Recent advances in TiO$_2$ nanoarrays/graphene for water treatment and energy conversion/storage

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ABSTRACT   Although TiO$_2$-based nanostructures with unique chemical and physical properties exhibit great promise in water treatment and energy conversion/storage, there still exist some limitations. In order to further improve the photochemical properties, one-dimension TiO$_2$ nanoarrays on the substrate are primarily combined with graphene by various preparation technologies. The composite coating has exhibited extraordinary photocatalytic abilities in the degradation of organic pollutants into less toxic compounds, antimicrobial activity and adsorption capacity in water treatment. Especially, it is easy to recycle after photocatalytic reaction. Additionally, TiO$_2$ nanoarrays/graphene on the substrate (especially flexible substrate) could provide potential opportunities for flexible-device fabrication with excellent photovoltaic conversion efficiency and electrochemical performance in energy conversion/storage devices. As far as we know, the relevant reviews have rarely been reported. Here, we present a comprehensive review on the preparation of TiO$_2$ nanoarrays or TiO$_2$ nanoarrays/graphene, and their application and mechanism in water treatment and energy conversion/storage.

Keywords: TiO$_2$ nanoarrays, graphene, photocatalysis, water treatment, energy conversion/storage

INTRODUCTION

While incredible progress in science and technology has indeed raised the quality and standard of human life and health, a multitude of problems have been brought about as well, such as energy shortage and environmental problem. Among them, water pollution is one of the biggest and the most alarming problems which demands formidable and effective solutions [1]. In the sea and lake, algal bloom caused by the eutrophication of the water, causes many concerns about water quality, because the presence of cyanobacteria can potentially produce toxins named cyanotoxins and off-odor compounds. Microcystins (MCs) are the most widespread cyanotoxins which exist in diverse aqueous environments [2]. MCs in water can cause acute and chronic toxicity to humans, bringing about mortality, loss of production, and decrement of productivity in aquaculture, and they also have the potential to harm consumers through the food web, *via* accumulation in freshwater fish [2]. In the recent years, there was a noticeable increase in the frequency of harmful algae blooms outbreaks in the sea and lake. Although huge initiatives have been already adopted to tackle the problem, further and thorough research dedicated to this issue is still required.

Moreover, in the case of water treatment technology, there are biodegradable technology, coagulation/precipitation techniques, and Fenton oxidation treatment technology [3–8], which are shown in Table 1. Although the treatment efficiency of these methods is high, the use of chemicals will bring about other environmental problems such as pipe blockages and water deterioration. Therefore, the advanced technology using photocatalysis is attracting more attention, owing to ·OH with strong oxidizing properties, which completely degrades almost all organic pollutants and has great antimicrobial activities in water treatment [9].

Simultaneously, the ever-increasing demand for energy is accompanied by the rapid growth of the global population and urbanization. Rapid energy consumption has resulted in the search for green and renewable alternative energy solutions. Ideally, solar energy, a clean and inexhaustible energy source, has great potential to meet the stringent energy demands [10]. Fundamentally, how to efficiently utilize and convert abundant solar energy remains a significant and urgent challenge for researchers. Solar cells are regarded as a suitable choice for harnessing and utilizing sunlight to drive chemical

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Table 1 Comparing the advantages and disadvantages of photocatalytic system and existing water treatment methods [4,7,8]

	Advantage	Disadvantage
Biological treatment technique	(1) High reliability of the method (2) High load operation can be processed	(1) Efficiency is low (2) Limited by biological species
Coagulation/precipitation	(1) High efficiency of processing	(1) Pipe blockages and water deterioration (2) Environmental problems
Fenton oxidation technology	(1) ·OH break down organic pollutants (2) Process is simple and easy to manage	(1) Limited by the Fenton's reagent (2) Remove the iron salts (3) Need the acidic conditions, pH<4
Photocatalytic oxidation technology	(1) Complete waste water treatment is possible (2) Low cost (3) Green, friendly to environment (4) Antimicrobial and degrading all compounds	(1) Limited by UV absorption (2) Photocatalyst powder is difficult to recover

reactions and produce electricity. Additionally, energy storage such as lithium-ion batteries (LIBs) has also been widely applied in portable digital products instead of the consumption of fossil fuels [11]. However, the energy density of LIBs is inadequate to satisfy the continuous growth in demand. It is essential to explore cathode/anode materials with high specific capacity, excellent rate capability and long cycle life.

TiO$_2$ is widely used mainly due to its non-toxicity, hydrophilicity, low cost, high photocatalytic activity, strong optical absorption, high chemical stability, and its suitable flat band potential (V_{fb}) that can induce desired redox reactions without bias potential [12,13]. The excitation of TiO$_2$ by photons with light energy greater than the band gap is the primary process underlying its vast area of photochemistry and photo-electrochemistry, as shown in Fig. 1 [14]. Therefore, TiO$_2$ has attracted significant attention because of its promising applications in wastewater purification as well as energy conversion/storage. The various applications of TiO$_2$ photocatalysis in recent years are shown in Fig. 2.

In the case of the advanced water treatment technology, the photocatalytic TiO$_2$ produces reactive oxygen-containing radicals (·OH, ·OOH, ·O$_2^-$). Among them, the hydroxyl radical (·OH) is the most reactive and powerful oxidant that decomposes the organic compounds into relatively harmless compounds, such as CO$_2$, H$_2$O, as shown in Table 2 [15]. In addition, the operating cost can be reduced dramatically. However, TiO$_2$ particles, the typical photocatalytic materials, have some shortcomings in the process. Firstly, TiO$_2$ can be only activated under the irradiation with photons of light in the UV domain (≤387 nm), and thus the light utilization efficiency to solar irradiation is limited, which causes the low photocatalytic properties. Secondly, when used as photocatalyst, particles have some disadvantages, such as
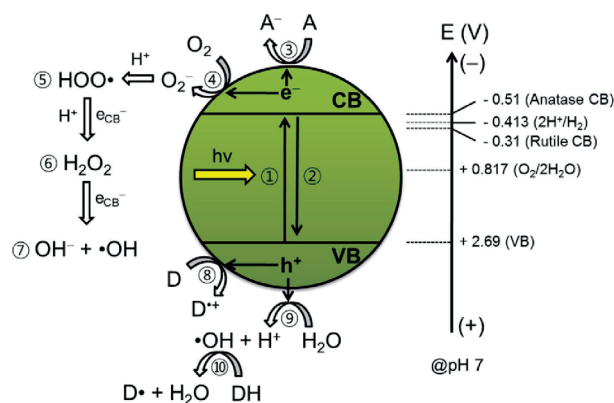
Figure 1 Schematic illustration for energetics and primary reaction mechanism of TiO$_2$ photocatalysis. 1: Bandgap (E_g) excitation and electron–hole charge pair creation, 2: the charge pair recombination, 3: electron transfer to electron acceptor (A: usually dissolved oxygen), 4: electron transfer to oxygen molecule, 5: formation of hydroxyperoxyl radical *via* a reductive pathway, 6: formation of hydrogen peroxide, 7: formation of hydroxyl radical, 8: hole transfer to electron donor (D: usually organic pollutants), 9: hole transfer to surface hydroxyl group to generate OH radical, 10: hydroxyl radical-mediated oxidation of organic substrate. Note that the energy levels (right arrow) shift according to the Nernst equation: $E(V_{NHE}) = E^0(@pH\ 0)–0.059pH$. Reprinted with permission from Ref. [14], Copyright 2013, Elsevier.

the particle defects, large grain boundaries, surface states and a low light response. These undesirable phenomena might decrease the electron transport rate, and eventually lead to poor charge collection efficiency. Additionally, TiO$_2$ particles are difficult to disperse, and are not easy to recover after photocatalytic reaction, which cause environmental pollution. Therefore, it is necessary to introduce a novel form of TiO$_2$ to solve these problems.

