Transparent conductive oxides in photoanodes for solar water oxidation

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Introduction

Water splitting using PEC systems has received increasing interest, because this conversion fulfils the sustainable goal for the storage of solar energy in chemical bonds. 1–4 The approach avoids the carbon cycle, and it therefore leads to almost zero impact on the environment. 5–8 Water oxidation at photoanode is normally the rate determining reaction for overall water splitting, since this oxidation reaction involves 4 electrons and 2 oxygen atoms. 7 To achieve an efficient photoanode, three general issues should be considered in the order (1) light absorption, (2) charge separation/transport and (3) surface reactions. 9 Among them, charge separation and transport are of particular importance. As the oxidation and reduction reactions are physically separated in two different chambers, 10 the photoexcited electron from the photoanode must migrate through the semiconducting films to the cathode for hydrogen production. 11 In other words, low conductivity of the semiconducting films could extensively limit the performance due to the effect of charge recombination. For instance, a pristine hematite photoanode presented excellent visible light absorption up to 590 nm, but the minority carrier diffusion length is short (2–4 nm) and thus hinders its efficiency. 11 Therefore, its solar conversion efficiency is far below the state-of-the-art. 12 What is worse, the incident photoenergy would release in other forms of non-collective energies, including thermal energy and photoluminescence energy. The emissions of these energies not only reduce the PEC conversion efficiency, but also degrade the photoactive films themselves, and thus likely reduce the working life. 13 As such, a few strategies were developed to overcome this issue, for instance, the improvement of the crystallinity and optimization of conductivity with doping. 15–17

Beyond the photocatalytic films, the conductive substrate is the other key part of the PEC electrode, and the materials of which are normally TCOs. 18–21 For a typical photoanode, TCO films normally bind the photocatalytic films and the substrate support to collect photoexcited electrons, which are then transferred to the cathode on the other side for the reductive reaction. 22–23 Typical TCOs include fluorine/indium doped tin oxide (FTO/ITO) and aluminum doped zinc oxide (AZO), which are already commercialized by coating flat films on glass or polymer substrates. 24 In the past few years, novel designs of TCO textures were also developed to promote charge separation and transfer and internal light scattering.

An example of one-dimensional (1D) TCO nanorods (NRs) and the corresponding hybrid structure are shown in Fig. 1b. In a comparison of flat films (Fig. 1c), this nanostructure, on one hand, could increase the effective interfacial surface area for improving the rate of charge injection and increases the area for surface reactions (Fig. 1a). On the other hand, a careful selection of the material for the formation of the hybrid structure would encourage charge migration to the cathode and minimize the recombination probability. Type II hetero-band structures of the photoanode are ideal for solar water oxidation (Fig. 1d), where the photoexcited electrons are transferred to the TCOs and carried to the cathode with a sufficient reduction potential. The appropriate relative positions of the electronic states are significant to achieve an efficient photoanode for solar water oxidation. 25 Despite a few reports being presented focusing on the TCOs in photoanodes, a comprehensive analysis is still absent. The merit of TCOs for photoanodes should be analyzed; only then can the possible way be proposed for further developing them in photoelectrodes and other optoelectronic applications.

In this mini review, the designs of nanoscale TCOs are reviewed for the development of efficient photoanodes for solar...
water oxidation. The principle of TCOs is introduced. Typical examples of nanostructured TCOs and their synthesis are presented. In addition, the hybrid structures formed by coating visible-active photocatalytic films on nanostructured TCOs are also reviewed, highlighting the favorable band structures for improving charge separation and transfer, thus optimizing the performance of solar water oxidation. Along this line, the importance of 1D TCOs in PEC systems is emphasized. In the future, the prototypical nanostructured electrodes may inspire a series of optoelectronic applications. 

**The fundamentals of TCO materials**

Excellent TCO materials should only absorb light shorter than 400 nm, so that they are visible light transparent. The ideal free carrier concentration should be above $10^{19}$ cm$^{-3}$. The use of TCOs for electronics was initially realized for a transparent display, which can be traced back to the 1930s, when H.G. Wells imagined such a material in his fiction novel called ‘The Shape of Things to Come’. With modern technology, this prototypical material is widely applied in electronics, such as mobile phones, electronic skin, solar cells and many more. Many such metal oxides have large bandgaps which only absorb in the ultra-violet (UV) spectrum. The materials are mainly based on SnO$_2$, TiO$_2$, In$_2$O$_3$, ZnO, and more, which have bandgap values of 3.49, 3.20, 3.00 and 3.20 eV, respectively. However, the pristine semiconducting metal oxides normally present limited diffusion length for the minority charges with insufficient conductivity. 

