly measures the electrochemical surface potential while the electrochemical system is in operation. Laskowski et al. 2020 used this technique to quantitatively assess the surface voltage of metal-oxyhydroxide catalyst films on metal-oxide photoelectrodes. PS-EC-AFM spatially resolves the electronic properties of semiconductor electrode interfaces at nanoscale [57].

In this technique, a conductive tip attached to an electrically insulated cantilever is in direct contact with the sample film. Force feedback is utilised for the management of tip–substrate interactions by observing cantilever deflections for stable electrical connection between substrate and the AFM nanoelectrode tip. The advantage of a small tip being in contact with the electrolyte is that capacitive and surface electrochemical processes are minimized. Is it is assumed that the Fermi levels of the tip and catalyst coincide so that the surface of the catalyst can be probed. Photoelectrochemical water splitting reaction is caused by the accumulation or depletion of charge carriers at the surface of the semiconductor and interfacial electrochemical potential gradients lead to charge transfer. The nanoscale conducting tip of the cantilever senses the surface electrochemical potential of electrocatalysts. Liu et al. 2019 studied morphology and mechanical adhesive properties upper-layer using AFM to understand the component's roles at the nanoscale. It was possible to visualise all the nanoparticles of oxide overlayer present over $BiVO_4$ surface. Surface structural properties of the sample can be deduced by using the topography images with adhesion maps [58].

SUMMARY

In summary, the understating of semiconductor/electrolyte interface of photoelectrochemical water splitting process is reliant on the advancement of the experimental techniques. Powerful potentiometric and microscopic techniques are being developed to understand the in-depth charge carrier kinetics at the interface of the PEC cell. These techniques play an important role to apprehend the numerous reactions at the semiconductor/electrolyte interface affects the efficiency of the PEC cell such as charge transport, recombination rate, and photocorrosion and photovoltage generation. However, none of the single technique can provide a complete understanding of the mechanistic aspects of the semiconductor/electrolyte interface. Thus, a combination of these techniques can be an effective and powerful tool to understand and develop new vital knowledge of the interfacial process of the PEC water splitting reaction.

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