One-dimensional (1D) TiO$_2$ nanostructures, including nanorods [16,17], nanowires [18], nanotubes [19,20], nanofibers [21] and nanobelts [22], are recognized as one of the most promising materials to provide a direct electric transport pathway for efficient charge collection
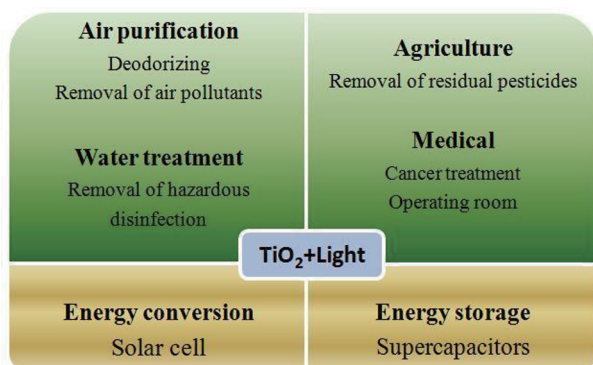
Figure 2 Various applications of TiO₂ photocatalysis in environment and energy fields.

Table 2 Redox potential of major oxidizing agents used in water treatment technology. Reprinted with permission from Ref. [8], Copyright 2017, Elsevier

Oxidizing agent	Oxidation potential (V)	Relative oxidation power
OH radical	2.80	2.06
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Perhydroxyl radical	1.70	1.25
Permanganate	1.68	1.24
Chlorine dioxide	1.57	1.15
Chlorine	1.36	1
Oxygen	1.20	0.88

[23]. Compared with their particles counterpart, 1D nanomaterials have unique chemical and physical properties which can be tailored by changing their nanoscaled 1D morphologies [24]. Firstly, the 1D nanostructures facilitate fast electron transport along the longitudinal dimension, significantly improving the charge separation efficiency; secondly, 1D nanoarrays are expected to have a larger specific surface area and pore volume as compared with the corresponding powder materials, providing more active sites; thirdly, based on the high length-to-diameter ratio for the 1D nanostructures, light absorption and scattering are thought to be significantly enhanced. In addition, fewer localized states due to the surface state of a specific facet of the nanocrystals also help to get the highly efficient photocatalysts. 1D TiO₂ nanostructures have shown outstanding performance and versatility in a wide range of applications [25–30]. Yu et al. [31] reported that 1D nanomaterial-based membranes possessing interconnected open pore structures and large surface

areas, were widely used to remove oily contaminants, toxic metal ions, emulsions, nanoparticles, small organic molecules such as antibiotics and dyes from water. Especially, 1D TiO₂ nanoarrays on the substrate are not only very easy to recover after the photocatalytic reaction, but also can increase the electron transport rate, and then improve the photocatalytic properties. In order to further limit the recombination of photoelectron-hole pairs during excitation state and maximize the light absorption, graphene is primarily combined with TiO₂ nanostructure by various preparation technologies. Furthermore, to highlight the research progress in the 1D TiO₂ nanoarrays/graphene and promote their better use, it is necessary to summarize the 1D TiO₂ nanoarrays and their nanocomposite in water treatment and energy conversion/storage.

Recently, several reviews have discussed some aspects of TiO₂-based nanomaterials and their applications [1,11,23,29]. However, review about 1D TiO₂ nanoarrays/graphene has rarely been reported until now. Here, we make great efforts to present a comprehensive review of 1D TiO₂ nanoarrays/graphene in water treatment and energy conversion/storage.

DESIGN OF TiO₂ NANOARRAYS/ GRAPHENE COMPOSITES

Owing to the 3.2 eV band gap of TiO₂, its photocatalytic activity is restricted to the ultraviolet region. Several strategies such as doping [32,33], introduction of defects [34,35] and combination with electron acceptor materials [36,37], have been tried to reduce the band gap to make it active in visible region. Graphene is the preferred candidates as electron acceptors owing to its outstanding physical, chemical and electronic properties [38].

Graphene, a novel two-dimensional carbon material with only one atom thick, is considered as the thinnest and hardest material known so far. Owing to single layer of sp² network of carbon atoms, graphene inherently displays a large number of intriguing and peculiar properties such as optical transparency, high room temperature charge carrier mobility (100,000 cm² V⁻¹ s⁻¹), excellent mechanical strength (2.4±0.4 TPa), theoretically large surface area (2,630 m² g⁻¹), high thermal conductivity (2,000 to 5,000 W m K⁻¹) and high capacity sustained at large current density (10⁸ A cm⁻²) [1,39], which make it exceptionally suitable for electron acceptor in versatile applications. In the last two decades, the term "graphene" has been used loosely in the literature to represent pristine graphene, graphene oxide (GO), and reduced

graphene oxide (rGO), which obtain immense interest among researchers and attract an inundation of studies devoted to various aspects of graphene [40].

Coupling TiO_2 with graphene could greatly enhance the photocatalytic performance [41,42]. On the one hand, the electric field integrally formed at the heterojunction interface can effectively separate the photoelectrons-holes in TiO_2 [43–46]. On the other hand, the combination of TiO_2 with graphene leads to the reduction in band gap of the TiO_2 by energy favored hybridization of O_{2p} and C_{2p} atomic orbitals which result in the formation of new valance band [36]. Compared to pure materials, TiO_2/graphene composite materials exhibit enhanced activities due to the synergistic effect of graphene and TiO_2 [47–49]. For instance, self-assembly of TiO_2 nanorods on the graphene oxide sheets (GO-TiO_2 NRCs) has been achieved by a water/toluene two-phase process. Compared with GO-P25 and the original TiO_2 nanorods, the GO-TiO_2 NRCs exhibit higher photocatalytic activity toward degradation of contaminant methylene blue and acid orange 7 under UV light irradiation [50]. Photocatalytic activities of the composite highly depend on the interface between TiO_2 and graphene. An intense coupling between TiO_2 nanorods and graphene facilitates charge separation and so retards the recombination of the photogenerated hole-electron pairs in the composite [51]. Therefore, coupling TiO_2 nanoarray with graphene on the substrate has wonderful prospect in water treatment and energy conversion/storage, which deserves further rigorous research in the future.