In principle, improving their conductivity is realized by introducing a shallow donor/withdrawer. Such doping would not lead to significant differences in the band edges, but injected electrons can be readily transported by the shallow donor or withdrawer. Whether to use a shallow donor or withdrawer depends on the type of semiconductor (p- or n-types) and the properties of the dopants. For example, in AZO, the major composition of ZnO is an n-type semiconductor. When doping Al into ZnO, Al ions replace Zn ions in the ZnO crystal to introduce extra electrons as shallow donors in the conduction band near the band edge, as shown in Fig. 2, which allows the charge to migrate (Fig. 2b). Despite the wide range of TCO materials available, limited species of TCOs were used for PEC applications. Most of the metal oxide based TCO materials and the corresponding dopants are summarized in Table 1 and their nanostructures can be developed for highly effective PEC water splitting in the near future.

**From planar to nanoscale TCOs for PEC water oxidation**

To the best of our knowledge, Nb doped TiO$_2$ (Nb:TiO$_2$) films are the first case for the investigation of TCO materials in the PEC water oxidation, reported in 1991. In this research, the effects of firing temperature, membrane thickness and Nb-doping level on quantum efficiency were examined. The performance of PEC water oxidation is improved with Nb doping, achieving the optimal PEC performance at a doping concentration of ca. 5 mol%, when the efficiency for charge separation and transfer approaches was balanced. The principle for the improved charge mobility in Nb:TiO$_2$ is similar to that of AZO. TiO$_2$ is an n-type semiconductor. Nb was the substitutional dopant in the TiO$_2$ crystal and delocalizes charge from Nb onto neighboring Ti ions. In more detail, the Nb 4d orbital would affect the Ti 3d orbital to induce shallow donors, thus resulting in the improved conductivity.

Recently, owing to the rapid developments of nanostructured materials, TCO based nanostructures, especially their 1D nanostructured version, were also widely reported. Nb:TiO$_2$ nanotubes were synthesized through traditional self-organizing anodization of Ti–Nb alloys. It is found that with respect to undoped TiO$_2$, ca. 5 times photocurrent density can be achieved using optimal Nb:TiO$_2$ nanotubes (ca. 5 at%), resulting in the optimal value of ca. 1.0 mA cm$^{-2}$ at the applied

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**Fig. 1** (a) Illustration of the hybrid visible photoanode by coating a visible light photocatalyst on TCOs. Comparison of (b) 1D hybrid structure with (c) flat films. (d) Illustration of a type II hetero-structured photoanode by coating a visible photocatalyst on TCOs for solar water oxidation.

**Fig. 2** The illustration of band structures of (a) ZnO and (b) Al:ZnO.
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Table 1  Typical metal oxides and dopants for TCOs

| Metal oxides | Dopants |
|--------------|---------|
| SnO₂         | Sb,³⁵ F,³¹ As,³² Nb,³³ Ta,³⁵ |
| TiO₂         | Nb,³⁴ Ta,³⁳ In³⁶ |
| ZnO          | Al,³⁷ B,³⁸ Cl,³⁹ Y,⁴⁰ V,⁴¹ Si,⁴² Ti,³³ Zr,⁴⁴ |
| CdO          | In,⁴³ Sn,⁴⁶ |
| In₂O₃        | Sn,⁵⁷ Mo,⁵⁸ F,⁴⁹ Ti,⁵⁰ Zr,⁵¹ Nb,⁵² Ta,⁵³ W,⁵⁴ |

Increasing surface area. The mechanism for the improved charge migration is illustrated in Fig. 3B. In addition, the band structure of the pristine ZnO and Y:ZnO samples is also shown in Fig. 3C, revealing that their band edges and gap are mainly preserved after doping. The product presented an optimal photocurrent of 0.84 mA cm⁻² at 1.23 V vs. RHE with 0.1% Y doping. This result corresponds to a 47% enhancement compared to pristine ZnO in solar conversion.

