A polarized liquid–liquid interface meets visible light-driven catalytic water oxidation†

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Bismuth vanadate (BiVO4) is one of the most interesting visible-light-driven photocatalysts for water oxidation, because it has a suitable position of the valence band (VB) edge at ca. 2.4 eV vs. RHE, a sufficiently narrow bandgap for visible light absorption, is stable, abundant and of low cost. However, it suffers from poor charge transport properties causing excessive electron–hole recombination.13–17 Furthermore, the hole transfer kinetics for WOR is sluggish.14 One direction for further improvement is size and shape control in order to facilitate the collection and separation of electron–hole pairs at the semiconductor/solution interfaces.14

Our approach herein is the use of hyperbranched BiVO4, at a chemically polarized ITIES for enhancing the rate of photo-catalytic WOR (Fig. 1). The nanoscale branches minimize the charge carrier diffusion length to the interface where they are converted before recombining. This is further supported by [Co(bpy)3](PF6)3 as an electron-acceptor in the organic phase. By efficient relaying of the photo-excited electrons from BiVO4 to the electron acceptor the electron/hole pair separation is facilitated after photoexcitation in BiVO4. This function is analogous to that of the electron transport chain between photosystems I and II.1 Interestingly, the driving force for electron transfer to [Co(bpy)3]3+ can be controlled easily by changing the polarization of the ITIES, which then clearly influences the efficiency of electron transfer from water to photogenerated holes (yielding O2).

In the present work, the interfacial photo-induced electron transfer (ET) reaction is studied by means of scanning electrochemical microscopy (SECM), which has quickly become an important tool for probing rapid processes at ITIES, including ET,19–22 ion transfer,23–26 and molecular transfer27 with high sensitivity. SECM is used here for recording the scavenging of photoelectrons by reduction of [Co(bpy)3]3+ at the BiVO4/butyronitrile interface. The SECM microelectrode (ME) oxidizes the resulting [Co(bpy)3]2+. Finally, WOR by photo-generated holes of BiVO4 at the chemically polarized ITIES is followed by online detection of O2 while the cell is irradiated using visible light (λ > 420 nm).

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cc04275a

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11382 | Chem. Commun., 2016, 52, 11382–11385

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The composition of the cell with the ITIES is schematically shown in Fig. 1A. Tetrabutylammonium chloride (TBACl) and tetrabutylammonium hexafluorophosphate (TBAPF6) are the supporting electrolytes in water and butyronitrile phases, respectively. Tetrabutylammonium (TBA+) is highly hydrophobic and acts as a common ion which induces the specific potential difference across the interface according to the Nernst–Donnan equation. 23–28

The BiVO4 nanocrystals are initially well-dispersed in the aqueous phase. The ITIES polarized immediately by ion-transfer and then BiVO4 nanocrystals are driven electrostatically to the interface. The synthesized BiVO4 nanocrystals resemble the shape of trunks with nano-scaled branches (so-called hyper-branched structure). Detailed data on the synthesis and characterization of BiVO4 and [Co(bpy)3]2+/3+ are provided in the ESL.†

Photoinduced ET from nanocrystalline BiVO4 to [Co(bpy)3]3+ is investigated using SCEM. A Au ME with radius rT = 12.5 μm is placed in the upper, organic phase at a distance d = 20 μm to the ITIES at a potential E0 = +0.5 V (vs Ag quasi-reference electrode (AgQRE)). The butyronitrile phase contained 0.5 mM [Co(bpy)3](PF6)3 and 0.05 M TBAPF6, and the aqueous phase contained 0.1 M NaCl and 0.01 M TBACl.

Clearly, band-gap illumination of the interface leads to interfacial ET to [Co(bpy)3]3+ in the organic phase. The generated photoinduced electron–hole pairs with quasi-Fermi levels approach the energy levels of the conduction band (CB) and valence band (VB) of BiVO4. The CB energy of BiVO4 is +0.02 V 29 and the redox potential of [Co(bpy)3]3+ in butyronitrile is +0.34 V vs. RHE. Therefore, heterogeneous ET of CB electrons from BiVO4 to [Co(bpy)3]3+ appears thermodynamically feasible.