In particular, some mechanisms of photocatalytic activities of TiO_2/graphene composites have been proposed. As a p-type semiconductor, graphene can act as extremely effective electron sinks, which can create a Schottky barrier at the TiO_2/graphene interface (a space charge region) [52]. TiO_2 acts as an n-type semiconductor, but in the presence of graphene, photoinduced electrons may migrate freely to the graphene surfaces, which might have a lower Fermi level like a metal. Another possible mechanism is that graphene may act as a photosensitizer. This might be responsible for extending the TiO_2 photocatalytic activity to the visible light range [53]. In addition, a range of hypotheses have also been proposed. Graphene is used as a two-dimensional photocatalyst owing to its excellent redox properties. High quality graphene makes the electrons travel without scattering at higher mobility than 15,000 m^2 V^{-1} s^{-1} at room temperature, meaning that it acts as an ideal electron sinks and electron transfer bridge [54]. This is possibly because mobility that the conductivity is affected by the electron delocalized behaviors in the conjugated π-π interaction of TiO_2/graphene composites, resulting in rapid photo-induced charge separation and slow charge recombination in the electron transfer process [55]. The band gap behavior of TiO_2/graphene composites has a wide range (2.66–3.18 eV), according to the graphene content from 0.25 to 10 wt.% [56]. This suggests that the newly formed Ti–O–C bands of TiO_2/graphene composites can extend to the absorption edge, which can absorb the long wavelength light of the visible region [57].

SYNTHETIC STRATEGIES OF TiO_2 NANOARRAYS/GRAPHENE COMPOSITES

In recent years, many researchers paid considerable attention to controlling the morphologies of TiO_2 nanoarrays via various methods, since the size and shape of TiO_2 nanoarrays determine the electrochemical properties and photocatalytic activities. TiO_2 nanoarrays/graphene composite coating can be obtained in three different ways, one of which is coating the graphene dispersion on the substrate by spin coating, followed by growing the TiO_2 nanoarrays on the graphene; the second way is coating the graphene dispersion on the TiO_2 nanoarrays by spin coating. Additionally, sandwich-type TiO_2 nanoarrays/graphene composite coating shown in Fig. 3c, can also be obtained by coating graphene dispersion on the TiO_2 nanoarrays grown on the graphene. Spin coating method is a simple technique where the loaded solvent drops on the center of substrate, and will be deposited uniformly under high speed rotation. A uniform thin film will be formed on the substrate by centrifugal force [40]. Therefore, it is very important to prepare TiO_2 nanoarrays on the substrate, in order to prepare TiO_2 nanoarrays/graphene composite coating.

To date, a variety of preparation methods have been developed for the synthesis of TiO_2 nanoarrays, such as chemical vapor deposition [58], sol-gel method [59], template method [60], and hydrothermal/solvothermal method [61]. Among them, the hydrothermal method is very simple to produce TiO_2 nanoarrays. For instance, as shown in Fig. 3, the sandwich heterostructures of TiO_2 nanorods were obtained by hydrothermal method. Another efficient technique to prepare the graphene/TiO_2 composite with excellent photocatalytic properties is direct growth process. Recently, Xu et al. [62] reported that graphene quantum dots could directly grow on 3D micropillar/microwave arrays of rutile TiO_2 nanorods to form the graphene-TiO_2 composite.
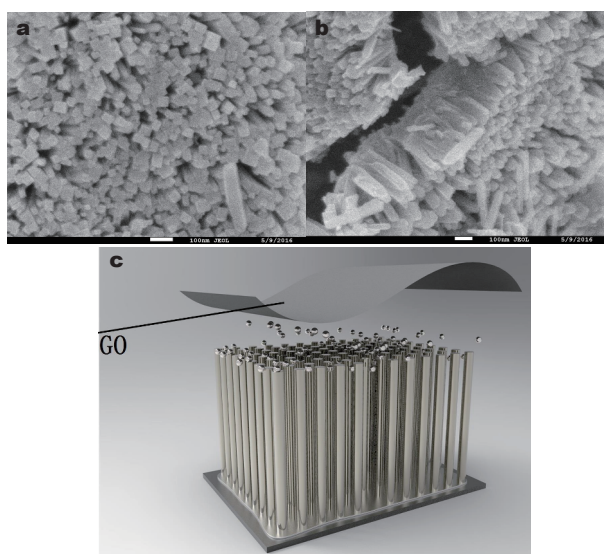
Figure 3 (a) Scanning electron microscopy (SEM) surface images and (b) SEM cross section images of TiO_2 nanorods obtained by the hydrothermal route; (c) schematic of sandwich GO/TiO_2 nanorods/graphene heterostructures.

Hydrothermal method/solvothermal method

Hydrothermal processing refers to any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high temperature and pressure conditions in a sealed or closed system. Solvothermal processing is almost the same as hydrothermal processing except that the solvent is nonaqueous. Thus, we put the two methods together, namely hydrothermal/solvothermal method.

Patel *et al.* [63] successfully synthesized TiO_2 nanorods by hydrothermal method. This method was also employed by Lv *et al.* [64], where densely aligned TiO_2 nanorod arrays with tunable thickness were synthesized. The property of substrates plays a key role in the synthesis of TiO_2 nanorods array, and lots of substrates have been applied to support TiO_2 nanorods. Liu *et al.* [65] introduced a mild hydrothermal method to fabricate single-crystalline rutile TiO_2 nanorod arrays directly on fluorine-doped tin oxide substrates. Dubal *et al.* [66] synthesized polycrystalline rutile TiO_2 nanorods by controlling precipitation routes on glass and indium tin oxide substrates.

The *in situ* growth of TiO_2 on graphene or graphene on TiO_2 can provide much more efficient hybrid photocatalysts. Wang *et al.* [67] developed a method for the *in situ* preparation of graphene-like carbon structures on TiO_2 which show nearly 2.5 times enhanced photodegradation of methylene blue dye, when compared with

pristine P25 TiO_2. Liang *et al.* [68] reported the uniform growth of TiO_2 nanocrystals directly on graphene oxide substrate *via* hydrolysis coupled hydrothermal treatment. The prepared GO-TiO_2 hybrids showed a three-fold photocatalytic activity for the degradation of Rhodamine B dye as compared to P25 TiO_2. This enhancement was attributed to an improved electronic coupling between graphene oxide and TiO_2 nanocrystals and the higher surface area of this hybrid material.

In addition, Zou *et al.* [69] prepared sandwich-like TiO_2/graphene/TiO_2 heterostructures by a simple and general nanocrystal-seed-directed hydrothermal route, which realized a large-scale growth of TiO_2 nanorod arrays on both sides of flexible graphene sheets. They found that in the hydrothermal process, the TiO_2 nanocrystals seeded on the graphene sheet played a key role in growth of the nanorod arrays on the graphene surfaces; the size of the TiO_2 nanocrystal seeds on the graphene sheets had an obvious effect on the size of the nanorods. The photocatalytic property of the TiO_2/G/TiO_2 had been evaluated by the degradation of methylene blue under UV/vis irradiation. Compared with P25 and TiO_2 nanorods, TiO_2/G/TiO_2 catalysts exhibited remarkably enhanced photocatalytic activities, indicating that the heterostructures could serve as promising candidates for photocatalytic decontamination. Furthermore, for 1D TiO_2 nanorod arrays, as shown in Fig. 4 [70], the recombination rate of e^- and h^+ in TiO_2 nanoarrays is lower than that in TiO_2 nanoparticles, which would enhance the photocatalytic activity [71].

