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Recent Progress in Design, Synthesis, and Applications of One-dimensional TiO_2 Nanostructured Surface Heterostructures: a Review

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One-dimensional TiO_2 nanostructured surface heterostructures (1DTiO_2NSHs) have been comprehensively studied during the past two decades because of the possible practical applications in various fields, including photocatalysis, dye-sensitized solar cells, sensors, lithium batteries, biomedicine, catalysis, and supercapacitors. Combining extensive advancements in materials science and nanotechnology, a 1DTiO_2NSH material with well-controlled size, morphology, and composition, has been designed and synthesized. More importantly, its superior properties, including a high aspect ratio structure, chemical stability, large specific surface area, excellent electronic or ionic charge transfer, and a specific interface effect, have attracted a great deal of interest in improving current performance and exploring new applications. In this tutorial review, we introduce the characteristics of 1D TiO_2 nanostructures, the design principles for the fabrication of 1DTiO_2NSHs, and we also summarize the recent progress in developing synthesis methods and applications of 1DTiO_2NSHs in different fields. The relationship between the secondary phase and the 1D TiO_2 nanostructure and between the performance in applications and the excellent physical properties of 1DTiO_2NSHs, are also discussed.

Introduction

Titanium dioxide (TiO_2) is a common multifunctional material, which has been used in a wide variety of applications in many fields: from glass, ceramic to paper industries, from cosmetics, refractory coating to painting, from medicine, food technology to farming, to painting, from medicine, food technology to farming, from electronic components to chemical catalysis.[1] Over the past four decades, TiO_2 nanostructured materials have attracted a great deal of research attention because of their potential application in the photodegradation of organic pollutants, photocatalytic water splitting for hydrogen generation, dye-sensitized solar cells, and even gas sensors and biosensors. Among the various TiO_2 nanostructures, granular TiO_2 nanoparticles represent the most popular morphology and are the most commonly used in various applications. Compared with bulk TiO_2, granular TiO_2 nanoparticles have a large surface area and a broadened band gap, and so they contain more active sites and display improved photocatalytic activity, photoelectrochemical

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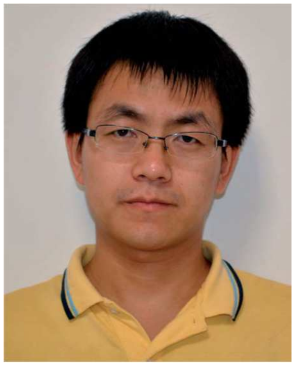
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properties and gas sensitivity.[2] Even though potential applications of TiO_2 nanoparticles exist in various fields, they still possess undesirable disadvantages: a large interfacial area that causes slow charge carrier transport, a wide optical band gap that leads to limited applications using solar light, and single phase and nanoscale features that induce fast recombination of photo-reduced carriers. More importantly, nanosize granular TiO_2 nanoparticles are hard to recycle and re-utilize in water when they are used in the photo-decomposition of organic pollutants, and may cause the secondary pollution of water.[3] As an example, consider the well-known commercially made product P25. It is a bi-phase form of TiO_2 (ca. 80 wt% anatase and ca. 20 wt% rutile) nanoparticles, and the photocatalytic reaction has to be performed through a pot-by-pot process. The collection cost of the TiO_2 nanoparticles from suspension after reaction is even higher than the original price of the P25 product. Much effort has been spent in trying to overcome the above disadvantages of this granular TiO_2 nanoparticle material, including doping with hetero-atoms, introducing oxygen vacancies, changing the physical and chemical surface properties via surface modification, tuning the band gap, etc.[4] However, none of the above strategies can effectively overcome all the problems when TiO_2 nanoparticles are used as photocatalysts, solar cell electrodes, or gas sensors. Most of the above methods induce a partial sacrifice of UV photocatalytic performance when they endow TiO_2 with visible light photocatalytic activity. Moreover, the modified TiO_2 nanoparticle products using the above methods are not stable. Some other methods have been also developed, such as forming Schottky junctions or introducing surface-plasmon resonance absorption, extending the light absorption from the UV range to the visible light range by sensitization with quantum dots and chalcogenides, and also by decoration with noble metal nanoparticles.[5] Indeed, these methods lead to many advantages, such as enhanced light harvesting, efficient charge carrier separation and transport, and suppressed charge carrier recombination, and so they can significantly improve the photocatalytic performance of TiO_2. However, due to the complicated synthesis procedure and resulting uncontrollable properties, in reality their practical application is limited. For example, it is hard to control the coverage and distribution of the secondary phase on the surface of TiO_2 nanoparticles, leading to the unexpected formation of a core-shell structure that blocks light absorption and restricts the diffusion of photo-induced charge carriers to the TiO_2 surface.

In recent years, one-dimensional (1D) TiO_2 nanostructures have been extensively studied because of their specific morphology and novel properties.[3] Generally, a 1D nanostructure is constructed with a high aspect ratio, and at least one of its dimensions should be in the 1-100 nm range, no matter whether it is rod-, wire-, belt- or tube-shaped. Therefore, in comparison with TiO_2 nanoparticles, 1D TiO_2 nanostructures not only inherit almost all the typical features of the nanoparticles, but also display some new properties and improve performance in specific areas. The diameter along the radial dimension of a 1D TiO_2 nanostructure is comparable to many important physical parameters, such as the exciton Bohr radius, the wavelength of light, the phonon mean free path, the excitation diffusion length, etc. On the one hand, the confined dimension of a 1D TiO_2 nanostructure produces quantized particles, such as electrons, phonons and photons. On the other hand, the unconfined dimension of a 1D TiO_2 can provide a highway for the transfer of these quantum particles.[6] The TiO_2 nanobelt is one of the ideal 1D TiO_2 nanostructures for potential applications in many fields related to photo-electrics or semiconductors.[3, 7] First, the high crystallinity of the TiO_2 nanobelt allows it to transport charge carriers very well along the axial direction. Second, the relatively large surface area and chemical stability make it an ideal building block for assembling various surface heterostructures, thus broadening its range of application. Third, the ease of synthesis is relatively advantageous. The length of a TiO_2 nanobelt can be varied from several micrometers up to the millimeter range, and an ultra-long TiO_2 nanobelt can be manipulated to construct a paper-like structure for sensors and continuous applications in photocatalysis.[8] However, some negative aspects of 1D TiO_2 nanostructures still exist, including a relatively low specific surface area, a smooth surface, a single crystal phase, and a broad band gap, which in turn lead to the lack of an active site, a relatively high recombination rate of photo-induced charge carriers, and a shortage of visible light photocatalytic activity.

Fortunately, thanks to the remarkable morphological features of 1D TiO_2 nanostructures, especially in the case of the belt-like 1D TiO_2 nanostructure, a special structure, named the "one-dimensional TiO_2 nanostructured surface heterostructure" (1DTiO_2NSH), can be designed and fabricated by assembling secondary phases with special morphology, such as nanoparticles, nanowires, nanorods or other nanostructures, on the surface of the 1D TiO_2 nanostructure. Several published reports have demonstrated that well designed 1DTiO_2NSHs can preserve the intrinsic characteristics of TiO_2, overcome the above-mentioned problems, and even endow the material with some new properties.[7] These new properties include broadening the light absorption band from the visible to the near infrared region, plasmon-enhanced light absorption and highly efficient separation of photo-induced charge carriers, with some special properties that are useful for gas sensors, solar cells, and biomedical applications. Therefore, by using careful design and synthesis techniques, the prepared 1DTiO_2NSH can feature the following characteristics: 1. maintenance of all the properties of 1D TiO_2 nanostructures; 2. possession of the surface heterojunction

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between properties of the secondary phase materials; 3. contribution of synergistic effects and improved performance that originate from the the secondary phase and the TiO_2 surface.

1. Design principles of one-dimensional TiO_2 nanostructured surface heterostructure

As mentioned above, the $1DTiO_2NSH$ has a very wide range of application, especially in photodegradation, water splitting, solar cells, photoelectrodes, and gas sensors. However, in this review paper, we would like to address only the principles and design techniques for $1DTiO_2NSH$ that mainly apply to photocatalytic applications, including photodegradation, water splitting, and photocatalytic disinfection. For other applications, such as electrochemical applications, the design principles for producing the $1DTiO_2NSH$ can follow this design method but with alterations to match the special requirements needed to improve the desired property of the material, which will also be briefly introduced.

In an ideal nanostructure that is to be used in photocatalytic applications, the following criteria must be met: 1. it must possess a sufficiently large surface area. In particular, one that contain enough photocatalytically active sites; 2. it must have high light absorption efficiency over a broad light absorption band to make full use of the solar spectrum; 3. there must be effective separation of the photo-induced charge carriers to produce more active radicals for photodegradation, or to generate more hydrogen gas. However, at present, no single material can match all of the above criteria. Fortunately, the synergistic effects of the $1DTiO_2NSH$ can definitely compensate for the deficiencies of an individual photocatalyst. Therefore, in the following section we introduce an outline intended to give some guidance to designing high performance $1DTiO_2NSH$ materials for future applications.

1.1 Enlargement of the photocatalytically active surface

Generally, some important parameters must be considered to increase photocatalytic activity; for example "the specific surface area and the active site concentration" of a photocatalyst affect the efficiency of the photocatalysis process. Based on these major points, two corresponding measures must be taken into account for the successful design and synthesis of a $1DTiO_2NSH$ for use in photocatalysis applications.

1.1.1 Increase of the specific surface area of 1D TiO_2 nanostructures

It is well known that the photocatalytic degradation of organic molecules and photocatalytic water-splitting for hydrogen generation occur on the surface of the photocatalyst. For highly efficient photocatalysis, a sufficient amount of surface area for absorption of the organic molecules must be created. One of the main disadvantages of the 1D TiO_2 nanostructure is the low specific surface area when compared with TiO_2 nanoparticles. The problem of how to enlarge the specific surface area of the 1D TiO_2 nanostructure and still maintain the wire-like morphology is a great challenge for obtaining good photocatalysis performance. The effective approaches to enlarging the surface area can be divided into two different kinds of method: the first is to decorate second phase nanoparticles on the surface of the 1D TiO_2 nanostructure, and the second is *in-situ* construction of a studded surface with uniformly distributed nanoparticles of the same composition through an acid corrosion process. Both approaches represent appropriate methods for building 0D nanoparticle-assembled 1D TiO_2NSHs. The resulting $1DTiO_2NSH$ obtained through this process possesses at least three qualities that improve photocatalysis: first, the surface area is significantly increased due to the large specific surface area of the nanoparticles on the surface of the 1D nanostructure; second, the nanoparticles possess a high surface energy which is beneficial for the absorption of organic molecules; third, the nanoparticles on the 1D TiO_2 nanostructure surface connect with the surface lattice of the 1D TiO_2 nanostructure, and form surface heterostructures which enhance the separation of photo-induced charge carriers, and so improve the photocatalytic properties of the 1D nanostructure. The above-mentioned methods used to synthesize nanoparticle-decorated $1DTiO_2SHs$ possess different advantages and drawbacks. For the first method, one type of nanoparticle is easily replaced by another, thereby producing different $1DTiO_2SHs$ with tunable structures and properties. However, in this method it is hard to control the coverage rate of the nanoparticles on the surface of the 1D TiO_2 nanostructure, and it is also difficult to control the particle size and uniformity distribution of the nanoparticles. In the second method, it is very easy to obtain well distributed TiO_2 nanoparticles on the surface of the 1D TiO_2 nanostructure, and it is beneficial for getting perfect contact between the nanoparticles and the 1D nanostructure, which is an important factor in obtaining a high performance photocatalyst. The drawback of this method is that it is impossible to obtain a heterojunction with two different compositions, and the 1D nanostructure can be destroyed if the corrosion time, acid concentration, or acid treatment temperature is not precisely controlled.