Hybrid visible light photoanode with nanoscale TCOs

Despite the TCO material approaching high quantum efficiency in photocatalytic water oxidation, the nature of its large bandgaps (>3.00 eV) restricts its solar light absorption within the UV spectrum, corresponding to ca. 5% of solar energy.⁷⁸ Therefore, even with much improved charge mobility, this conversion is still far below the requirements (10%) for practical applications. Although increasing the doping level could potentially narrow the bandgap, it is normally accompanied by the reduction of crystallinity. Too many crystal defects could reduce charge mobility and thus decrease photo-oxidation performance. To overcome the wide bandgap issue, a hybrid photoanode is designed by coating narrow bandgap photocatalysts on the surfaces of nanostructured TCOs. The structure offers the benefits of both good electron conductivity and visible light absorption. The nanomorphology will add extra benefit of a large effective surface area to facilitate oxidation at the electrolyte/photoanode interfaces. Most of the narrow bandgap photocatalysts have a short charge diffusion length. The design of the hybrid photoanode can effectively avoid such a problem. Within such a hybrid structure, the light absorption is determined by the thickness of the TCO films, while the charge transfer is determined by the thickness of the films of the narrow bandgap photocatalysts. Hence, the light absorption can be maximized without affecting the charge mobility.

A typical example is visible light sensitive hematite, because it has an extremely short diffusion length for charge carriers (ca. 2 nm).¹¹ As early as 2012, Gratzel and coworkers synthesized a 3D porous Nb:SnO₂ host electrode to facilitate charge transport and improve the PEC water oxidation efficiency of hematite.⁷¹ The structure of the photoanode is shown in Fig. 4.⁷² The Nb:SnO₂ host is fabricated by atomic layer deposition (ALD) and it was crystallized by high temperature annealing to achieve

Fig. 3 (A) Illustrations of the Y:ZnO NRs with different concentrations of Y. (B) Schematic explaining the increased electron mobility with increasing Y doping concentration. (C) The details of the band structure of pristine ZnO and Y doped ZnO with different concentrations of Y. Reproduced with permission from ref. 68; Copyright (2019) American Chemical Society.

Fig. 4 Illustration of the host–guest PEC system by coating hematite films on Nb:SnO₂. Reproduced with permission from ref. 71; Copyright (2012) American Chemical Society.
high transparency and conductance with good chemical stability over a wide range of pH. The optimized Nb:SnO₂ films showed a high electrical conductivity of up to 37 S cm⁻¹ concomitant with a low optical attenuation coefficient of 0.99 μm⁻¹ at 550 nm. This 3D nano-electrode is used as a host to support the deposited hematite layers on the surface and achieves a photocurrent density of ca. 1 mA cm⁻² with a voltage bias of 1.2 eV (vs. RHE). Zou and co-workers reported the synthesis of another core–shell structure by coating hematite on ITO NRs for PEC water oxidation.⁷² ITO NRs were synthesized through chemical vapor deposition (CVD) on a quartz substrate. The hematite layer is then coated on the surface of the ITO NRs, with a layer thickness of 30 to 40 nm. The boundary between hematite and ITO was clearly distinguished with high-resolution transmission electron microscopy (HR-TEM). The hybrid core–shell photoanode reached a current density of ca. 1.1 mA cm⁻² at 1.23 V (vs. RHE), which is double that of planar hematite films. The stability of the photoanode was tested in 1 M NaOH aqueous electrolyte under AM1.5 illumination. The photocurrent density was maintained for as long as 40000 s. This result indicated that with improved charge transport, the stability of the photoanode is also significantly improved.

Conductive Sb:SnO₂ NRs were also synthesized by thermal vapor deposition and hematite NRs were grown on the surface of the conductive NRs for enhanced PEC water oxidation. By annealing the hybrid photoanode at 650 ºC, a photocurrent density of 0.88 mA cm⁻² was achieved at 1.23 V (vs. RHE). This result is 3 times higher than that of hematite NRs on FTO glass annealed at the same temperature. More recently, an extra TiO₂ coating was applied on the hematite/Sb:SnO₂ NRs, as shown in Fig. 5.⁷³ This photoanode presented an optimal photocurrent density of ca. 1.75 mA cm⁻², which is double that of the hematite/Sb:SnO₂ photoanode.