Template-based synthesis method

Usually, nanoarrays synthesized by this method have a well-defined size and shape, benefiting from the directing effect of the templates. The template-based synthesis method includes three primary steps: template preparation, synthesis of nanoarrays using the template and template removal. The most common templates for the preparation of TiO_2 nanoarrays are anodized alumina membranes (AAMs). The template is placed in colloidal dispersions which are prepared by the sol-gel method. Then, the template pores are filled with the colloidal dispersions because of the capillary forces. Followed by drying and calcining, 1D TiO_2 arrays can be synthesized. However, it is difficult to guarantee the complete filling of the template pores.

Yuan *et al.* [72] successfully prepared TiO_2 nanotube and nanowire arrays by this method. In this method, $Ti(OC_4H_9)_4$ (TBT) dissolved in *n*-butyl alcohol and deionized water immersed the AAM template for six
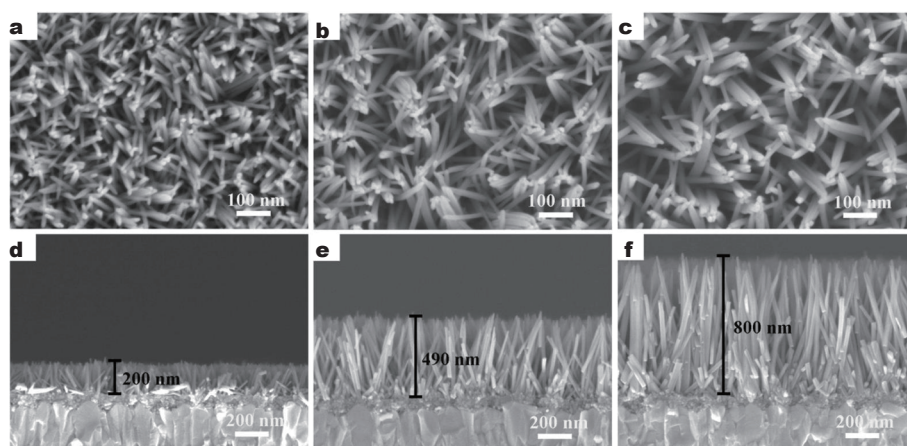
Figure 4 Surface and cross-sectional SEM images of TiO$_2$ nanorod arrays with growth time of 75 min (a, d), 105 min (b, e), and 115 min (c, f). Reprinted with permission from Ref. [70], Copyright 2017, Elsevier.

hours, followed by drying and calcining, and a continuous series structure from nanotubes to nanowires can be synthesized just by adjusting the concentrations of TBT solutions from 0.1 to 2.0 mol L^{-1}. TiO$_2$ nanorod arrays with tunable diameters were prepared by Mirdamadi *et al.* [73]. The pressure by a syringe was used to increase the driving force, in order to fill the template pores. In a typical experiment, a TiO$_2$ sol was prepared by dissolving titanium isoporpoxide (TTIP) in ethanol with a small amount of water. Then the sol was injected by a syringe into the AAM templates several times, and the samples were immediately immersed into boiling TiO$_2$ sol for 20 min. After being calcined at 400°C for 2 h, the AAM templates were removed in NaOH solution. Therefore, combining the sol-gel method with template-based synthesis methods has been investigated to prepare 1D TiO$_2$ arrays.

On the base of an AAM template, TiO$_2$ nanotube arrays can be prepared by electrochemical deposition [74]. Typically, the deposition process was carried out under potentiostatic conditions in 0.1 mol L^{-1} TiCl$_3$ aqueous solution, whose pH was maintained at 2.0 by adding Na$_2$CO$_3$ aqueous solution. After calcination processing and template removal, anatase TiO$_2$ nanotube arrays were obtained. Similarly, TiO$_2$ nanowires can also be obtained by this method.

Electrophoretic deposition is also an electrochemical method which has been widely explored in film deposition from colloidal dispersions [75]. It includes two steps, electrophoresis and precipitation. In the first step, an electric field is applied between two electrodes, the charged particles move toward the opposite electrode.

In the second step, the charged particles accumulate at the deposition electrode and form a relatively compact film. A combination of sol-gel method and electrophoretic deposition with AAM or PC templates has been used to synthesize TiO$_2$ nanowires and nanorods [76]. In a typical experiment, TiO$_2$ sol was formed by dissolving TTIP in acetic acid, followed by the addition of deionized water. Nanorod growth occured on a working electrode of aluminum. TiO$_2$ sol was deposited into the pores of the PC membrane under a potential of 5 V for 1 h. After calcining the PC membrane at 500°C for 1 h, dense anatase TiO$_2$ nanorods were obtained. TiO$_2$ nanowires can also be prepared using an AAM template with long pores.

Direct anodization of Ti metal
Direct oxidation of Ti metal using anodization can be employed for the preparation of 1D TiO$_2$ nanotube arrays on Ti substrates. Anodization is an useful method for modifying surface structures to obtain nanoporous or nanotubular structures. Fabrication of TiO$_2$ nanotubes *via* direct anodization of Ti foil in a H$_2$O-HF electrolyte was first reported by Grimes *et al.* [77]. Typically, a cleaned Ti foil was anodized in a 0.5% HF solution under a direct current voltage of 20 V for 20 min. The obtained nanotubes had an average tube diameter of approximately 60 nm and a tube length of only 250 nm. The formation of nanotube arrays appears to be three simultaneously occurring processes: (1) field-assisted oxidation of Ti metal to form TiO$_2$; (2) field-assisted dissolution of Ti metal ions in the electrolyte; and (3) chemical dissolution of Ti and TiO$_2$ due to etching by fluoride ions [78].

Further studies concentrate mainly on precisely controlling the nanotube length, pore size, and wall thickness [79]. These parameters strongly depend on the electrolyte. Electrolyte composition and its pH determine the formation rate of both nanotube arrays and the resultant oxide dissolving. In most situations, TiO$_2$ nanotube arrays are obtained by anodization in the existence of electrolyte containing fluoride ions.

TiO$_2$ NANOARRAYS/GRAPHENE COMPOSITES FOR WATER TREATMENT

This part complements the earlier work [80] by extending to the application of TiO$_2$ nanoarrays/graphene composite in water treatment. TiO$_2$ nanoarrays or TiO$_2$ nanoarrays/graphene composite coating on the substrate have unique properties in water treatment, owing to their fast electron transport and being easy to recycle after photocatalytic reaction. The combination of graphene with TiO$_2$ nanoarrays limits the electron-hole recombination, extending the life time of the photoelectron hole pairs. Also, the formation of π-π stacking between aromatic rings of graphene and organic pollutants also facilitates the adsorption of pollutants on the photocatalyst thereby enhancing the quenching of pollutants [81]. Therefore, the coupling of graphene with photoactive TiO$_2$ greatly enhances the photocatalytic activity of TiO$_2$ for the degradation of various waterborne pollutants such as pathogens, organic dyes and heavy metal ions. The unique properties of graphene, in combination with size-dependent properties of TiO$_2$ nanoarray induce further functionalities for the composites such as extended light absorption range, high adsorption capacity and improved charge separation properties.