The driving force of the interfacial photo-induced ET reaction is determined by this thermodynamic energy difference and the galvanic potential difference (∆G°) across the ITIES. 30,31 The influence of ∆G° is investigated by adjusting it by means of the concentration ratio of TBA+ between the aqueous and organic phases. Cyclic voltammograms (CVs) of [Co(bpy)3]3+ reduction were recorded in the butyronitrile solution as part of a biphasic system containing 0.01–0.1 M TBA+ in the aqueous phase and a fixed concentration of 0.05 M TBA+ in the organic phase. As shown in the inset of Fig. 2, the reduction potential of [Co(bpy)3]3+ shifts positively by nearly 60 mV per concentration decade of TBA+, in good agreement with the Nernst–Donnan equation. Please note that the electroneutrality of the two phases is maintained by insertion of the hydrophobic, potential-determining ion TBA+ into the organic phase. In addition, the influence of ∆G° is observed clearly by photocurrent responses at the Au ME which grows with the TBA+ concentration in the aqueous phase (Fig. 2). This causes a more positive potential across the interface contributing to a higher driving force for photo-induced ET.

Interestingly, changing the aqueous electrolyte from acidic to alkaline media dramatically influences the photocurrent responses. As depicted in Fig. 3, the transient signal increases significantly in neutral (pH 7, 0.1 M NaCl) or alkaline (pH 9, 0.01 mM NaOH) aqueous electrolytes compared to the acidic solution (pH 3, 0.02 M HClO4).

It is known that the energy levels of the CB and VB of the BiVO4 semiconductor shift with pH, whereas the redox potential of [Co(bpy)3]3+/2+ is independent of pH. 32 A higher pH of the reactant solution yields a negative shift of the band-levels of

![Photoinduced ET from nanocrystalline BiVO4 to [Co(bpy)3]3+](image)
BiVO₄ (on the electrochemical scale). Consequently, the CB electrons in BiVO₄ attain more reductive power towards the approximately pH-independent formal potential of [Co(bpy)₃]³⁺ and the photo-induced ET proceeds more easily (Fig. 3). Furthermore, the photocurrent signal is enhanced when using tetrahexylammonium (TH₂A⁺) instead of TBA⁺ as the common ion because the more hydrophobic TH₂A⁺ has a higher tendency to transfer to the organic phase and, therefore, contributes to a higher driving force for the photo-induced ET reaction from BiVO₄ to [Co(bpy)₃]³⁺.

Parallel to the ET reaction between photo-excited electrons of BiVO₄ and [Co(bpy)₃]³⁺, photo-generated holes in the VB of BiVO₄ cause the WOR which is energetically possible. The reaction product, O₂, can be detected by online mass spectrometry (ESI-6, ESI†) as the main product of photooxidation of water. Table 1 summarizes the O₂ evolution rates per gram catalyst within the first 10 min of irradiation. The O₂ evolution rate is improved drastically under polarization of the ITIES with TBA⁺ compared to batches without either potential-determining ion.

Table 1  Oxygen evolution rate in a batch reactor depending on additions of common ion and electron acceptor

| Batch  | [Salt]₀ | [Co(bpy)₃]³⁺ | O₂ evolution rate (µmol h⁻¹ g⁻¹) |
|--------|---------|--------------|---------------------------------|
| 1      | None    | 0            | 0                               |
| 2      | 0.1 M NaCl + 0.01 TBACl | 0            | 5                               |
| 3      | None    | 0.5 mM      | 218                             |
| 4      | 0.01 M NaCl + 0.01 TBACl | 0.5 mM      | 336                             |
| 5      | 0.1 M NaCl + 0.01 TBACl | 0.5 mM      | 0                               |

a Details of the photoreactor and GC detection in ESI-6, ESI. b 30 mg BiVO₄ was dispersed in 35 mL water. c 35 mL organic phase contained 0.05 M TBAPF₆. d Per gram of catalyst. e Hyperbranched BiVO₄. f Powdered catalyst synthesized by the sol-gel method. g

Fig. 3 Photocurrent transients for the detection of [Co(bpy)₃]²⁺ in butyronitrile at a Au ME (r = 12.5 µm, E₁ = +0.5 V vs. AgQRE) with different aqueous supporting electrolytes. The butyronitrile solution contained 0.5 mM [Co(bpy)₃]PF₆ and 0.05 M TBAPF₆. The aqueous solution contained 0.1 M NaCl and additionally from bottom to top, 0.02 M HClO₄, no addition, 0.01 mM NaOH and 0.01 M TH₂ACl.