1.1.2 Increase of active facet exposure

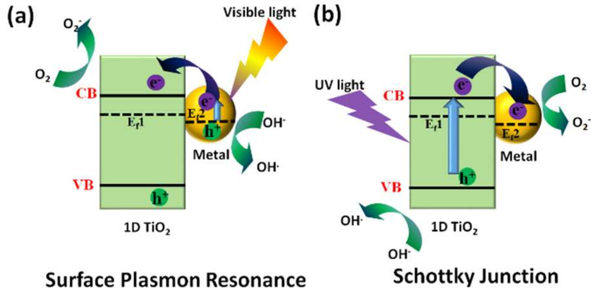
According to reports in the literature, different facets of anatase TiO_2 show different chemical activity, a property that is determined by the surface energy of the facet. It is reported that the ranking of the surface energy of the TiO_2 facets is γ (001) (0.90 J m^{-2}) >γ (100) (0.53 J m^{-2}) >γ (101) (0.44 J m^{-2}),[9] which means that the highest photocatalytic capability is exhibited by the highly energetic (001) facets. However, exposing the (001) facets in TiO_2 nanostructures (especially in nanobelts) is difficult prepare due to the reduced stability of the (001) facets. Although some researchers have reported that exposed (001) facets in TiO_2 nanoparticles can be obtained by carefully controlling the growth process by adding surfactants, the synthesis method is time-consuming with high cost, and difficult to scale-up. Normally, the anatase TiO_2 nanobelt grows along the [101] direction, the facet with very low activity, and only on the top of the nanobelt is the (001) facet exposed, which explains the very low photocatalytic ability of TiO_2 nanobelts. By tuning the synthesis procedure and the crystallization process, TiO_2 nanobelts grown along the [101] direction with two dominant (101) facets exposed can be obtained. It has already been demonstrated that the dominant (101) facet of the 1D TiO_2 nanobelt has preferable reactivity with O_2 molecules, and hence enhances photocatalytic activity.[3] From the above analysis, it can be concluded that exposing the more active facets of the 1D TiO_2 nanostructure is the key problem to overcome in obtaining high performance $1DTiO_2SH$ hybrid photocatalysts.

1.2 Enhancement/broadening of light absorption

The energy distribution of solar light is 4% UV light, 44% visible light and 52% infrared (IR) light. It is well known that the wide band gap of the TiO_2 (about 3.2 eV) nanostructure can only absorb UV light, which largely limits the harvesting of solar light. The ability to enhance the absorption of the 1D TiO_2 nanostructure, and thus improve the light harvesting ability is one of the most important challenges for building high performance hybrid photocatalysts. There are two main approaches to enhance the light harvesting ability of 1D TiO_2 nanostructures: one is to enhance the light absorption ability by utilizing the surface plasmon resonance (SPR) effect of metallic nanoparticles that are assembled on the surface of the 1D TiO_2 nanostructure, another is to broaden the light absorption from UV light to the visible light range, or even to the near-infrared range by assembling nanoparticles with visible or IR light photocatalytic activity, and forming $1DTiO_2SHs$ with them. These two important promising approaches are briefly introduced below.

1.2.1 Enhancement of light harvesting

Recently, fundamental research on the SPR enhanced photocatalytic activity of TiO_2 have greatly increased. The materials used for this purpose have mainly focused on noble metals, such as Au, Ag, Pt, and Pd and their alloys.[10] As an alternative but effective way to improve the photocatalytic activity of TiO_2 semiconductor photocatalysts, SPR can greatly improve solar light conversion because of enhanced light absorption and scattering at the interface of the heterostructure. The scattered light at the interface caused by noble metal nanoparticles can be further absorbed by the 1D TiO_2 nanostructure, which induces two processes for enhancing light absorption. It has already been demonstrated that SPR can transfer energy from a metal to a semiconductor, and this energy transfer induces two different kinds of charge separation: direct electron-hole separation and plasmonic energy-induced electron-hole separation. Both processes can greatly increase solar light conversion efficiency. It should be pointed out that light absorption and scattering at the interface are largely dependent on the size, morphology, and distribution of the noble metal nanoparticles. Also, assembling noble metal nanoparticles on the 1D TiO_2 nanostructure can broaden the light absorption band from UV to visible light. Fig. 1a shows a schematic of photogenerated charges transfer for metal-1D TiO_2 NSHs under visible light irradiation due to the surface plasmon resonance (SPR) effects. Therefore, assembling noble metal nanoparticles on the surface of a 1D TiO_2 nanostructure is one of the prominent design methods used for adapting $1DTiO_2NSH$ to the purpose of enhancing the light harvesting capacity of TiO_2. It has already been demonstrated that the morphology and size of the noble metal nanoparticles can be used to tune the SPR absorption wavelength. Therefore, this design idea is universal for obtaining high performance photocatalysts and solar cell electrodes.



Surface Plasmon Resonance Schottky Junction

Fig. 1 Schematic illustration of photogenerated charges transfer for metal-1D TiO_2 NSHs (a) under visible light irradiation due to the surface plasmon resonance (SPR) effects and (b) under UV light irradiation due to the existence of the schottky junction.

1.2.2 Broadening light absorption to visible light

As mentioned previously, the 1D TiO_2 nanostructure possesses high photocatalytic activity with good recycling prospects, but the broad band gap of TiO_2 only permits photocatalysis in the UV region, which limits the efficient use of solar energy for the power source in photocatalysis. Because UV light makes up only about 4% of the entire solar energy spectrum, more than 95% of the solar spectrum cannot be used for TiO_2 photocatalysis. Therefore, one of the most important design principles for fabricating $1DTiO_2NSHs$ is to broaden the photocatalytically active wavelength region to include visible light. A practical approach to expanding the light absorption spectrum of TiO_2 can be summed up in two approaches: the first approach is to tune the physical and chemical properties without changing the crystalline phase and morphology of the TiO_2 nanostructure, such as by introducing oxygen vacancies, or by doping with anions or cations. The other approach is to construct surface heterostructures using oxide or chalcogenide semiconductor materials or other visible light active materials with narrower energy gaps. As shown in Fig. 2, because the good visible photocatalytic property of Ag_2O and the construct of surface heterostructure, the Ag_2O nanoparticles/TiO_2 nanobelts heterostructure presents excellent UV and visible photocatalytic properties.[11] The possibility of using the former approach is limited, not only because the ability to tune the light absorption band is limited, and the photocatalysis efficiency in the visible region is not very high, but also due to lowered UV light activity because doped TiO_2 is not stable for long term applications. In the latter approach, the ideal route to overcome such problems is the combination of the high UV photocatalytic properties of TiO_2 with the visible photocatalytic properties of semiconductor nanoparticles or specially shaped noble metal nanoparticles with a narrower band gap. However, in this design, if the TiO_2 substrate consists of granular nanoparticles, the heterostructures normally form as core-shell structures. Although the shell of visible light active semiconductor nanoparticles can endow the hybrid photocatalyst with visible light photocatalytic activity, it can block UV light from reaching the TiO_2 core. On the other hand, compared with granular nanoparticles, the 1D TiO_2 nanostructure has a large surface. If visible light active semiconductor nanoparticles are assembled on the 1D TiO_2 nanostructure to form a $1DTiO_2NSH$, a well-designed synthesis process can ensure that the nanoparticles distribute themselves on the surface of the 1D TiO_2 nanostructure without completely covering the surface. This type of $1DTiO_2NSH$ should possess both UV light activity from the TiO_2 nanobelts and visible light activity from the surface nanoparticles, resulting in a broadened active light spectrum for the hybrid photocatalyst.

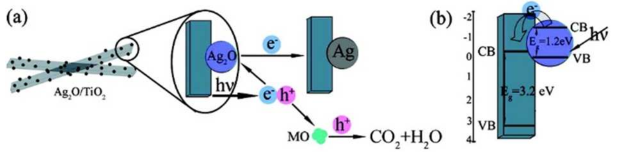


Fig. 2 Schematic view for electron-hole separations and energy band matching of Ag_2O nanoparticles/TiO_2 nanobelts heterostructure under (a) UV- and (b) visible-light irradiation.[11]

Based on the above design principles, forming visible light-active nanoparticles assembled on $1DTiO_2NSHs$ has become one of the most popular methods of broadening the light absorption from UV to visible light. Theoretically, almost any semiconductor with a band gap less than 3.2 eV with visible light photocatalytic activity can be selected as a candidate for construction of the $1DTiO_2NSH$ to obtain an active light wavelength-broadened photocatalyst. These materials can mainly be divided into transition metal oxides, transition chalcogenides and their corresponding complex oxides and complex chalcogenides. The synergistic photocatalytic capability obtained can be optimized by controlling the particle size and distributing the visible light photocatalyst on the 1D TiO_2 nanostructure surface.

1.2.3 Broadening light absorption to near-infrared light

Infrared light comprises a major part (almost more than 50%) of solar light energy. However, because there is a lack of photocatalysts that can use infrared light, to fully use the solar energy spectrum for photocatalysis or photocatalytic water splitting for hydrogen generation has remained unexplored for a long time. In recent years, several infrared light-active photocatalysts and ideas to use infrared light that make full use of the solar energy spectrum for photocatalysis have become more of a reality.[12] The assembly of some nanostructures with visible-infrared light photocatalytic activity to form a 1DTiO$_2$NSH is the basic principle for the construction of UV-visible-infrared active hybrid photocatalysts.

There are several infrared light photocatalysis techniques or infrared active materials that can be used to design a 1DTiO$_2$NSH that impart infrared light activity to the 1D TiO$_2$ nanostructure. The first approach to incorporate infrared light activity in TiO$_2$ is to use up-conversion fluorescence technology, in which absorbed long wavelength light can be converted to shorter wavelengths that lie within the visible and UV regions. Up-conversion usually occurs in materials containing d-block or f-block elements, such as Yb^{3+}, Er^{3+}, Tm^{3+}, etc.[13] The most widely used up-conversion materials are Yb^{3+} and Er^{3+}: NaYF$_4$ nanoparticles. By simply assembling the up-conversion nanoparticles onto the 1D TiO$_2$ nanostructure, it is easy to obtain photocatalysis under near-infrared light irradiation. The main problem for this method is low light conversion efficiency and a very narrow excitation wavelength band for up-conversion. The fluorescence can only be excited by laser stimulation. Although this system has been used to demonstrate infrared photocatalysis, it is not useful for the practical application to solar light driven photocatalysis. Another kind of important up-conversion material is carbon or graphene quantum dots, a newly emerging material with up-conversion fluorescence. Carbon or graphene quantum dots can convert infrared light to visible light, and then to UV light.[14] Therefore, they represent another choice for the synthesis of 1DTiO$_2$NSHs having infrared light photocatalytic activity or in preparing full solar spectrum photocatalysts. This kind of 1DTiO$_2$NSH possesses some advantages, such as low cost, continuous high absorption from UV, visible to infrared, non-toxicity, and environment-friend. However, because the light up-conversion efficiency is very low, the problem becomes how to improve rare earth-doped NaYF$_4$ and carbon/graphene quantum dot's up-conversion performance. Solving these questions is the great task that must be addressed in order to obtain practical 1DTiO$_2$NSHs that can be applied to this purpose. The second method for building a UV-visible-infrared light active 1DTiO$_2$NSH photocatalyst is to assemble infrared light active photocatalysts on the surface of the 1D TiO$_2$ nanostructure. Although this solution is quite obvious, no such photocatalyst had been reported until last year.[12] Recently, due to the appearance of a new infrared light active photocatalyst (Bi_2WO_6), a new future for the fabrication of a real solar light photocatalyst has been opened.[12] By assembling visible-infrared active Bi_2WO_6 nanosheets on TiO$_2$ nanobelts, a high performance and broad spectrum light active 1DTiO$_2$NSH has been obtained.[12]

There is also a new idea that should be addressed. Nonlinear optical materials, which are often used as frequency doubling materials in lasers, can be used to build a 1DTiO$_2$NSH. It is very well known that nonlinear optical materials can convert infrared light to visible light, and visible light to UV light by frequency doubling. Although, no published work has been reported for the construction of such 1DTiO$_2$NSH nanostructures, in the near future it is quite possible that a well-designed non-linear optical nanomaterial-decorated 1D TiO$_2$ nanostructure will attract more research attention and can serve to be a practical broad light active photocatalyst.