Especially, in recent years, algal blooms in sea and lake cause microcystins (MCs) which can cause acute and chronic toxicity to humans [2]. TiO$_2$ nanoarrays or TiO$_2$ nanoarrays/graphene composite coating on the substrate can not only kill the algal in the sea and lake to inhibit the reproduction of algal, but also decompose the MCs in the water, as shown in Fig. 5.

Compared with other substrates, flexible substrate has been considered as a good choice, because catalyst recovery can be solved by anchoring the TiO$_2$ photocatalyst onto the substrate. Besides, these heterostructures with highly ordered nanoarrays on flexible substrates provide potential opportunities for flexible-device fabrication with optimal performance, such as photocatalysis devices and energy conversion/storage devices. Therefore, recycled TiO$_2$ composite on the substrate is a very important advanced oxidation technology, playing an
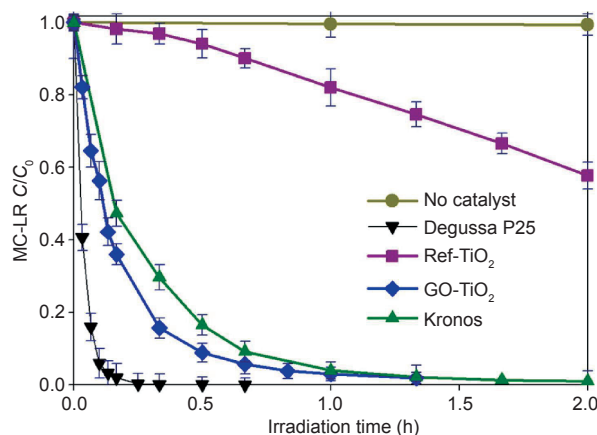

Figure 5 Photocatalytic degradation of 10 mg L^{-1} of MC-LR under solar light irradiation in the presence of different TiO$_2$ based nanostructured materials, 200 mg L^{-1} (Degussa P25, Kronos, GO- TiO$_2$, and ref-TiO$_2$), Degussa P25 and Kronos are used as standard materials for comparison. Reprinted with permission from Ref. [2], Copyright 2013, American Chemical Society.

important role in water treatment in the future.

Antimicrobial treatment

Recently, the research on antimicrobial activity of nanomaterials has gained great attention. Moreover, graphene has emerged as one of the most promising materials for application as antimicrobial materials [82–85]. Other than the presence of organic pollutants and heavy metals in water, waterborne pathogens are also deleterious to human health, which need to be killed. For this, nanomaterials with antimicrobial activity can be employed for remediation and sterilization of water. Further coupling of graphene with TiO$_2$ greatly enhances its antimicrobial activity, because TiO$_2$ can contribute to the antimicrobial activity by producing active oxidative species which destructs the cell, and by increasing the surface area of graphene to promote the adherence of more cells to graphene (Fig. 6) [86]. Therefore, TiO$_2$ nanoarrays/graphene composite exhibits excellent antimicrobial activity due to their synergistic effects.

Xu et al. [87] synthesized the filtration membranes by combining TiO$_2$ with graphene. Despite of the encouraging findings, the application of the nanocomposite to kill bacteria in a recyclable and synergistic manner remains to be further explored. Recyclable antibacterial TiO$_2$ nanoarrays/graphene composites are eco-friendly and low cost, because of reducing the usage of raw materials. It is observed that the lateral dimensions and morphology of the graphene oxide sheets play a key role in its efficacy
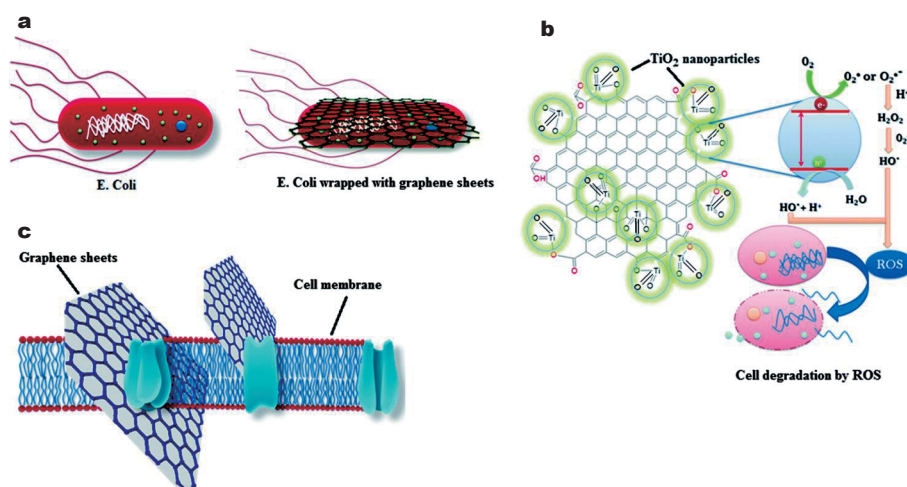
Figure 6 (a) Wrapping of *E. coli* by graphene sheets. (b) Slicing of cell membrane by sharp edges of graphene. (c) Mechanism involved in photoinactivation of cells by metal oxide/graphene composite. Reprinted with permission from Ref. [86], Copyright 2013, The Royal Society of Chemistry.

as antimicrobial agent [84]. Compared to the smaller sheets, the larger sheets exhibit higher antimicrobial activity. The reason is as follows: firstly, this complete wraping of bacterial cells by larger graphene sheets ($>0.4\ \mu m^2$) could block all the available active sites, disallowing the cell proliferation. Secondly, smaller sized graphene oxide sheets ($<0.2\ \mu m^2$) do stick to the cell membrane, which are not capable of occupying and isolating the whole cell surface, leading to low efficiency.