In addition to hematite, TiO₂ was also widely used as a photocatalyst, due to its negative conduction band minimum. TiO₂ NRs coated on Sb:SnO₂ NRs achieved enhanced PEC water oxidation.⁷⁴ In this case, the TiO₂ NRs were formed on the Sb:SnO₂ NRs by the chemical bath deposition method. A maximum photocurrent of ca. 0.6 mA cm⁻² was achieved for this hybrid structure. A similar result was achieved by depositing a TiO₂ layer via ALD on the Sb:SnO₂ nanoparticles on FTO glass as a photoanode, which presented an optimal photocurrent density of ca. 0.58 mA cm⁻² at 1 V (vs. RHE) under AM 1.5G illumination.⁷⁵ A similar idea was also reported by replacing Sb:SnO₂ nanoparticles with FTO colloid films. A further increase of the photocurrent density is achieved (0.7 mA cm⁻²) under the same conditions. The improved PEC efficiency can be attributed to the improved charge collection by the nano FTO colloid films, together with an increased surface area from the nanotextured photoanode.⁷⁶

CdS and CdSe are well established visible-light sensitive photocatalysts and thus have potential for improved solar PEC applications. By integrating them with highly conductive NRs, both good visible light absorption and excellent charge transportation can be achieved. Lee and co-workers⁷⁷ demonstrated the coating of CdS and CdSe based photocatalysts on the outside of vertically aligned conductive ITO NRs for PEC water oxidation. The structure of their photoanode is shown in Fig. 6.⁷⁷ ITO NRs were produced using the CVD approach. A thin layer of TiO₂ was coated on ITO NRs in order to control the charge recombination on the ITO surface. The photoactive layer of CdS and CdSe was coated by successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) methods, respectively. This multi-shell photoanode presented a significant increase in solar conversion with a photocurrent density of 16.2 mA cm⁻². This result is unexpectedly higher than most of the other similar reports. In this system, three key points determine this high efficiency: (1) the ITO NRs play a key role in charge transport to improve the quantum efficiency; (2) the heterostructure of the bandgap ensures the migration of the electrons and ‘holes’ to the right direction; (3) strong visible light absorption of CdS and CdSe allows the use of the majority of solar illumination.

Recently, Zou and co-workers developed conductive, vertically aligned AZO NRs by doping Al into ZnO NRs through a hydrothermal approach. A CdS layer is then coated on the surface of the AZO NRs by SILAR. Thin Al₂O₃ films were further deposited on the surface of the as-prepared core–shell NRs using the magnetron sputtering technique for improving the stability of the NRs. It results in a photocurrent density of ca. 10.4 mA cm⁻² at 1.23 V (vs. RHE). Meanwhile, the photocurrent density of an optimal photoanode can be preserved at ca. 75% for a 3600 s test, which is excellent for a CdS based photoanode.

BiVO₄ is a relatively new emerging visible light photocatalyst; the major issue to apply it for PEC applications is also the short diffusion length of minority carriers. The typical approach is to dope Mo into BiVO₄ to increase charge mobility, which could significantly improve the photocurrent density to ca. 2.73 mA cm⁻². Yang and co-worker doped TiO₂ NRs with Ta to achieve conductive NRs.⁷⁸ In this research, a solid state diffusion approach based on ALD was used to achieve Ta:TiO₂. With
With the traditional hydrothermal method, this method requires a high processing temperature (823 K) to achieve homogeneously doped Ta on the surface of TiO₂. The quantity of doping can be facilely controlled. The improved charge mobility was measured through electrochemical impedance spectroscopy and analyzed with Mott–Schottky plots. The NRs were further coated with BiVO₄ nanoparticles to achieve visible light absorption. The valence band edges of Ta:TiO₂ and BiVO₄ were identified using ultraviolet photoelectron spectroscopy (UPS). It is shown that a typical type II heterostructure was formed at the interfaces. As such, under light illumination, the photoexcited electrons were ready to migrate from BiVO₄ to Ta:TiO₂, which led to higher carrier separation and transfer, thus improving the performance of solar water oxidation. The development of nanoscale TCOs might inspire a series of applications in optoelectronics, sensors, photocatalysts, and more.

**Conflicts of interest**

There are no conflicts to declare.

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