1.3 Prohibiting charge carrier recombination

The photocatalytic capacity of a semiconductor mainly originates from photo-induced charge carriers. Under a given amount of light illumination for a specific material, the effective number of charge carriers contributing to photocatalytic reaction is governed by several processes: 1. the excitation of electrons from the valence band to the conduction band; 2. the diffusion of charge carriers from the bulk to the surface; 3. the recombination/separation of charge carriers that occurs at the surface or in the bulk. Although the enhancement or extension of light absorption can be designed to increase the concentration of photo-generated charge carriers, the matter of how to prohibit the recombination of these carriers is the key in the next step of the photocatalysis process, which also dominates photocatalysis efficiency. In following section, several design principles for a 1DTiO$_2$NSH with improved photo-induced carrier separation are introduced.

1.3.1 Schottky junction

When a metal and semiconductor come in contact, an energy barrier is formed at the interface. If the Fermi levels of the metal and semiconductor are comparable, it termed a Schottky junction. The main feature of the Schottky barrier is the barrier height, which is the energy difference between the work function of the metal and the electron affinity of the semiconductor. With reasonable manipulation, photo-induced charge carriers in the semiconductor may either accumulate at the interface in the depletion region or flow into the metal leaving holes in the valence band of the semiconductor, and hence significantly separate the charge carriers. Therefore, based on the Schottky junction effect, assembling metal nanoparticles on a 1D TiO$_2$ nanostructure to form a hybrid system that prohibits photo-induced carrier recombination is one of the most important design principles for building a 1DTiO$_2$NSH. As shown in Fig. 1b, due to the existence of the schottky junction, the equilibrium alignment of the Fermi level for metal and 1D TiO$_2$ nanostructure forms a built-in electric field near the interface, which is in favor of the separation of photogenerated charge carriers.[15]

1.3.2 p-n junction

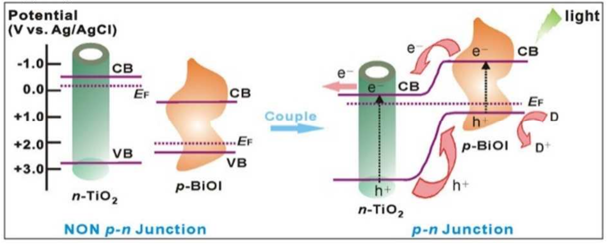


Fig. 3 Schematic diagrams for the energy bands of p-type BiOI and n-type TiO$_2$ nanotube before and after coupling, as well as the specific charge transfer process at the formed p-n junction under visible-light irradiation.[16] (Reprinted from ref. 16. Copyright 2014, with permission of Nature Publishing Group)

Another important 1DTiO$_2$NSH design principle that is aimed at improving photo-induced carrier separation is to use the p-n junction effect between the surface nanoparticles and the 1D TiO$_2$ substrate. A p-n junction is usually formed between the two types of semiconductor, p-type and n-type. As shown in Fig. 3, when a p-n junction is formed, a local electric field across the space charge region is formed. Driven by the electric force, photo-generated electrons move to the p-type semiconductor side, and holes to the n-type semiconductor side.[16] The charge carriers can also diffuse into the space charge region. The result of these two processes is the effective separation of photo-induced electron-hole pairs, always leading to enhanced photocatalytic activity. It is well known that TiO$_2$ is an n-type semiconductor. Hence, using some p-type semiconductor such as NiO, Ag$_2$O, and BiOI, to form a p-n junction heterostructure on the surface of the 1D TiO$_2$ nanostructure to form a

1DTiO$_2$NSH is an effective approach to enhance photocatalytic activity.[17]

1.3.3 Band structure matching

Although the p-n junction and the Schottky junction can efficiently separate charge carriers to increase photocatalytic activity in semiconductors, most of the high performance photocatalytic semiconductors are of n-type, which means they cannot be used to follow the above design principles. With the rapid development of knowledge and new techniques in this field, it has become easier to tune or design the band structures of two semiconductors to match each other through the nano-engineering process. Through alignment of the band structures of the two semiconductors used in 1DTiO$_2$NSHs, the photo-induced electron-hole pairs will be driven to different parts of the heterostructure and can achieve charge carrier separation. This design principle is most applicable to the synthesis of 1DTiO$_2$NSH.

1.4 Structural design of one-dimensional TiO$_2$ nanostructured surface heterostructures

In Section 1.3, we discussed the design principles for fabricating 1DTiO$_2$NSHs based on physical mechanisms. The structure of 1DTiO$_2$NSHs is also affected by the resulting properties of this kind of hybrid semiconductor.

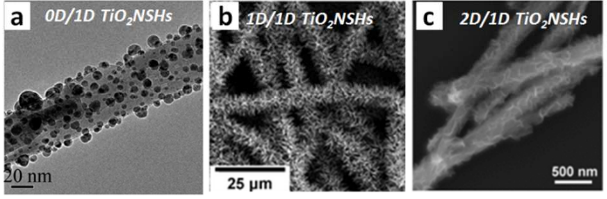


Fig. 4 SEM of different microstructures of 1DTiO$_2$NSH: (a) Ag$_2$O nanoparticles/TiO$_2$ nanobelts heterostructure (0D/1D TiO$_2$NSHs)[11]; (b) ZnO nanorods/TiO$_2$ nanofibers heterostructure (1D/1D TiO$_2$NSHs)[18]; (c) MoS$_2$ nanosheets/TiO$_2$ nanobelts heterostructure (2D/1D TiO$_2$NSHs).[19] (Reprinted from ref. 19. Copyright 2013, with permission of Wiley)

1.4.1 Morphology/microstructure design of one-dimensional TiO$_2$ nanostructured surface heterostructures

The topological properties of 1DTiO$_2$NSH are also very important. Based on the morphology of the nanoparticles assembled on the 1D TiO$_2$ nanostructure, a 1DTiO$_2$NSH can be designed with the following microstructures:

0D/1D TiO$_2$NSHs: This heterostructure consists of granular or semi-spherical nanoparticles and the 1D TiO$_2$ nanostructure, such as Ag$_2$O nanoparticles/TiO$_2$ nanobelts heterostructure[11] (Fig. 4a). The advantage of this kind of heterostructure is ease of synthesis which can be expanded for large-scale production. Therefore, most 1DTiO$_2$NSHs can be designed as 0D/1DTiO$_2$NSHs.

1D/1D TiO$_2$NSHs: This heterostructure is constructed by growing secondary 1D nanostructures, such as nanorods or nanowires, on the surface of the 1D TiO$_2$ nanostructure in the perpendicular or parallel direction.[18] (Fig. 4b) Perfect crystalline characteristics of the secondary 1D structure can increase charge transfer along the axial direction and increase the contact area, hence improving photocatalysis. However, if the length of the second phase nanowires is too large, the photo-induced carriers have to pass a long way to get to the TiO$_2$ substrate, so recombination is difficult to control. Moreover, if the length of the surface nanowires is greater than the light wavelength, it will block the passage of UV light into the TiO$_2$, and the total photocatalytic efficiency will decrease. Therefore, controlling the direction, length, and density distribution of the secondary phase nanowires on the surface of the 1D TiO$_2$ nanostructure is an important aspect that must be considered in the synthesis of 1D/1DTiO$_2$NSH.

2D/1D TiO$_2$NSHs: For this heterostructure, the secondary material on the surface of 1D TiO$_2$ is a 2D structure like graphene, MoS$_2$, BN, etc.[19] (Fig. 4c) 2D structures are materials possessing some special properties, which could endow some novel properties to the 1DTiO$_2$NSHs.

1.4.2 Multi-heterostructures for multi-functional enhancement

Sometimes, single heterostructured 1DTiO$_2$NSH cannot fulfill the requirements for high performance photocatalysis and complete utilization of the solar energy spectrum. Therefore, the design and synthesis of a multi-heterostructure is one of great importance. Here, from two different standpoints, structural and functional, we illustrate the potential advantages of the multi-heterostructure material and the anticipated enhancement in the photocatalytic performance of TiO$_2$.

Structural design: 1. two different nanostructures are uniformly or randomly distributed on the surface of a 1D TiO$_2$ nanostructure; 2. a sandwich nanostructure is formed on the surface of a 1D TiO$_2$ nanostructure, i.e., the third phase is assembled on the surface of the secondary phase that is attached to the 1D TiO$_2$ nanostructure surface.

Functional design**:** In order to compensate for the disadvantages of the 1D TiO$_2$ nanostructure and obtain multi-functional 1D TiO$_2$NSHs, based on the single role of each part of the heterostructure, several multi-heterostructures can be designed using the following approaches:

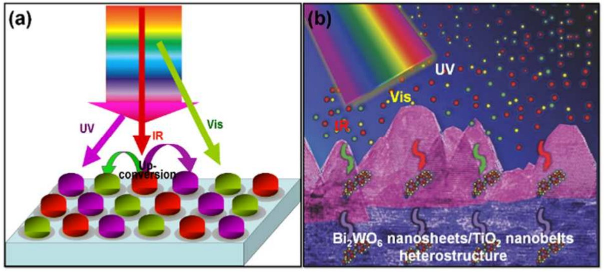


Fig. 5 Schematic diagram of (a) up-conversion nanoparticle/visible light-active nanoparticle/1D TiO$_2$NSH and (b) visible and near-infrared light-active nanoparticle/1D TiO$_2$NSH.[12]

A. Visible light-active nanoparticle/near-infrared light-active nanoparticle/1D TiO$_2$NSH. In this process, the 1D TiO$_2$NSH displays broad spectrum light activity, from UV, visible to near-infrared. Therefore a potentially broad application of this type of 1DTiO$_2$NSH to solar light photodegradation and water splitting for hydrogen generation is anticipated. However, due to the scarcity of near-infrared photocatalysts, discovery of a suitable material in this category represents the main problem rather than development of a heterostructure assembly technique.