Ahmed *et al.* [40] investigated the effect of graphene oxide on wastewater borne microbial community. They found the fact that graphene oxide impaired the metabolic activity of microorganism, thereby restricting the cell proliferation and ultimately leading to the cell death. Reduced metabolic activity caused a reduction in the consumption of oxygen which would decrease the value of biological oxygen demand (BODs) [88]. The bacteria effectively interact with the graphene (oxide) nanosheets through direct contacting with such sharp edges. The cytoplasm of some bacteria leaks off thoroughly, indicating both outer and inner membrane damaged (Fig. 7). When bacteria directly contact with graphene, intensive physical interactions between graphene and bacterial cells may cause physical damages on cell membranes, leading to the release of intracellular contents [88]. This can be assigned to a stronger interaction between the more sharpened edges of graphene and the cell membrane of bacteria, or a better charge transfer between bacteria and the edge of graphene which finally result in further damage of the cell membrane of bacteria during the contact interaction.
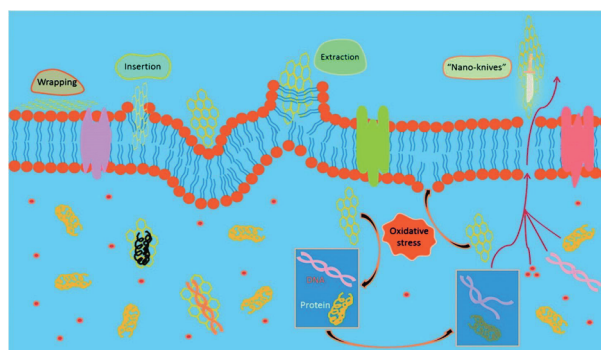
Figure 7 Mechanism of the antimicrobial activities of single-component graphene materials. Reprinted with permission from Ref. [88], Copyright 2017, The Royal Society of Chemistry.

Akhavan *et al.* [83] also contended that direct contact interaction of bacteria with the very sharp edge of graphene would result in much more damage to the cell membrane of Gram-positive *S. aureus* bacteria, which was lack of an outer membrane as compared to the Gram-negative *E. coli* ones.

The composites of graphene with TiO_2 have also been explored as an antimicrobial agent for the sensitization and disinfection of water. Akhavan *et al.* [89] reported that graphene oxide/TiO_2 thin films annealed at 400°C could photo-inactivate *E. coli* 25% more efficiently, as compared to bare TiO_2. In this case, graphene oxide served as an electron acceptor for the removal of electron from electron hole pair which generated by the exposure of photoactive material to light. Simultaneously, the quantum efficiency of the photocatalysis was enhanced by

an increase in life time of the hole and a reduction in the electron-hole recombination. The graphene oxide/TiO_2 thin films exhibited significantly improved antibacterial activity by factors of 7.5, 3.7, 1.7 and 1.1, as compared to unsupported TiO_2, Ag-SiO_2, Ag nanorods and Ag-TiO_2/Ag/TiO_2 films [89].

The cytotoxicity of graphene/TiO_2 composite in miniscule nematodes was investigated by Thakur *et al.* [90]. Nearly 98.4% of the nematodes were inactivated, when exposed TiO_2/graphene composite whose ratio of surface area to volume (S/V) is 10, to the solar radiation within 4 h. Cao *et al.* [23] reported that TiO_2/graphene composite with 4.2 wt% graphene showed photoactivity in visible spectrum as well, which was attributed to the formation of Ti-C bond between TiO_2 and graphene. The photocatalytic properties of TiO_2/graphene composite were tested against *E. coli*. It was observed that the composite showed excellent antibacterial activity and the bacterial cell viability was reduced to 9.5% after 12 h exposure in visible light.

It was further revealed that the major inactivation of nematodes was due to the interaction with reactive oxygen species (ROS) generated by the composite. Reactive oxygen species generated by TiO_2 was also responsible for microbial cell inhibition, hindering the activity of ammonia by oxidizing bacteria and polyphosphate accumulating organisms, which were responsible for the removal of the following two nutrients: nitrogen (as NH_3–N) and phosphorous (as PO_4^-) from waste water [91,92]. Also, the modification of the surface of graphene with molecules and functional groups, effectively prevented sheets folding and helped to maintain a stable dispersion. The presence of certain active groups such as –COOH and –OH can increase the surface roughness, which could thereby enhance the antimicrobial activity by damaging the outer membrane of cells *via* attrition and rubbing. Increasing the number of active groups on the surface of graphene effectively improves antimicrobial activity of graphene based composite. Sharp edges of graphene also contribute to its antimicrobial activity, wherein the atomically sharp edges can slice through the cell membrane [86].

One-dimensional nanomaterials such as nanorods, have also been utilized in combination with graphene oxide for photocatalytic degradation of microorganisms. Liu *et al.* [93] prepared TiO_2 nanorod hybrids with graphene oxide and investigated their bactericidal activity by monitoring the effect of solar radiation exposure on the *E. coli* bacterial colony, in the presence of hybrid material. The TiO_2 nanorods/graphene oxide composite showed significantly higher bacteriocidal activity as compared to the TiO_2 nanoparticles/graphene oxide hybrid. TiO_2 nanorods/graphene oxide composite inactivated 90% *E. coli* within 27 min, but TiO_2 nanoparticles/graphene oxide hybrid took 52 min to achieve same performance. Therefore, specific structures and morphologies are very important because they could provide a high degree of edge planes.

To some extent, graphene coated on TiO_2 nanoarrays may reduce the light absorption, which is the potential drawbacks. But on the basis of the above advantages of TiO_2 nanoarrays/graphene and the suitable composite structure, the influence of the reduced light absorption by graphene itself on photocatalytic reaction is weak. Moreover, graphene coated on TiO_2 nanoarrays greatly improves the adsorptive and antimicrobial activities in water treatment. Therefore, TiO_2 nanoarrays coupling with graphene have greatly enhanced the photocatalytic properties and antimicrobial efficiency in water treatment.

Adsorption

Adsorption is one of the most important phenomena for desalination of water. As compared to other water treatment, the advanced water treatment technology with TiO_2 nanoarrays/graphene composites can remove nearly all types of pollutants from waste water, offering several advantages such as ease of recycling, and no harmful generation of by-products during the treatment [94]. As the metal ions cannot be degraded by photocatalysis or any other chemical reaction, adsorption is a preferred approach due to its effective removal of toxic heavy metal ions. More importantly, graphene exhibits a much higher surface area than activated carbon, and thus can act as an efficient adsorbent. In addition to unprecedented surface area, graphene derivative also provides functionalities which can favour selective adsorption of pollutants [95]. Graphene oxide is highly acidic in nature, therefore it can readily adsorb basic molecules and cations. Moreover, when graphene is modified with surfactant, the presence of active groups such as carbonyl, epoxy and hydroxyl groups on the surface of graphene oxide enables it to interact with a wide variety of molecules [96]. Until now, graphene has been explored as an adsorbent for the removal of various dyes, heavy metal ions [97] and other aromatic pollutants [98].

Recently, numerous studies were devoted to utilization of self-assembled TiO_2 on graphene or reduced graphene oxide for removal of different water pollutants. The incorporation of TiO_2 nanoarrays on graphene can

reduce their restacking and aggregation, thereby enhancing the surface area of the composite [99,100]. At the same time, *in situ* growth of TiO_2 nanoarrays on graphene results in less agglomeration. Furthermore, the functional groups and defect sites of graphene can act as the nucleation and growth sites for TiO_2. The combination of graphene with TiO_2 nanoarrays extends the life time of the adsorbent material by acting as support material, which inhibits leaching of fine TiO_2 into treated water.

As a hot issue, photocatalysis has witnessed an enormous change over the past two decades, which makes significant advancements in the preparation of novel form nanomaterials and the design of efficient photodegradation processes in water treatment. Thus, the development of a simple recyclable photocatalyst not only prevent the excessive use of photocatalysts, but also contribute to the recovery of photocatalysts, which is green and benefit to water environment. Therefore, one of the great challenges of photocatalyst study is to devise recycled new catalysts that exhibit high activity under illumination by visible light.

