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Synchronization of charge carrier separation by tailoring the interface of Si–Au–TiO_2 heterostructures via click chemistry for PEC water splitting

Dilip Kumar Behara [a], Gyan Prakash Sharma [a], Arun Prakash Upadhyay [a], Maurya Gyanprakash [a], Raj Ganesh S Pala [a,b,*], Sri Sivakumar [a,b,c,*]

[a] Department of Chemical Engineering, Indian Institute of Technology Kanpur, India
[b] Material Science Programme, Indian Institute of Technology Kanpur, India
[c] Centre for Environmental Science & Engineering, Thematic Unit of Excellence on Soft Nanofabrication, Indian Institute of Technology Kanpur, India

HIGHLIGHTS

- Versatile technique to devise Si–Au–TiO_2 heterostructure for PEC water splitting.
- Capitalizing energized photo electrons of Si and preventing surface oxide formation.
- Synchronized charge carrier transport to overcome electron–hole recombination.
- Achieved photo-conversion efficiency (ABPE) of ~0.4% at 0.9 V applied bias.

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ABSTRACT

Electrochemical potential gradients that are established due to appropriate band edge alignment in heterostructures can synchronize the movement of electron and hole in opposite direction. Such synchronization is critical for efficient photoelectrochemical devices and can be achieved by tailoring the interface of heterostructures. To this end, we fabricate a tailored interface of Si–Au–TiO_2 heterostructure over stainless steel ((Si–Au–TiO_2)/SS) for effective charge carrier separation. The fabricated electrode possesses the following tailored interfaces to enhance the charge-carrier separation/transport: 1) gold nanoparticles form interface (sandwiched) with Si as well as TiO_2; 2) Si, Au, and TiO_2 form the interface with SS, 3) Si–TiO_2, and Si–Au interface facilitates the quenching of h^+ generated in Si (via electron transfer from TiO_2 and Au to Si) which facilitates electron transport to counter electrode for hydrogen generation, and 4) TiO_2 forms the interface with the electrolyte solution to facilitate hole transport. Photoelectrochemical (PEC) measurements of (Si–Au–TiO_2)/SS heterostructure exhibits higher performance compared to other heterostructures ((Au–Si)/SS, (Au–TiO_2)/SS, (Si–TiO_2)/SS, TiO_2/Au/Si/SS, and Si/Au/TiO_2/SS), substantiating the importance of synchronized charge transport in PEC systems. Further, electrochemical impedance spectroscopy (EIS) studies also support the synchronized charge transport in the tailored heterostructure ((Si–Au–TiO_2)/SS) compared to control samples. The calculated applied bias to photo-conversion efficiency (ABPE) of ~0.4%@~0.9 V applied bias, intrinsic solar to chemical conversion efficiency (ISTC) of ~0.085 (or 8.5%) @1.66 V vs. RHE and electrical and solar power-to-hydrogen (ESPH) conversion efficiency of ~3.3%@~1.0 V applied bias.

1. Introduction

Charge carrier separation is one of the main factors in determining the performance of photoelectrochemical (PEC) water splitting systems (Abdi et al., 2013) and is limited by bulk and surface charge recombination rate. Several reports attempt to enhance the charge-carrier separation through the fabrication of heterostructures, (Qu et al., 2013; Wang et al., 2014; Zhu and Lian, 2012) in which the interface facilitate the charge-carrier separation (Linic et al., 2011). Charge-carrier separation can be promoted if the interfaces are tailored to facilitate the charge-transport with lesser energy barriers (Chen et al., 2007; Kargar et al., 2013; Zhang et al., 2009). In addition, tailored interfaces extract existing

* Corresponding authors at: Department of Chemical Engineering, Indian Institute of Technology Kanpur, India.
E-mail addresses: rpala@iitk.ac.in (R.G. Pala), srisiva@iitk.ac.in (S. Sivakumar).

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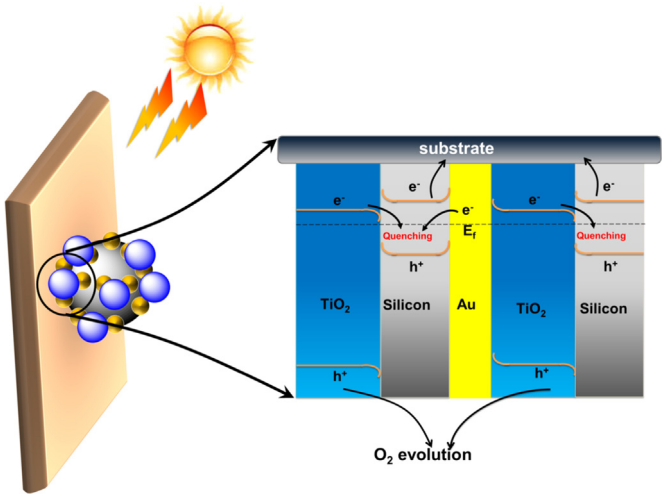
electric-field strength/or flux across the interface (~several million volts/cm) (Bard, 2001) and help to transfer/translate the fluxes of precursor/electrolyte to the electrode (Myung et al., 2011). This interfacial electric field may synchronize the charge carrier movement in opposite directions, which is essential for PEC devices. Therefore, it is useful to develop nanostructures with tailored interfaces which are stable for longer term operation without changes in their molecular configurations during charge transfer process.