B. Up-conversion nanoparticle/visible light-active nanoparticle/1D TiO$_2$NSH. As shown in Fig. 5a, The design of this kind of 1D TiO$_2$NSH aims at harvesting infrared light and converting it to visible light by up-conversion nanoparticles, and then transferring it to visible light-active photocatalytic nanoparticles on the surface of a 1D TiO$_2$ nanostructure. Although up-conversion nanoparticles do not display near-infrared photocatalytic activity, their up-conversion property can ensure that the near-infrared energy in solar light is used for photocatalysis. Hence, this kind of 1DTiO$_2$NSH also has expected applications in solar light photocatalysis. However, more attention must be paid to the narrow absorption band of the up-conversion materials and the low up-conversion efficiency of carbon quantum dots. Some challenges still exist in developing new up-conversion materials that show a wider absorption band with high light conversion efficiency. Organic up-conversion materials with tunable band gaps are the right choice for the design and development of this kind of heterostructure for photocatalysis applications.

C. Noble metal nanoparticle/visible light active nanoparticle/1D TiO_2NSH. In this kind of 1DTiO_2NSH, both UV light activity that originates from the 1D TiO_2 nanostructure and visible light activity that originates from the narrower band gap nanoparticles on the nanostructure can lead to the enhancement of light absorption by the SPR effect. Based on this design principle, well designed multi-nanoparticle 1DTiO_2NSHs can display excellent UV/visible light photocatalytic activity by assembling noble nanoparticles of different size or morphology, because the SPR-enhanced light absorption wavelength largely depends on size and morphology.

D. Metal nanoparticle or visible and near-infrared light-active nanoparticle/1D TiO_2NSH. This kind complex 1D TiO_2NSHs can be designed for utilizing SPR enhanced light absorption both in the visible and infrared regions.[12] (Fig. 5b) To enhance the light absorption by SPR in the infrared and visible region, some noble metal particles of a special morphology such as nanorods, nanotriangles, or nanoflowers need to be considered. This complex surface heterostructure merits special and careful experimental design, because it is hard to assemble the specially shaped nanoparticles onto the designated sites of the 1D TiO_2 nanostructure surface. Undoubtedly, this complex heterostructure will possess the advantages of the above three kinds of complex 1D TiO_2NSHs mentioned in this section.

1.5 Principles and design techniques of 1DTiO_2NSHs for electrochemical applications

For electrochemical applications, the design principles for producing the 1DTiO_2NSH can follow some design methods of photocatalytic applications, such as large surface area, but it also need to meet the electrochemical requirements, such as the improvement of the electronic and ion transport property.

Electrochemical energy storage is the main electrochemical applications, which is realized by electron and ion charge-discharge. Batteries and supercapacitors are two kinds of typical electrochemical energy storage devices, both of which store electricity in electrochemical process. So many criteria, such as improving the electron and ion mobility and expand the contact area between electrode and electrolyte, can be used to design the 1DTiO_2NSHs for electrochemical applications.

(1) Increase the specific surface area. Large surface area not only helps the transportation of ions and facilitate double-layer charging, but also provides a large interface for contacting with the electrolyte in electrochemical applications. So increasing the specific surface area can be used to improve the electrochemical property of 1DTiO_2NSHs.

(2) Increase the percentage of active facet exposure. An electrochemical study on crystal engineering of TiO_2 nanotube arrays having different percentages of surface shows that [001]-oriented TiO_2 nanotube arrays have enhanced lithium ion insertion/extraction behavior, including better reversibility and excellent capacity at high current rates. The origin of the enhanced performance of the [001]-oriented TiO_2 nanotube arrays is confirmed by the investigation of the lithium storage performance, electrochemical impedance, and the kinetics of lithium ion insertion/extraction.[20] So rational design of active facet exposure can enhance the performance of 1D TiO_2 nanostructure in electrochemical applications.

(3) Porous structure. Porous structured 1DTiO_2NSHs electrodes can provide a large contact area between electrode and electrolyte for charge transport, and a shorten diffusion path for lithium, which is beneficial for short charging-discharging times in batteries. The structure of electrode materials, especially the surface porous structure, is a crucial factor that determines the rate for ion insertion/extraction. So design porous structure of 1DTiO_2NSHs is also important for the electrochemical applications.

(4) Assembling some high electrical conductivity materials. In lithium-ion batteries and supercapacitors, the electrochemical activity of TiO_2 is negatively impacted by its low electronic conductivity. Therefore, assembling some high electrical conductivity materials on the 1D TiO_2 nanostructures, have been employed to enhance the electrochemical performance of 1D TiO_2 nanostructure anodes.

A. Carbon assembling. The carbon assembling method has been proven to be very efficient to improve the electrochemical performance of 1D TiO_2 nanostructures. A better cycling stability and high rate capacity could be achieved with the coated carbon material.[21] The carbon assembling can also suppress the agglomeration of 1D TiO_2 nanostructures and allow better contact with the electrolyte leading to a better electrochemical performance.

B. Metal assembling. Many metals, such as Ag, Cu, Sn, and Co, were integrated with 1D TiO_2 nanostructures to improve the electric conductivity and charging/discharging rates, and thus to further improve the electrochemical performance.[21] This type of 1DTiO_2NSHs can decrease the polarization of the anode and also improve the stability and fast-cycling ability of 1D TiO_2 nanostructures.

C. Metal oxide assembling. Metal oxide, such as RuO_2, Fe_xO_y, and SnO_2,[22] on the surface of 1D TiO_2 nanostructures formed into the 1DTiO_2NSHs, which can provide highly conducting paths for electrons, then result in negligible diffusion times, enhanced local conductivities, and faster phase transformation reactions, and hence appear to be the key to the good electrochemical performance for the 1DTiO_2NSHs.

2. Synthesis of 1D TiO_2 nanostructures

As the substrate and one of the most important parts of the 1D TiO_2NSH, the synthesis of the 1D TiO_2 nanostructure is important for the construction of 1D TiO_2NSHs. There are many methods that have been developed to prepare 1D TiO_2 nanostructures with various morphology types, including nanotubes, nanorods, nanowires, nanobelts and nanofibers, all of which have already been discussed in a previous review article.[3] In this section, we briefly introduce the four main preparation methods, including the hydrothermal method, the sol-gel method, the vapor deposition method, and the electrospinning method, to give the reader a full picture of the synthesis techniques for 1D TiO_2 nanostructures.

2.1 Hydrothermal method

The hydrothermal method is usually conducted in a closed system, such as a sealed Teflon-lined autoclave enclosed in a stainless steel vessel. By heating the sealed vessel, the inner temperature can be elevated to above the boiling point of water, producing high pressure. 1D TiO_2 nanostructures can be obtained under such harsh reaction conditions. Fig. 6 shows the various kinds of 1D TiO_2 nanostructures prepared by the hydrothermal method, including TiO_2 nanotubes,[23] TiO_2 nanorods,[24] TiO_2 nanobelts,[25] and TiO_2 nanowires.[26] Nowadays, the hydrothermal synthesis of 1D TiO_2 nanostructures is a well-established technique and typically yields a large amount of 1D TiO_2 nanostructures from solution.

In terms of the reactants used for the hydrothermal synthesis of 1D TiO_2 nanostructures, the synthesis method can be divided into the acid-hydrolysis hydrothermal and alkali-hydrothermal approaches. In the former method, the reactants are usually titanium salts like chlorides and titanium alkoxide with inorganic acids, and normally lead to the formation of a rutile 1D TiO_2 nanostructure. The reactants in the latter method are usually TiO_2 nanoparticles and hydroxide solution. The product in most cases is anatase, and dissolution-recrystallization is always involved in this process. Different reaction mechanisms are involved in these two methods, which produces different morphology types and different crystalline phases of the product 1D TiO_2 nanostructure.

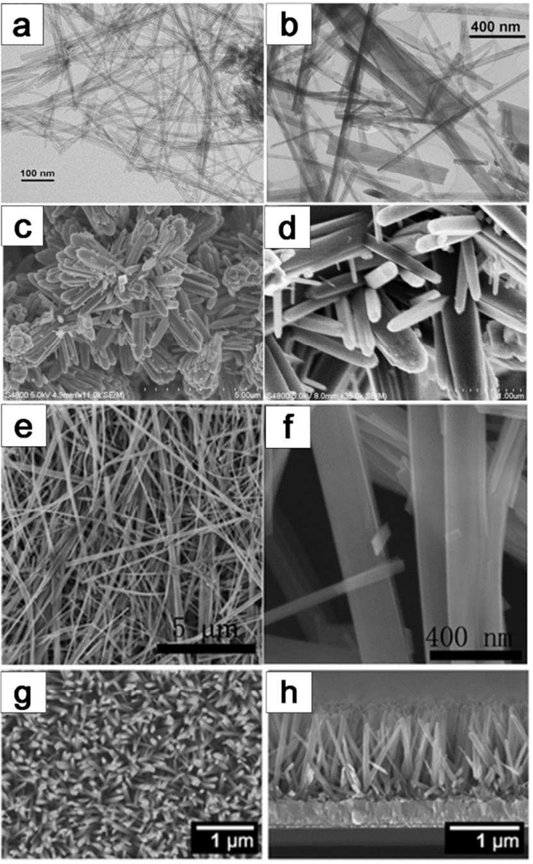


Fig. 6 Different morphology types of 1D TiO_2 nanostructures synthesized through hydrothermal methods: (a, b) TiO_2 nanotubes,[23] (c, d) TiO_2 nanorods,[24] (e, f) TiO_2 nanobelts,[25] (g, h) TiO_2 nanowires.[26] (Reprinted from ref. 24. Copyright 2013, with permission of InTech.)

2.2 Sol-gel method

The sol-gel method has been used for the preparation of TiO_2 nanoparticles by using the manufactured hydrolyzed product of an organic titanium complex as the titanium precursor. In the case of the synthesis of 1D TiO_2 nanostructures, the process typically requires special confinement to achieve growth of the 1D nanostructure. In a typical example, TiO_2 nanorods were synthesized via a novel direct sol filling and heating sol-gel template method using titanium (IV) isopropoxide ($Ti_4(OCH_3)_{16}$) as a precursor.[27] The as-prepared TiO_2 nanorods exhibited the anatase phase with a 10 nm diameter.

Through the sol-gel method, TiO_2 nanoparticles can be aligned according to their crystal orientations and so form a TiO_2 nanowire. This process is also known as the "oriented attachment" mechanism. For example, Rodríguez-Reyes *et al*[28] demonstrated that using titanium tetraisopropoxide ($Ti(OC_3H_7)_4$), isopropanol and acetic acid as the sol is a successful way to prepare the TiO_2 nanowires. To obtain the xerogel, the sol was dried at 100 °C for 24 h. Finally, the xerogel was calcined in a conventional furnace in normal atmosphere at 400, 500 and 600 °C for 1 h in order to densify and crystallize the TiO_2 nanowires.

2.3 Vapor deposition method

Vapor deposition techniques, including chemical vapor deposition (CVD) and physical vapor deposition (PVD) have been developed for the preparation of high quality 1D TiO_2 nanostructures. Compared with ordinary chemical methods, both CVD- and PVD-derived 1D TiO_2 nanostructures display a high degree of crystallinity (usually single crystal TiO_2). Chen *et al*[29] have grown well-aligned rutile TiO_2 nanorods via the CVD method by using titanium tetraisopropoxide ($Ti(OC_3H_7)_4$) as the source reagent. The rutile TiO_2 nanorods were grown with a very high density and exhibited uniform height. However, this method requires expensive equipment and the cost is too high for mass production.