## TiO₂ NANOARRAY/GRAPHENE COMPOSITES FOR ENERGY CONVERSION/STORAGE

Solar cell

Over the last decades, TiO_2 nanoarrays have been widely applied as one of the efficient charge separation and electron transporting materials in the fields of dye sensitized solar cells (DSSC) [65,101], quantum dot sensitized solar cells [102], and organolead halide perovskite solar cells [103]. As one of the important components of solar cells, the TiO_2 photoanode has a great effect on light conversion efficiency. The length, diameter, surface hydroxyl group content and areal density of TiO_2 nanoarrays strongly affect the interface charge separation and photovoltaic performance of the corresponding solar cells. The TiO_2 nanoarrays/graphene composite with unique properties have been used in photovoltaic studies, in which highly ordered nanoarray structure accelerates electron transport and ordered surface increases sensitizer absorption [70,104].

Clearly, oriented single-crystal TiO_2 nanowires or nanorods on FTO glass would be most suitable for fast electron transport [30,105]. Moreover, among these preparation techniques, growing the 1D TiO_2 nanorods/wires directly on FTO glass by hydrothermal/solvothermal method is the most promising technique due to its
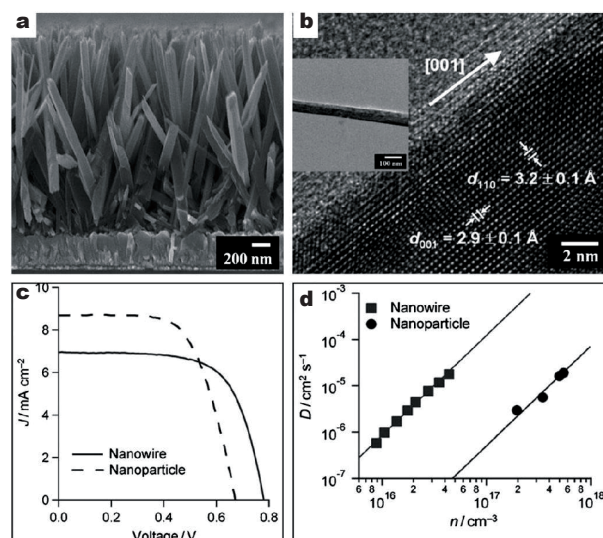
Figure 8 DSSCs with TiO_2 nanorod arrays. (a) Field emission SEM (FE-SEM) cross-sectional image of rutile TiO_2 nanorod arrays grown on an FTO substrate, (b) high-resolution transmission electron microscopy (HR-TEM) image of a single nanorod array shown in the inset. (c) $J–V$ characteristics of DSSCs based on a 4.5 μm long rutile TiO_2 nanowire arrays and a rutile TiO_2 nanoparticle film, (d) comparison of electron diffusion coefficients (D) as a function of the photoelectron density (n) for rutile nanowire- and nanoparticle-based DSSCs with a laser illumination at 680 nm. Reprinted with permission from Ref. [30,65,106], Copyright 2014, Elsevier.

simplicity and low cost. As shown in Fig. 8, nanorods with ~90 nm in diameter and 1.9 μm in length were formed at 150°C for 20 h [65]. These nanorods were polycrystalline rutile and grew along the [001] direction with the growth axis parallel to the substrate surface normal (Fig. 8a, b). The photoelectric conversion efficiency (PCEs) were almost the same (3.68% for nanowires and 3.74% for nanoparticles), while the short-circuit current values (J_{sc}) were distinct (6.95 mA cm^{-2} for nanowires and 8.70 mA cm^{-2} for nanoparticles). The 20% lower J_{sc} value for nanowire-based DSSCs primarily resulted from their lower surface area than the nanoparticle-based cell. Shi *et al.* [70] successfully prepared a TiO_2 nanorod array with a length of 200 nm, a diameter of 13 nm and an areal density of 1,100 μm^{-2} using a hydrothermal method, as shown in Fig. 9. It showed that the structure of nanorod array was beneficial to the infiltration of ion and hole transport in the solar cell. Feng *et al.* [105] prepared the rutile TiO_2 nanowire arrays with the length of 900, 600 and 400 nm. And they found that the corresponding performance of perovskite solar cells gave the PCEs of 11.7%, 10.8%, and 9.7%, respectively. This is a good evidence that the 1D nanostructures may offer better charge transport than
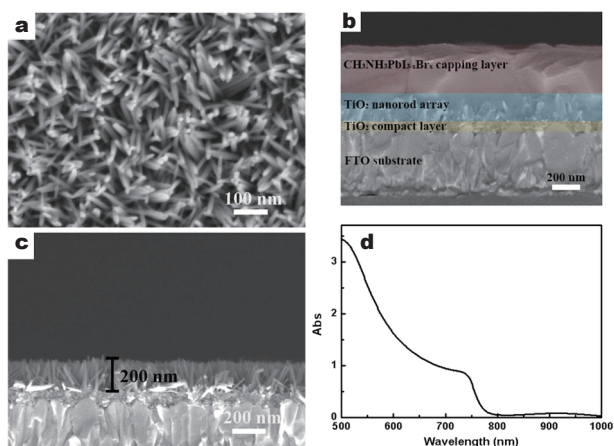
Figure 9 Surface (a) and cross-sectional (c) of TiO$_2$ nanorod array, cross-sectional (b) and UV-Vis-NIR spectrum (d) of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ thin film based on the TiO$_2$ nanorod array. Reprinted with permission from Ref. [70], Copyright 2017, Elsevier.

nanoparticles. Further increment in PCEs of 1D nanostructures most likely depends on the enhancement of surface area.

However, ordered TiO$_2$ nanorods/wires arrays also suffer from the drawbacks such as high electron-hole pair recombination which leads to low charge density in the photoanode. Considering this fact, hybridization of graphene and TiO$_2$ nanoarrays could enhance the photoanode activity by increasing electron mobility and reducing the recombination of the electron and hole. Lee et al. [40] reported that graphene/TiO$_2$ photoelectrodes could display enhanced dye adsorption properties with lower internal resistances and faster transport time. The maximum power conversion efficiency of DSSCs was 9.32% with optimized DSSC parameters, which represented that the addition of GR would increase dye loading and enhance DSSC efficiency. Wang et al. [99] showed that printing TiO$_2$/graphene nanocrystals on TiO$_2$ nanoarrays to prepare the photoanode of solar cells could achieve the increased absorbability for dye and the increased absorption of visible light, and enhanced efficiency of the cell by 35%, compared with the TiO$_2$/graphene nanocrystals film. This transparent graphene/TiO$_2$ nanoarray photoanode exhibited a high conversion of light to electricity.