Systematic organization or integration of nanoparticles can form tailored interfaces. However, existing approaches such as vapor-deposition techniques (Abdi et al., 2013; Coridan et al., 2014; Shaner et al., 2014), spin-coating (Su et al., 2011), electrospraying (Park et al., 2013), self-assembly (Gao et al., 2013), and electrochemical (Kleiman-Shwarsctein et al., 2008)/electroless (Oh et al., 2011) techniques are challenging to fabricate multi-nanostructures with tailored interfaces, as they are not binding specific. In addition, they may not be stable due to their weak van der waals/hydrogen bonding/non-specific electrostatic interaction at the interface (and with the substrate). To overcome these limitations, we utilise "click chemistry" as a tool to form highly stable tailored/specific interfaces between nanostructure assemblies to facilitate synchronized charge transport for longer time (Upadhyay et al., 2013). Silicon, an earth abundant semiconductor is a potential material for water splitting reaction due to its low optical band gap (E_g~1.1 eV) which helps in absorbing visible fraction of solar light and has been used in "tandem" configuration wherein Si is present both in the photocathode and photoanode (Boettcher et al., 2011). However, its use is limited in PEC water splitting reaction due to 1) band gap $<$1.23 eV, which is the minimum thermodynamic driving force required for water splitting and hence, Si cannot drive water splitting if used in the photoanode, 2) unsuitable band edge positions w.r.t redox levels of water, 3) formation of insulating surface oxide layer (silica) which prevents the electron transport, and 4) photocorrosion problem as the photo generated holes will oxidise itself due to slow charge transport across the material interface. These limitations restrict utilization of Si either combination with other electro/photoactive materials (tandem cell or heterostructures) (Reece et al., 2011) or with a suitable protecting layer for water splitting reaction (Kenney et al., 2013; Sun et al., 2015; Nielander et al., 2013). Therefore, there is a large thrust to improve charge carrier separation and transport problem of Si semiconductor for efficient utilization in solar energy conversion applications. Herein, we fabricate Si–Au–TiO_2 heterostructure over stainless steel (SS) substrate via click chemistry. Stainless steel (SS) is chosen as conducting substrate for electro/photoelectrochemical applications as it is cheaper and good conducting electrode under alkaline conditions (Benck et al., 2014).

The rationale behind choosing these materials for heterostructure is as follows: n-Si forms Type-II heterostructure with n-TiO_2 as per band alignments, thereby facilitating charge transfer (by quenching the photo generated holes in Si) with the Si–TiO_2 heterostructure geometry (Maiolo et al., 2007; Behara et al., 2015). The following tailored interfaces of the fabricated electrode will enhance the charge-carrier separation/transport: 1) gold nanoparticles are sandwiched between Si and TiO_2 for quenching the energised holes of Si; 2) all the three materials (i.e. Si, Au, and TiO_2) form the interface with SS facilitating the electron transport to the counter electrode; 3) Si–TiO_2 and Si–Au interfaces facilitate the quenching of h^+ generated in Si (electron transfer from TiO_2 →Si and Au→Si) which enables electron transport to counter electrode for hydrogen generation, and lastly 4) hole transport is facilitated by TiO_2 which forms an interface with the electrolyte solution. Overall, the energized electron from Si and hole from TiO_2 were effectively used for hydrogen evolution reaction and oxygen evolution reactions respectively (Scheme 1). Therefore, the proposed methodology is effective for utilizing Si in photoelectrochemical water splitting in two ways: 1) Enhanced capture of majority charge carriers (e^-) for hydrogen evolution reaction, 2) the minimization of surface oxide layer due to more coverage of alkyne groups on surface anchored via click chemistry.



Scheme 1. Proposed charge carrier transfer mechanism of Si–Au–TiO_2 heterostructure for photoelectrochemical (PEC) water splitting reaction.

Photoelectrochemical measurements of these heterostructures yield an applied bias to photo-conversion efficiency or applied bias photon to current conversion efficiency (ABPE) of ~0.4% for Si–Au–TiO_2 in comparison to 0.31%, 0.27%, and 0.11% for Au–TiO_2, Au–Si, and Si–TiO_2 heterostructures, respectively. Further, the intrinsic solar to chemical i.e. ISTC efficiency of ~0.085 (or 8.5%) at 1.66 V vs. RHE potential under light illumination is observed for Si–Au–TiO_2 heterostructures. We note that ABPE and ISTC efficiencies are mainly based on the photocurrent and total power input from solar light (Hodes, 2012). In order to evaluate the PEC cell performance based on the total current density observed, we have included the contribution of externally supplied energy along with solar light energy to the total power input and proposed a new efficiency as "electrical and solar power to hydrogen conversion (ESPH)". The calculated ESPH for Si–Au–TiO_2 heterostructure is found to be ~3.3% and 12.24% at 1.0 V and 1.56 V applied bias respectively. Further, to prove the versatility of the approach, we have extended the fabrication of Si–Au–TiO_2 heterostructure over ITO and silicon wafer substrates.

2. Experimental section

2.1. Materials and methods

Titanium iso-propoxide (97%), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC.HCl, 98.0%), 4-pentynoic acid (95.0%), 3-bromopropyltrichlorosilane (96.0%), 3-chloro-1-propanethiol (98.0%), 1,8-nonadiyne (98.0%), 3-aminopropyltriethoxysilane (APTES, 98.0%) were purchased from Sigma Aldrich and used without further purification. Trisodium citrate and thiourea were purchased from Fisher Scientific and used without any further purification. Sodium borohydride (95.0%), copper sulfate pentahydrate ($CuSO_4.5H_2O$, 95.0%), ascorbic acid, dichloromethane (DCM, 99.5%), dimethyl sulfoxide (DMSO, 99.5%), toluene, methanol, acetonitrile, tetrahydrofuran (THF, 99.5%), hydrogen peroxide (H_2O_2), sulfuric acid (98%), and absolute ethanol were purchased from Merck's chemicals. Silicon wafers (n-type) were purchased from Sigma Aldrich. Sodium azide (NaN_3), chloroauric acid ($HAuCl_4.xH_2O$), and hydrofluoric acid (HF) were purchased from