2.4 Electrospinning method

Compared with the above-mentioned methods for generating 1D TiO_2 nanostructures, electrospinning represents a simple and versatile method for the scalable production of 1D TiO_2 nanostructures, especially ultralong TiO_2 nanofibers and hollow TiO_2 nanofibers. The method uses electric fields and a spin force to eject the liquid precursors through a fine orifice, forming fibrous structures. Post heat treatment is usually needed to remove the solvent and solidify the fiber structure. Generally, the synthesis of electrospun TiO_2 nanofibers involves the following four steps: (1) preparation of a sol with titania precursor; (2) mixing of the sol with a polymer template to obtain the solution for electrospinning; (3) electrospinning of the solution to obtain composite nanofibers, and (4) calcination of the as-prepared nanofibers to obtain single-phase crystalline TiO_2 nanofibers. Li *et al*[30] prepared electrospun TiO_2 nanofibers of anatase by using titanium tetraisopropoxide ($Ti(OC_3H_7)_4$), polyvinyl pyrrolidone (PVP), acetic acid, and ethanol as starting chemicals. In this study, the TiO_2 nanofibers that are produced can have a variable average diameter of 20-200 nm by varying the applied electric field, PVP concentration, $Ti(OC_3H_7)_4$ concentration, and feeding rate. Although electrospinning is an efficient method for mass production, the high resistance caused by the polycrystalline characteristics of the product nanofibers limits its applications.

3. Synthesis of one-dimensional TiO_2 nanostructured surface heterostructure

As discussed in Section 1, although 1D TiO_2 nanostructures have unique properties for different applications, their performance still cannot match the continuously increasing demand in many fields of application. Using a 1D TiO_2NSH is the most efficient approach to tune the properties and improve the performance of the 1D TiO_2 nanostructure, because it combines the properties of the surface nanoparticles and the TiO_2 substrate to get enhancement through the heterojunction effect. Most recently, the growing interest in engineering 1D TiO_2NSHs has intensified the research on assembling different materials in a single architecture for the realization of new or improved properties. Various 1DTiO_2NSHs have been designed and synthesized, and have demonstrated that assembling surface heterostructures on a 1D TiO_2 nanostructure is a versatile and powerful tool for enhancing the properties of TiO_2 nanostructures. Almost all the published reports on 1DTiO_2NSHs follow the design principles discussed in Section 1. In this section, we summarize the methods and mechanisms for the synthesis of 1D TiO_2NSHs, and give a full picture of this field to the reader. We classify 1D TiO_2NSHs according to the type of materials used in the surface heterostructure.

3.1 Metal nanoparticle-1D TiO_2 nanostructured surface heterostructures

As we mentioned in Section 1, the metal nanoparticle-assembled 1D TiO_2NSH is one of the most important 1D TiO_2NSHs that has been developed so far, with the advantage of accelerated photo-induced carrier separation because the electron work function is much higher in a metal than in a semiconductor. Because of the excellent controllability of the electron transfer process by means of storing and shuttling photo-induced electrons, noble metals such as Au, Ag, Pt, and Pd have been used to couple with the 1D TiO_2 nanostructure to construct a 1D TiO_2NSH. The wet-chemical *in situ* reduction method is most often used to synthesize metal nanoparticle assembled 1D TiO_2NSHs. The synthesis process is very simple, consisting of dropping the reducing agent into a metal-salt solution, in which the synthesized 1D TiO_2 nanostructures were dispersed in advance. When the reduction reaction occurs between the reducing agent and the metal ions, the elemental metal particles that are formed can attach to the surface of the 1D TiO_2 nanostructure to form a 1D TiO_2NSH. The main drawback of this simple method is that the particle size and size distribution of the nanoparticles is too uncontrolled on the surface of the 1D TiO_2 nanostructure, and aggregation of intact nanoparticles poses a problem. To overcome this problem, speeding up the nucleation rate and suppressing the growth rate, especially by controlling the nucleation sites on the surface of the 1D TiO_2 nanostructure are necessary steps in order to acquire high performance 1D TiO_2NSHs.

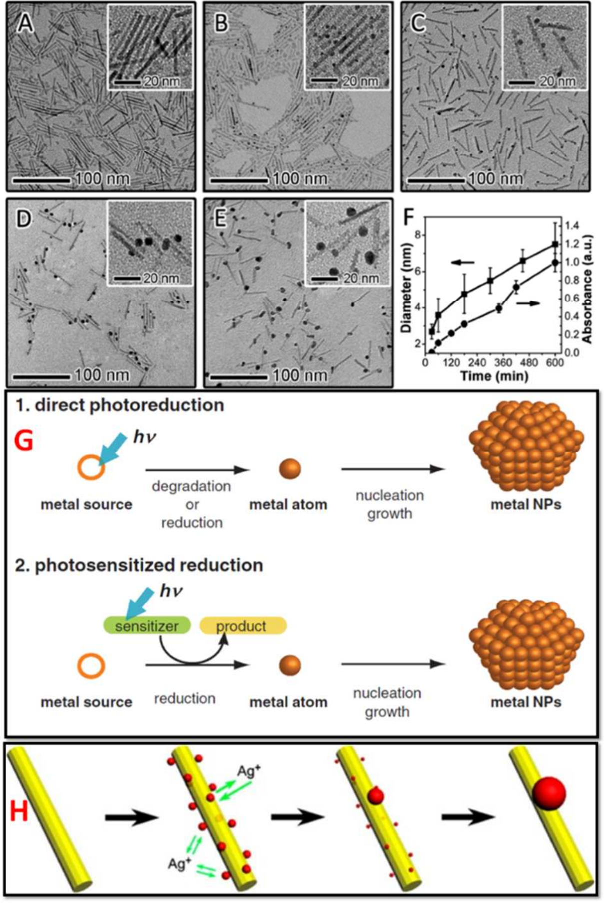


Fig. 7 (A) TEM image of TiO_2 nanorods. (B-E) TEM images of Ag-TiO_2 nanorod composites formed by UV irradiation for (B) 30 min, (C) 60 min, (D) 180 min, and (E) 600 min; (F) dependence of intensity of the plasmon band at 440 nm and the size of AgNPs on irradiation time;[31] (G) schematic of photo-induced synthesis of metal nanoparticles. This scheme shows the different routes in which metal nanoparticles are formed;[32] (H) The proposed formation mechanism of Ag-TiO_2 nanorod composites.[31] (Reprinted from ref. 31. Copyright 2013, with permission of American Chemical Society; Reprinted from ref. 32. Copyright 2010, with permission of Chemical Society of Japan)

The photo-reduction method was proposed to synthesize metal nanoparticles *in situ* on the surface of a 1D TiO_2 nanostructure. This method is performed by irradiating a metal-salt solution with synthesized 1D TiO_2 nanostructures dispersed under vigorous stirring. During this process, hydroxyl radicals produced by the photocatalysis of TiO_2 reduce the metal ions to elemental form. Because the reduction reaction occurs on the interface between TiO_2 and water, the locally high concentration of elemental metal atoms uniformly initiates the nucleation process only on the surface of the 1D TiO_2 nanostructure, and the metal nanoparticles on the TiO_2 surface are small and therefore uniformly distributed. Using this method, noble metal nanoparticles synthesized on the surface of a TiO_2 nanobelt are only 3-5 nm in diameter, which is much smaller than those synthesized by the conventional wet-chemical method.[31] Most importantly, the photo-reduction method is free of toxic reducing agents, and so avoids the use of organic capping agents that degrade the electronic properties. Fig. 7 illustrates that noble metal nanoparticles can be synthesized *in situ* on TiO_2 nanorods either through the direct photo-reduction of a metal precursor, or through the reduction of a metal precursor using a photosensitizer to adsorb the light. The synthesis mechanism of the photo-reduction method is schematically described in Fig. 7G and H.[31, 32]

Another important approach to the fabrication of metal nanoparticle assembled 1D TiO_2NSHs is the immobilization of prepared metal nanoparticles on the surface of the 1D TiO_2 nanostructure. In most cases, the metal nanoparticles and/or the 1D TiO_2 nanostructure are modified to aid in the attachment of capping ligands. The main advantage of this immobilization method is precise control over the metal nanoparticle size and morphology, which can in turn control the wavelength of the SPR effect. However, in this method, in order to connect the noble metal nanoparticles to the 1D TiO_2 nanostructure, some surface modification to aid in the interattachment of both nanomaterial surfaces is essential. For even more precise control, "biological surfaces" have been used to fabricate Au nanoparticle/TiO_2 nanotube heterostructures,[33] however because the nanoparticles connect with the substrate through chemical bonding, this kind of hybrid structure is not a true surface nanoheterostructure.

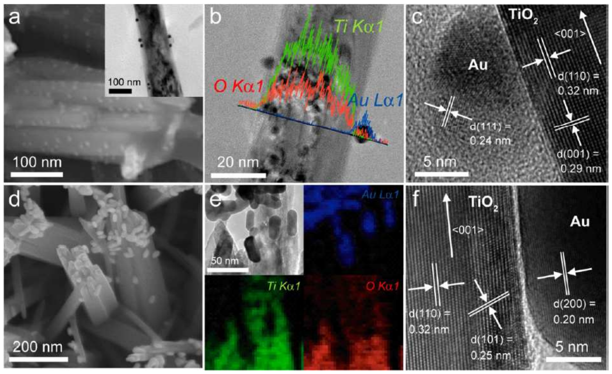


Fig. 8 (a) SEM and TEM (inset) images of Au NP-decorated TiO_2 nanowires; (b) EDS line profile recorded on an individual Au NP-decorated TiO_2 nanowire; (c) HRTEM image taken at

the interface between Au NP and TiO_2 nanowire; (d) SEM images of Au NR-decorated TiO_2 nanowires; (e) TEM images of Au NR-decorated TiO_2 nanowires and corresponding EDS element-mapping data: Au (blue), Ti (green), and O (red); (f) HRTEM image taken at the interface between Au NR and TiO_2 nanowire.[34] (Reprinted from ref. 34. Copyright 2013, with permission of American Chemical Society)

Although some literature reports have demonstrated that metal nanoparticle/1D TiO_2NSHs prepared from either of the two above approaches are highly efficient for the separation of photo-induced charge carriers, it should be pointed out that the metal nanoparticle/1D TiO_2NSH is different when the metal nanoparticle is synthesized *in situ* on the 1D TiO_2 nanostructure rather than immobilized there. In the former case, it appears that the lattices are connected, but in the latter it appears that the nanoparticle is simply somehow physically attached to the surface of the 1D TiO_2 surface with a large gap between them.[34] (Fig. 8)

3.2 Metal oxide-1D TiO_2 nanostructured surface heterostructures

As stated in Section 1, we have described p-n junction, band matching, and visible light photocatalyst assembled 1DTiO_2NSHs as very efficient approaches to the construction of hybrid nanophotocatalysts. Most of the materials needed for building such 1DTiO_2NSHs are metal oxides; therefore metal oxide/1D TiO_2NSHs represent one of the most important areas in the discussion of1DTiO_2NSHs. There are many oxides that can be used as assembly particles for 1DTiO_2NSHs. Among the oxides, some are p-type semiconductors, which can be used to build p-n junction 1DTiO_2NSHs; some are n-type semiconductors, which can be used to build 1DTiO_2NSHs for band matching; some are photocatalytically active in the visible, and so can be used to build light wavelength broadened 1DTiO_2NSHs. In fact, normally the oxides for building 1DTiO_2NSHs often take on two or more functions that enhance the photocatalytic efficiency of the 1D TiO_2 nanostructure.

Metal oxide semiconductors with different band gaps can be used to tune the photocatalytically-active light band of a 1D TiO_2 nanostructure in the form of a 1DTiO_2NSH by prohibiting photo-induced carriers or by broadening the light harvesting wavelength. Suitable metal oxides for assembly on a 1D TiO_2 nanostructure to form 1DTiO_2NSHs comprise a very large family. Many methods have been developed to synthesize metal oxide/1D TiO_2NSHs, including sol-gel, solution decomposition, wet chemical deposition, hydrothermal reaction, and electrodeposition.