Fig. 4 Oxygen evolution rate over the reaction time. The inset figure is the cumulated amount of generated O₂ assuming a linear change of O₂ concentration in the exhaust gas stream between the sampling. The initial oxygen production rate at t = 0 is assumed to be the same as that at the first sampling after 10 min: (●) hyperbranched BiVO₄, 0.01 M TBACl aqueous phase, 0.5 mM [Co(bpy)₃]PF₆ + 0.05 M TBAPF₆; (●) hyperbranched BiVO₄ aqueous phase without TBACl, 0.5 mM [Co(bpy)₃]PF₆ + 0.05 M TBAPF₆.

In conclusion, a completely new approach has been proposed by which the photochemical behavior of BiVO₄ semiconductor nanostructures can be improved for visible light-driven oxidation of water. The nanoparticulate BiVO₄ semiconductor is assembled at the water/butyronitrile interface polarized by the common, highly hydrophobic tetraalkylammonium cation partitioning between the two liquid phases. A CoIII complex acts as an electron acceptor in the organic phase. The high surface area of nanosized BiVO₄ crystals with a specific hyperbranched structure along with the defect free ITIES minimizes the interfacial recombination of photo-excited electron–hole pairs by driving force due to the polarization of the ITIES by a common ion increases the O₂ evolution rate.

The removal of the electrons from the BiVO₄ nanostructures inhibits the otherwise fast recombination of electron–hole pairs. This requires nanostructured BiVO₄ for efficient transport of electrons to the solid–liquid interface. When using the same mass of powdered BiVO₄ without hyperbranched structures, the O₂ evolution rate is below the detection limit. So far, many strategies have been developed to increase the efficiency of visible light-driven oxygen evolution at BiVO₄ semiconductor materials applied as photocatalyst powders or modified solid electrodes in aqueous solutions with electron acceptors such as Co⁢II or Fe³⁴,⁴⁰ complexes, morphology control and facet engineering of BiVO₄-based materials. Here, the extremely high rate of visible light-driven O₂ evolution allows detection within only 10 min of illumination of the hyperbranched photocatalyst powder by separation of photo-induced charge carriers at a molecular interface. A similar value of 238 µmol h⁻¹ g⁻¹ is also obtained with Ag⁺ as a scavenger in the first 15 min of operation and with a larger optical band (λ > 320 nm).

The very high initial activity decreased within 20–30 min to levels below the detection limit of our system (ca. 1 µmol h⁻¹). The data are shown in Fig. 4. The accumulated amounts of O₂ generated during the reaction time are plotted in Fig. 4. They compare favourably to amounts of O₂ detected within 1–5 hours for BiVO₄ systems as reported recently. ³²–³⁹

In conclusion, a completely new approach has been proposed by which the photochemical behavior of BiVO₄ semiconductor nanostructures can be improved for visible light-driven oxidation of water. The nanoparticulate BiVO₄ semiconductor is assembled at the water/butyronitrile interface polarized by the common, highly hydrophobic tetraalkylammonium cation partitioning between the two liquid phases. A CoIII complex acts as an electron acceptor in the organic phase. The high surface area of nanosized BiVO₄ crystals with a specific hyperbranched structure along with the defect free ITIES minimizes the interfacial recombination of photo-excited electron–hole pairs by driving force due to the polarization of the ITIES by a common ion increases the O₂ evolution rate.
rapidly transferring electrons to reactants in the adjacent liquid phases. The ET reaction can be characterized sensitively by oxidation of [Co(bpy)]$_{3}^{2+}$ originating from the photo-driven reaction at the ITIES using a SECM configuration in the organic phase.

Moreover, the driving force for the photo-induced ET reaction could be readily maximized by chemically controlling the polarization of the interface. This improves the WOR compared to recent reports on WOR using powdered BiVO$_4$ photocatalysts. It is expected that the new strategy developed in this work will promote efficient water splitting with powdered BiVO$_4$ photocatalysts in large-scale solar-to-hydrogen conversion. Further studies will be directed to address details of WOR mechanisms at BiVO$_4$ at ITIES, integrating other approaches such as doping of BiVO$_4$.

We are grateful to Prof. Dr Michael Wark and Sven Warfsmann (Institute of Chemistry, Carl von Ossietzky University of Oldenburg) for help with measuring O$_2$ evolution rates. S. R. thanks the Hanse Institute of Advanced Studies Delmenhorst and the Alexander von Humboldt Foundation for research fellowships.

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