The first metal oxide nanoparticles used to decorate 1DTiO_2NSHs were TiO_2 nanoparticles. The most efficient way to synthesize a metal oxide assembled 1DTiO_2NSH is through the acid corrosion method. This method is simple, low cost, and very efficient. The synthesized TiO_2 nanobelts are reacted with dilute sulfuric acid at about 90^{o}C. During the acid corrosion process, TiO_2 nanoparticles can form *in situ* on the surface of the TiO_2 nanobelts through a dissolution-precipitation process.[25] The TiO_2 nanoparticles on the surface of the 1D TiO_2 nanostructure are in intimate contact with the nanobelt substrate to form well-defined heterostructures, which is beneficial to increase the number of photocatalytically active TiO_2 nanobelt sites and to improve the separation of photo-induced charge carriers. In addition, TiO_2 nanoparticles or TiO_2 nanorods can be assembled on the 1D TiO_2 nanostructures to form a 1D-1DTiO_2NSH by assembling a layer of TiO_2 nanoparticles as crystalons, and then growing them into nanorods during the hydrothermal process that follows. As shown in Fig. 9, the precursor concentration and the hydrothermal temperature can be used to tune the size and morphology of the TiO_2 nanorods on the surface of the TiO_2 nanowire,[35] and the photocatalytic efficiency of the 1DTiO_2NSHs can be controlled.

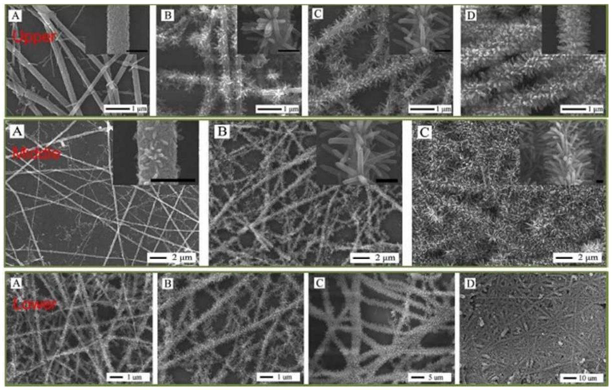


Fig. 9 SEM images of TiO_2 nanorods/1D TiO_2NSHs. Upper: prepared with different reaction time intervals: (A) 1 h, (B) 2 h, (C) 2.5 h and (D) 3 h; Middle: prepared in HCl solution containing 0.5 g titanium isopropoxide under hydrothermal reaction conditions for 2.5 h at temperatures of: (A) 130 ^{o}C, (B) 150 ^{o}C and (C) 170 ^{o}C; Lower: prepared under hydrothermal reaction conditions at 150 ^{o}C for 2.5 h in HCl solution containing different weights of titanium isopropoxide: (A) 0.4 g, (B) 0.5 g, (C) 0.7 g and (D) 1.0 g. For inset images, the scale bar is 200 nm.[35]

Although the TiO_2 nanoparticle- or TiO_2 nanorod-assembled 1DTiO_2NSH can improve the performance of 1D TiO_2 nanostructures, the scope is limited because the photocatalytically active wavelengths still lie only within the UV region, and the difference in band structure between the nanoparticles and the substrate is very small. To broaden the photocatalytically active wavelength band to the visible region, some other oxide semiconductor nanoparticles with visible light photocatalytic activity, such as Co_3O_4, Cu_2O, In_2O_3, MnO_2, Ag_2O, NiO, CeO_2, etc, have been considered to construct 1DTiO_2NSHs based on the above mentioned principle.[7] These 1DTiO_2NSHs have been shown to improve the UV and visible photocatalytic efficiency. Most of the oxide nanoparticle-assembled 1DTiO_2NSHs are synthesized by wet-chemical methods by dropping precipitant into a 1D TiO_2 nanostructure-dispersed precursor solution. The most important key for synthesizing these 1DTiO_2NSHs is to keep the particles at a small size and to have a proper density distribution in order to avoid having a thick dense layer of visible light photocatalytic nanoparticles blocking the UV light from the surface of the TiO_2 substrate.

3.3 Chalcogenide-1D TiO_2 nanostructured surface heterostructures

In contrast to metal oxide semiconductors, chalcogenides typically behave as narrow band gap semiconductors which respond to visible light irradiation. It has been reported that the band gap and band structure of chalcogenides can easily be tuned by the formation of a solid solution.[19] Therefore, coupling a chalcogenide with a 1D TiO_2 nanostructure to form a 1DTiO_2NSH cannot only increase the separation of photo-induced charge carriers (because of the alignment of the band structure of the chalcogenide and TiO_2), but also broaden light adsorption to the visible region in order to harvest more solar light. Therefore up to the present time, the fabrication and application of chalcogenide-decorated 1DTiO_2NSHs have been studied extensively. The chalcogenide in the heterostructure can either have a particulate shape with 1D morphology or a 2D structure. In the past 5 years, a large number of different chalcogenide nanoparticles, such as In_2S_3, CdSe, ZnTe, BiS_3, MoS_2, WS_2 quantum dots or 2D nanosheet-assembled $1DTiO_2NSHs$ have been successfully synthesized. Most recently, 2D sulfide nanosheets, several layered MoS_2 nanosheets, and assembled $1DTiO_2NSHs$ have proven to possess excellent properties, and should have many applications in a number of fields.[19]

Synthesis methods for chalcogenide nanoparticle-assembled $1DTiO_2NSHs$ can be divided into three main categories. The first involves the assembly of chalcogenide nanoparticles by the vapor deposition method. The second involves the synthesis of chalcogenide nanoparticles in advance, then the assembly of the synthesized nanoparticles onto the surface of the 1D TiO_2 nanostructure by an electrochemical method or a chemical bath method. The third method involves the *in situ* synthesis of chalcogenides on the surface of the 1D TiO_2 nanostructure by a wet-chemical method and hydrothermal process. All three methods possess their own advantages and drawbacks. The selection of a particular method must involve the desired properties and applications of the target $1DTiO_2NSHs$.

3.4 Complex compound-1D TiO_2 nanostructured surface heterostructures

The definition of a complex compound heterostructure in this section refers to a structure whose secondary phase on TiO_2 contains more than three elements in its formula, such as $Bi_4Ti_3O_{12}$, $SrTiO_3$, Bi_2WO_6, $BiVO_4$, $ZnTi_2O_4$, Ag_3PO_4, etc, as well as multi-component heterostructures. These ternary oxides are usually of the perovskite structure and have been found to be catalytically active. Many reports in the literature have covered the synthesis and application of these perovskite-decorated TiO_2 heterostructures.[12]

Recently, Cao *et al*[36] reported a simple two-step synthesis route to construct $Bi_4Ti_3O_{12}$/1D TiO_2NSHs. The route reported on is likely accessible to the formation of other ABO_3 material-decorated 1D TiO_2NSHs. In detail, the method involves an electrospinning process and a hydrothermal process. A TiO_2 nanofiber prepared by the electrospin method was used not only as the supporting material, but also as the Ti precursor for the hydrothermal *in situ* growth of $Bi_4Ti_3O_{12}$. This method can also be extended to the synthesis of other perovskites like $SrTiO_3$, $PbTiO_3$, and $BaTiO_3$ on 1D TiO_2nanostructures. In addition, doping with or solid solutions of oxides and chalcogenides are considered to be basic materials for building $1DTiO_2NSHs$. These complicated compounds provide more choices for the construction of high performance $1DTiO_2NSHs$ for different applications.

3.5 Conducting polymer-1D TiO_2 nanostructured surface heterostructures

In 2000, the Nobel Prize was awarded for work related to polyaniline (PANI). The prominent advantages of conducting polymers, such as high electrical conductivity, low energy optical transitions, low ionization potential and high electron affinity, have attracted the attention of many researchers, and numerous applications of conducting polymers in photocatalysis, photochemistry, energy conversion and energy storage have been reported.[37] The nature of the conductivity of conducting polymers mainly originates from the overlapping of molecular orbitals and on partially filled molecular orbitals which aids the free movement of electrons throughout the polymer structure. Coupling a conducting polymer with a 1D TiO_2 nanostructure can bring about remarkable improvement in the TiO_2 properties, such as increased electrical conductivity, increased flexibility, ability to manipulate the band structure, etc. Conducting polymers mainly include polyaniline (PANI), polypyrrole (PPy), polythiophene (PTH) and their derivatives. By contrast with the synthesis of inorganic materials, the preparation of conducting polymers often involves complex reactions. Until now, the synthetic methods that are used involve polymerization using designed procedures, such as the electrochemical method, chemical oxidation polymerization, the hydrothermal method, and vapor phase deposition. Because most conducting polymers are p-type, the p-n junction plays an important role in enhancing the performance of 1D TiO_2 nanostructures.

4. Applications of one-dimensional TiO_2 nanostructured surface heterostructures

As previously described in Section 3, various kinds of $1DTiO_2NSH$ have been fabricated using different kinds of simple but effective strategies. Because of the synergistic effect of multiple components, $1DTiO_2NSHs$ can exhibit multifunctional unique properties. Therefore, such $1DTiO_2NSHs$ are expected to have applications in many fields, such as photocatalysis, dye-sensitized solar cells, sensors, lithium batteries, biomedicine, catalysis, and supercapacitors. In this section, we briefly discuss the various applications of $1DTiO_2NSHs$.

4.1 Photocatalysis

Because the excellent basic UV light-sensitive photocatalytic activity of 1D TiO_2 nanostructures and the ease of assembly of various photocatalytic nanoparticles on its surface, the $1DTiO_2NSH$ is predetermined to be used in photocatalysis. As discussed in Section 1, a $1DTiO_2NSH$ endows TiO_2 with more light harvesting ability, a broadened absorption band, and a large amount of light-induced carrier separation, so it will have a great number of applications in the photocatalytic degradation of pollutants, photocatalytic water splitting for hydrogen generation, and photocatalytic disinfection.

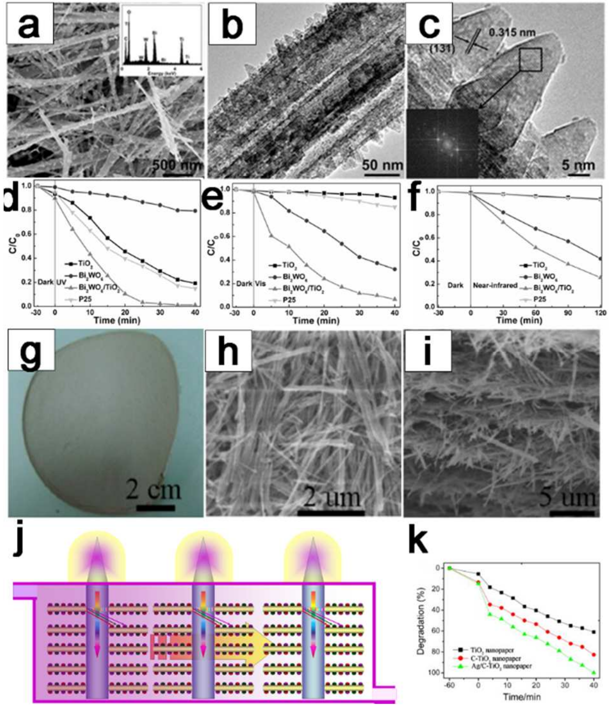


Fig. 10 (a) SEM image of Bi_2WO_6/TiO_2 nanobelt heterostructures. EDS of Bi_2WO_6/TiO_2 nanobelt heterostructures is shown in top inset; (b, c) TEM images of Bi_2WO_6/TiO_2 nanobelt heterostructures; Photocatalytic degradation of MO under (d) UV light, (e) visible light, and (f) near-infrared light irradiation;[12] (g) Optical photographs and (h,

i) SEM images of Ag/C-TiO$_2$ nanopaper; (j) Schematic diagram of continuous flow photocatalysis device; (k) continuous-flow photocatalytic treatment of methyl orange (MO) aqueous solution with different TiO$_2$ nanopapers.[8]

4.1.1 Photocatalytic degradation of pollutants

In Section 1, we demonstrated all of the design principles for high performance 1DTiO$_2$NSH photocatalysts. In fact, many different kinds of design principles have been employed in their synthesis and have subsequently been experimentally investigated. Noble metal nanoparticle (Ag, Pt, Pd)-assembled 1DTiO$_2$NSHs with a Schottky heterostructure, NiO and Ag$_2$O nanoparticle-assembled 1DTiO$_2$NSHs with a p-n heterostructure, CeO$_2$ nanoparticle-assembled 1DTiO$_2$NSHs with a band matching heterostructure and capture-degradation-release mechanism, ZnO and TiO$_2$ nanorod-assembled 1DTiO$_2$NSHs with a 1D-1D heterostructure, graphene and MoS$_2$ nanosheet-assembled 1DTiO$_2$NSHs with a 2D-1D heterostructure, and Ag$_2$S-Ag$_2$O and Bi$_2$O$_3$-Bi$_4$Ti$_3$O$_{12}$-assembled 1DTiO$_2$NSHs with a double heterostructure, have been successfully synthesized, and their application in photocatalysis has been thoroughly investigated.[7] The earliest work on a 1DTiO$_2$NSH photocatalyst was reported by Liu's group, which first demonstrated great improvement in the performance of TiO$_2$ nanobelts in a 1DTiO$_2$NSH constructed by taking Ag$_2$O nanoparticle-assembled 1DTiO$_2$NSHs as an example.[11] Recently, by assembling visible-infrared light photocatalytically active Bi$_2$WO$_6$ nanosheets on TiO$_2$ nanobelts, a UV-visible-infrared broad spectrum-active photocatalytic 1DTiO$_2$NSH material has been obtained, one which opens new doors in photocatalysis applications by using the entire solar energy spectrum (Fig. 10a-f).[12]

Because of the 1 D character and the abundance of hydroxyl groups in 1DTiO$_2$NSHs, they can be prepared in the form of a paper-like membrane structure (Fig. 10g-i), which has been used in a the design of a continuous flow photocatalysis device (Fig. 10j-k).[8] This device will undoubtedly have a practical applications in the environmental industry.

4.1.2 Photocatalytic hydrogen generation

The semiconductor band structure required for the degradation of organic pollutants and water splitting is different, although the photocatalysis mechanisms are similar. Clearly, photocatalytic water-splitting for hydrogen generation is a most important topic in the application of 1DTiO$_2$NSHs. Similarly, by using Schottky, p-n junction, band matching, visible light-active photocatalyst assembly, and other design principles, the water splitting ability and active light absorption band can be tuned over a large range, and the water splitting efficiency and hydrogen generation ability of the 1DTiO$_2$NSH can be improved.

Previous studies have shown that noble metal nanoparticle-assembled 1DTiO$_2$NSHs, some metal oxide, complex oxide, and chalcogenide nanoparticle-decorated 1DTiO$_2$NSHs, MoS$_2$ nanosheets and reduced graphene oxide-assembled 1DTiO$_2$NSHs, multi-heterostructured 1DTiO$_2$NSHs (such as In$_2$O$_3$-Pt-TiO$_2$ heterojunctions), and solid solution chalcogenide complex (CdSeS) 1DTiO$_2$NSHs, possess enhanced hydrogen generation ability under simulated solar light irradiation, compared to bare 1D TiO$_2$ nanostructures.[19] Because there is a great family of 1DTiO$_2$NSHs used for hydrogen generation photocatalysts as mentioned in Section 1, 1DTiO$_2$NSHs also represent one of the most important types of water splitting photocatalysts.

4.1.3 Photocatalytic disinfection

TiO$_2$-mediated disinfection has been considered a promising process compared to the common disinfection methods such as chlorination and UV disinfection, because of its strong oxidizing power, non-toxicity, and long-term photostability, and also because it requires negligible or no maintenance. Since, due the unique properties of 1DTiO$_2$NSHs, they can enhance the photocatalytic properties of TiO$_2$ under UV and visible-light irradiation, 1DTiO$_2$NSHs may potentially be used to enhance antibacterial activity. For example, Amna *et al.*[38] illustrated that NiO/TiO$_2$ nanofibers were able to destroy more than 80% of four common food-borne pathogenic bacteria viz., *Staphylococcus aureus*, *Escherichia coli*, *Salmonella typhimurium*, and *Klebsiellapneumoniae*. The antibacterial activity was attributed to the release of a reactive oxygen species (ROS) that caused cell membrane damage followed by damage to the interior molecules, eventually causing the death of the bacterium. The introduction of Ni dopant into TiO$_2$ nanofibers enhances the antibacterial performance.

4.2 Dye-Sensitized Solar Cells (DSSCs)

The nanostructured dye-sensitized solar cell (DSSC) is considered to be one of the most promising technologies for achieving the goal of high efficiency and low cost in the utilization of solar energy. When sensitized with organic dyes or inorganic narrow band gap semiconductors, TiO$_2$ can absorb visible light and convert solar energy into electrical energy. For solar cell applications, the TiO$_2$ nanoparticle network acts as the photoanode of the DSSC, with an overall efficiency of only ≈12% due to electron loss during percolation through the nanoparticle network and photo-induced carrier recombination.[39]

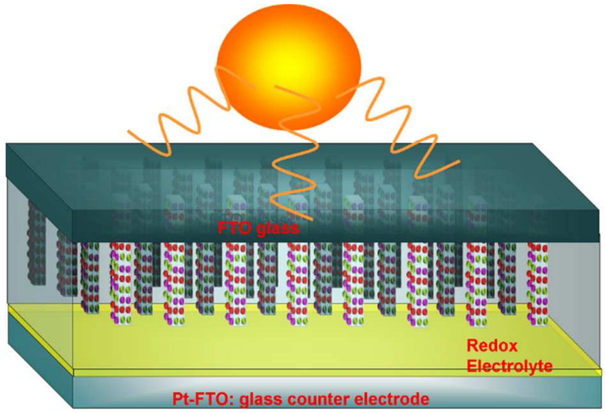


Fig. 11 Schematic diagram of 1DTiO$_2$NSH dye-sensitized solar cells

To overcome the drawbacks of granular TiO$_2$ nanoparticles, a 1D TiO$_2$ array is often used as the photoanode to improve electron transfer ability. However, the main drawback of the nanoarrays is the lack of photocatalytically active sites, with too long a path for electron transfer, which in turn favors photo-induced carrier recombination. As shown in Fig. 11, following the design, the 1DTiO$_2$NSH can solve all of the above problems by assembling specially selected compound nanoparticles. Recently, 1DTiO$_2$NSH dye-sensitized solar cells have been reported on extensively. They usually reduce optical reflection, improve absorption and charge carrier collection efficiency. Electrochemical TiO$_2$ nanotube array-based 1DTiO$_2$NSH photoanodes, such as SrTiO$_3$, CdSe, CdS, and Zn$_x$Cd$_{1-x}$Se sensitized 1DTiO$_2$NSH, have been prepared and demonstrated that they can improve DSSC efficiency.[40] It is believed that 1DTiO$_2$NSH will become a very important component in the development of high performance solar cells.

4.3 Sensor applications

Nanostructured sensors, including gas sensors and light sensors, are very important components for the *internet of things*. Many of the sensors are based on the chemical, physical and electrochemical properties of nanomaterials. The operation of the sensors relies on the density of active sites on the nanomaterial surface and on the electron transfer ability within the nanomaterial. 1D nanostructures are ideal building block materials for sensors, because of the high electron transfer rate along their length. However, their sensory capability is limited due to the lack of active sites. Assembling secondary phase nanoparticles on the surface of a 1D TiO_2 nanostructure can preserve its high charge transfer ability, increase the number of active sites, and even change the basic sensory properties. Therefore, $1DTiO_2NSHs$ can be used to enhance the sensory performance or to endow TiO_2 with new sensory properties by providing more gas adsorption sites, a larger surface area, and additional sensory capability from the second phase nanoparticles. Recent results illustrate that $1DTiO_2NSH$ can improve the gas sensing performance of TiO_2, including improvement in the sensitivity and lowering of the gas activity temperature.[41, 42] For example, Liu's group[41] reported that the sensitivity of Ag-TiO_2 nanobelt $1DTiO_2NSHs$ showed a strong dependence on ethanol exposure, even at relatively low concentrations (20 ppm). (Fig. 12) Beside TiO_2 nanobelts, TiO_2 nanotubes have also been used for building $1DTiO_2NSHs$ for gas sensor applications, such as α-Fe_2O_3/TiO_2 nanotube heterostructures, Co_3O_4/TiO_2 nanotube p-n heterostructures, and SnO_2-Pd/TiO_2 nanotube multi-heterostructures, all of which have demonstrated good enhancement of gas sensor properties.[42]

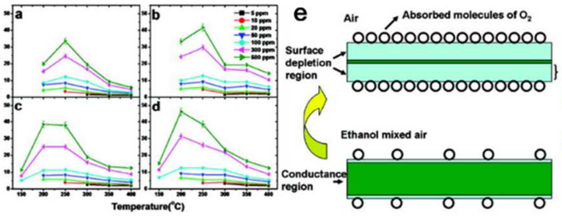


Fig. 12 Variation of sensitivity (R_a/R_g) with working temperature of four different kinds of sensor based on (a) TiO_2 nanobelts, (b) Ag-TiO_2 nanobelts, (c) surface-coarsened TiO_2 nanobelts, and (d) surface-coarsened Ag-TiO_2 nanobelts, to ethanol vapor of different concentrations; (e) sensing mechanism of Ag-TiO_2 nanobelts to ethanol.[41]

4.4 Electrochemical energy storage

$1DTiO_2NSHs$ received considerable research attention in development of electrochemical energy storage technologies, including lithium-ion batteries and supercapacitors, because of their high surface areas, favorable transport properties, and short ion path lengths. These merits could benefit these energy storage applications by (1) providing a large surface area to improve the electrochemical reaction at the interface, and (2) facilitating the electron or ion transport and electrolyte diffusion, which attribute to the high crystallinity or porous structure, so as to lead to higher capacities at high charge/discharge rates and ensure the electrochemical process occurs with high efficiency.

4.4.1 Lithium-ion batteries (LIBs)

Titanium dioxide (TiO_2) is one of the most promising anode materials available for lithium ion batteries due to its low cost and structural stability during Li insertion/extraction. In contrast to the general conversion mechanism exhibited by mixed metal oxide anodes, TiO_2 is a typical Li^+ intercalation compound. The reaction can be expressed as:

$$xLi^+ + TiO_2 + xe^- \leftrightarrow Li_xTiO_2\ (0 \leq x \leq 1) \qquad (1)$$

The Li insertion/extraction into TiO_2 causes very small volume change (<4%), and hence TiO_2 possesses good rate capability and stability during long duration charge/discharge processes. For granular TiO_2, the large interfacial area between the nanoparticles inhibits ion diffusion and so the volume variation may also be magnified during the charge/discharge process. The 1D TiO_2 nanostructure is a layered structure and has excellent mechanical properties, which ensure structural stability during Li-ion insertion/extraction. However, the energy storage ability of the 1D TiO_2 nanostructure is still not very high because of its inherently low electrical conductivity. One strategy to address these issues is the use of $1DTiO_2NSHs$. The large surface area of $1DTiO_2NSH$ materials increases the electrolyte/electrode contact area, which in turn leads to a decrease in the current density and an increase in the charge/discharge rate. Moreover, the nanostructure provides a shorter path for Li^+ transport, permitting the battery to use materials with lower ionic conductivity. The large surface area, on the other hand, incurs more side reactions with the electrolyte, and the thickness of the solid electrolyte interface layer may be larger than in the case of bulk TiO_2, thereby impeding electron and Li-ion transport in and out of the structure. Owing to their mesoporous structure, the large surface-to-volume ratio, the efficient transport of lithium ions, good ion-exchange ratio, and better accommodation of lithiation-induced stresses, $1DTiO_2NSH$ electrode materials exhibit a high charge/discharge capacity, good kinetic characteristics, and very good robustness and safety.

The performance of $1DTiO_2NSH$ electrodes at high discharge/charge rates is undesirable partly due to the aggregation tendency of the 1D TiO_2 nanomaterials, which leads to an increase in interparticle contact resistance. So, mixing the 1D TiO_2 nanostructure with highly conductive materials in a $1DTiO_2NSH$, such as C/TiO_2 nanowires, C/TiO_2 nanotubes, functionalized graphene sheet/TiO_2 nanorods, and Sn/TiO_2 nanotubes, can effectively solve this problem.[21]

Metal oxides have also been considered as anode materials for LIBs, and they have respective advantages when used as such. Thus metal-oxide/$1DTiO_2NSHs$ for LIBs most usually combine the 1D TiO_2 nanostructure, which has good cycling performance for enhancing LIB capacity with other metal oxides that enhance the LIB capacity such as, SnO_2, RuO_2, etc.[22] The objective of these studies is to obtain electrodes with high capacity and good stability upon cycling in order to meet the application requirements of LIBs for industry.

4.4.2 Supercapacitors

In recent years, electrochemical supercapacitors have attracted a great deal of attention for use in energy storage. Their performance is comparable to or superior to that of either regular batteries or the standard type of electrolytic capacitor due to their high power density, moderate energy density, safe operation, and long life cycle. One of the most important types of supercapacitor is the pseudocapacitor. Although the charge storage capacity of a pseudocapacitor is typically larger than that of other types of supercapacitor, or electrochemical double layer capacitors, the active materials in the faradic pseudocapacitor suffer from the disadvantages of higher cost, poor rate capability, and low conductivity. As the electrode material of a pseudocapacitor, a 1D TiO_2 nanotube array can overcome most of drawbacks of the pseudocapacitor, but the charge storage ability of TiO_2 nanotubes is too low to be practicable. Therefore, assembling RuO_2 and MnO_2 on a 1D TiO_2 nanostructure is an efficient approach to obtaining a low-cost, high performance pseudocapacitor.[43] For example, the symmetric supercapacitor formed by RuO_2 nanoparticle-decorated TiO_2 nanotube arrays using the gel polymer PVA-H_3PO_4-H_2O as the electrolyte have even attained a maximum specific capacitance of 1263 F/g.[43] As a new category of pseudocapacitor electrode, carefully designed $1DTiO_2NSHs$ will prove to be one of the most important hybrid electrodes for use in high performance supercapacitors.

In addition to metal oxides, conducting polymers have also been considered for use in the fabrication of supercapacitors. Polyaniline (PANI) has been extensively studied for this purpose because of its relatively high conductivity, low cost, facile synthesis and fast doping/dedoping rate. The research results show that a PANI nanowire/TiO_2 nanotube array synthesized by a low-cost electrochemical deposition method possesses excellent supercapacitor properties.[44]

4.5 Biological applications

Recently, research has demonstrated that $1DTiO_2NSHs$ have great potential for applications as biochemical sensors, in controlled drug delivery, and in the engineering of artificial tissue construction.[45] For biosensor applications, a well-designed $1DTiO_2NSH$ should exhibit enhanced electron-transfer kinetics and a strong adsorption capability, providing suitable micro-environments for the immobilization of biomolecules, resulting in enhanced electron transfer and improved biosensing characteristics. These materials can be used for the detection of biomolecules and some biomedicinal component molecules. The unique properties of $1DTiO_2NSHs$ offer excellent prospects for interfacing biological recognition events with electronic signal transduction and for designing a new generation of bioelectronics devices that could exhibit novel functions. Tang *et al*[46] reported a new glutathione biosensor based on IrO_2/hemin/TiO_2 nanowire arrays. The detected photocurrent capacity of the $1DTiO_2NSH$ array is double that of pristine TiO_2 nanowires, and exhibits label-free, real-time, sensitive photo-electrochemical detection of glutathione. The $1DTiO_2NSH$ array constructed by assembling p-type BiOI nanoflakes on an n-type TiO_2 nanotube array presented a sensitive detection of cancer biomarkers such as the vascular endothelial growth factor (VEGF).[16] The Liu group's research has shown that NiO-TiO_2 nanobelt p-n $1DTiO_2NSHs$ have an almost ideal capability for the electrochemical detection of anticancer drugs and their bio-interactions with cancer cells when compared with bare TiO_2 nanobelts.[47]

Another very important biological application of $1DTiO_2NSHs$ is in biomedical applications. Titanium and its alloys are one of the most important biomaterials used in implants for medical treatment. There has been a great deal of work on the construction of TiO_2 nanostructures, such as nanorods, nanotube arrays, and *in situ* grown nanobelt layers that can improve adhesion, the differentiation potential for stem cells, and biocompatibility. However, for implants, bacterial infection is a big postsurgical problem. By assembling Ag nanoparticles on the surface of a TiO_2 nanotube or nanowire, enhanced antibacterial performance can be realized. Pisareka *et al*[48] reported that Ag/TiO_2 nanotube arrays grown on a titanium substrate possess both biocompatibility and antibacterial activity, thus providing a promising technique for improving bio-implant design and preparation.

4.6 Catalysis

Titanium dioxide is at present among the most intensely studied oxides due to its interesting electrochemical properties. It is employed as a catalyst and metal catalyst support in various hydrogenation and selective oxidation reactions. There are many examples of using a $1DTiO_2NSH$ as a mesoporous catalyst support: Pd/TiO_2 nanotubes, Pt/TiO_2 nanotubes, Pt-Ru/TiO_2 nanotubes, and Pt-Ni/TiO_2 nanotubes as catalysts for the oxidation of methanol; Pt/TiO_2 nanotubes, Pt-Ni/TiO_2 nanotubes, and Pt-Co/TiO_2 nanotubes as catalysts for the reduction of O_2; Au/TiO_2 nanotubes and Au-Cu/TiO_2 nanotubes as catalysts for CO oxidation; RuO_2/TiO_2 nanotubes as an electrocatalyst for the reduction of CO_2; $Ru(OH)_3$/TiO_2 nanotubes and V_2O_5/TiO_2 nanotubes as catalysts for the selective oxidation of ethanol; Au/TiO_2 nanowires, Rh/TiO_2 nanowires, and Au-Rh/TiO_2 nanowires as catalysts for the decomposition of ethanol and the hydrogenation of CO_2; Cu^{2+}/TiO_2 nanotubes and Cu/TiO_2 nanotubes as catalysts for the selective reduction of NO with NH_3; and Pt-Ir/TiO_2 nanotubes as catalysts for the hydrogenation of cyclohexene (CHE).[49]

For example, Liu's group investigated the aerobic oxidation of benzyl alcohol by Au-Ag/TiO_2 nanobelt paper (Fig. 13).[50] It can be seen that the Au-Ag/TiO_2 nanobelts are active for catalyzing benzyl alcohol to benzaldehyde with high selectivity (>99%). The synergistic effect between the Au and Ag species endows improved catalytic activity to the bimetallic nanoparticles when compared to that of monometallic counterparts.

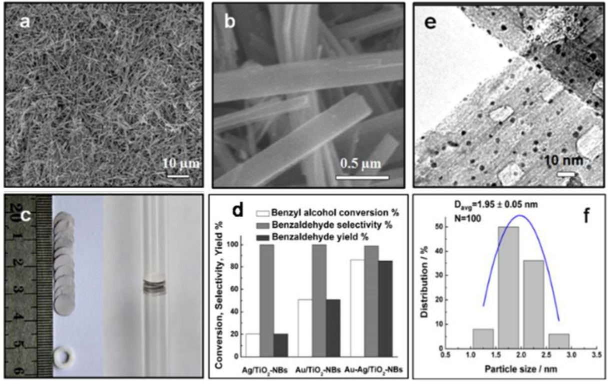


Fig. 13 (a, b) SEM images and (c) digital pictures of Au-Ag/TiO_2 nanobelts paper; (d) the benzyl alcohol oxidation over paper catalysts of Au-Ag/TiO_2 nanobelts, Au/TiO_2 nanobelts, and Ag/TiO_2 nanobelts; (e) TEM image and (f) corresponding particle size distribution of Au-Ag/TiO_2 nanobelts after reaction for 30 h at 240 °C.[50]

Summary and outlook

This review summarizes the design principles, synthesis and applications of $1DTiO_2NSHs$. It also discussed the many emerging opportunities for the application of $1DTiO_2NSHs$ in various fields. The information collected in this manuscript is trying to figure out the current applications and challenges associated with $1DTiO_2NSHs$, to give up whole image of $1DTiO_2NSHs$ and share the information in front of the world-wide research. There is little doubt that $1DTiO_2NSHs$ represent an important category of hybrid nanomaterials in energy and environmental applications, including photocatalysis, solar cells, sensors, lithium ion batteries, catalysis, and supercapacitors. However, until now, all of the design synthesis and useful properties of $1DTiO_2NSHs$ have been based on physics and solid-state chemistry. There is very little work that has demonstrated theoretical design using numerical simulation of these hybrid materials. In the near future, with the further development of the theoretical underpinnings and the enhancement of computational capability, researchers will be able to predict the properties of $1DTiO_2NSHs$ based on their material components, size and morphology. Therefore, the composition and morphology of the second phase component of the $1DTiO_2NSHs$ can be designed to fit the property requirements for different applications. After understanding the design of $1DTiO_2NSHs$, some specially designed $1DTiO_2NSHs$ with unique opto-electronic, energy harvesting, photocatalytic, and even biosensor properties can be synthesized, and will be able to be dedicated to more practical real-life application. The likelihood of more interdisciplinary effort in this area will be improved and will result in more applications of $1DTiO_2NSH$ materials in many new fields.

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Notes and references

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Key learning points

(1) Design principles of one-dimensional TiO_2 nanostructured surface heterostructures ($1DTiO_2NSHs$).
(2) Summary of synthesis methods of 1D TiO_2 nanostructures and $1DTiO_2NSHs$.
(3) Comprehensive overview of recent advanced applications of $1DTiO_2NSHs$.
(4) Relationship between the secondary phase and the 1D TiO_2 nanostructure, and between the performance in applications and the excellent physical properties of $1DTiO_2NSHs$.

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