Energy storage

Recently, our group have tried to use various morphologies of nanomaterials as the electrodes to enhance the electrochemical performance, in order to achieve the high power and energy density of electrochemical energy

storage devices [107–110]. Among them, well-defined 1D hetero-nanostructures combine the advantages and overcome the limitations of different electrochemically active materials. Mai et al. [111] reported that V$_2$O$_5$ nanowires/graphene (VOG) was synthesized using a liquid phase method. The highly interconnected vanadium oxide nanowires framework was supported by reduced grapheme oxide. The cycling performance of VOG indicated that a 71% of the maximum capacity was achieved after 900 cycles. The initial increase in capacity for the first 50 cycles might be attributed to the activation of bilayer V$_2$O$_5$ at a high current density of 6 A g^{-1}. An et al. [112] synthesized nanowires/GO nanocomposites via freeze drying and annealing process. This V$_2$O$_5$/GO aerogel exhibited excellent electrochemical performance in Mg^{2+} ions storage. Except the special structure that graphene was convolved by V$_2$O$_5$ nanowires, the crystal water molecules in layers also played an important role in Mg^{2+} ions diffusion.

TiO$_2$ has received much attention for Li-ion battery because of its several merits such as low cost and friendly environment. Importantly, TiO$_2$ is a quick and low voltage insertion host for Li, and its structure can keep stable during the Li insertion extraction process [113]. However, just like every coin has two sides, TiO$_2$ also has its weaknesses, for example poor cycling performance due to its poor electron transport ability. Therefore, lots of efforts have been made to overcome these disadvantages. Kim et al. [114] reported a hybrid supercapacitor combining the advantages of Li-ion batteries and supercapacitors based on anatase TiO$_2$-rGO (Fig. 10a). Fig. 10b clearly showed that the hybrid supercapacitor could deliver far higher power and energy densities. As an energy storage device as popular as batteries, supercapacitor can provide high power density because of fast surface reactions. However, general supercapacitors suffer from low energy density as a result of limited surface charge storage.

Therein, TiO$_2$ nanoarrays not only shorten the ion diffusion length, but also reduce the ionic diffusion resistance and charge transfer resistance. To make the structure more innovative, Ramadoss et al. [115] prepared rGO/TiO$_2$ nanorod/rGO sandwich electrode and confirmed the specific capacitance retention ratio was 85% even after 4,000 cycles (Fig. 10d, e). In this electrode, rGO nanosheets acted as an interconnector to improve the internal electrical conductivity and cyclability. In addition, the enhanced specific surface area of the electrode greatly improved the charge capacity. Simultaneously, the TiO$_2$ nanorod arrays acted as infrastructure
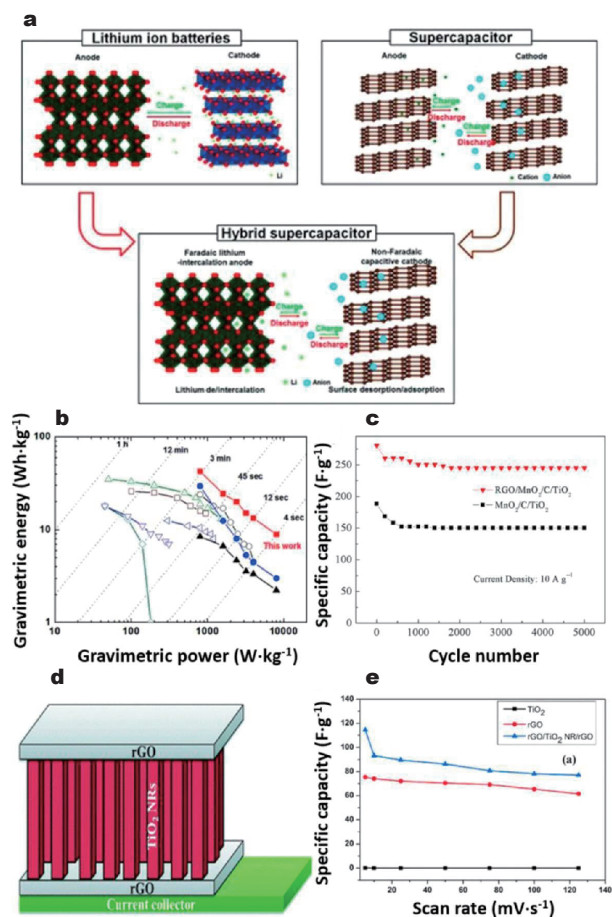
Figure 10 (a) Illustration of a typical hybrid supercapacitor. The hybrid supercapacitor uses a non-Faradaic capacitive cathode like those used in supercapacitors and a Faradaic lithium intercalation anode like those used in Li-ion batteries. (b) Ragone plots of various hybrid super-capacitors, (c) Cycle performance of the RGO/MnO$_2$/C/TiO$_2$ and MnO$_2$/C/TiO$_2$ electrode at a current density of 10 A g^{-1}. (d) Schematic diagram of an rGO/TiO$_2$ nanorod/rGO electrode. (e) Specific capacitance of TiO$_2$ nanorods, rGO and an rGO/TiO$_2$ nanorod/rGO electrode at various scan rates. Reprinted with permission from Ref. [116], Copyright 2017, Elsevier.

bridging the GR nanosheets, preventing them from serious swelling during the cycling process. These results suggested that the tested cell could exhibit superior performance in TiO$_2$ nanoarrays/graphene supercapacitors with aqueous electrolyte.

CONCLUSION AND OUTLOOK
This review focuses on TiO$_2$ nanoarrays and TiO$_2$ nanoarrays/graphene composite as photocatalysis and photoanode with their practical use in water treatment and energy conversion/storage. The foremost goal on photovoltaic materials is to explore the light harvesting,

limit the electron-hole pairs recombination and electron losses. Owing to its excellent physical and chemical properties, TiO$_2$ nanoarrays/graphene is undoubtedly suitable to act as the perfect material for photocatalysis and energy conversion/storage. According to the literature reviews, their conversion efficiency based on TiO$_2$ nanoarrays and TiO$_2$ nanoarrays/graphene are promising as compared to the pure TiO$_2$ and graphene. Some have ascribed the excellent catalytic activities to better accessibility of reacting molecules into TiO$_2$ nanoarrays. And some papers assume that the intimate interaction between TiO$_2$ and graphene leads to efficient electron transfer. This article presents a comprehensive review on the application and mechanism of TiO$_2$ nanoarrays or TiO$_2$ nanoarrays/graphene composites in water treatment and their role as photocatalyst, anti-microbial activities and adsorbent in water remediation. Through this review, we discuss the current state of TiO$_2$ nanoarrays/graphene composite for water purification and also provide a comprehensive analysis of these composites about their photocatalytic, adsorptive and antimicrobial activities on various types of pollutants. Also, due to its excellent electrical and thermal conductivity, mechanical strength and high surface area, TiO$_2$ nanoarrays/graphene composite on the substrate is an ideal photoanode applied in energy conversion/storage.

A brief perspective on the challenges and new directions in the area is also provided for researchers interested in designing advanced photochemical materials for water treatment and energy conversion/storage. Anchoring TiO$_2$ nanoarrays/graphene on the substrate (especially flexible substrate) has been considered as a good choice because of easy recovery of the photocatalyst in water treatment, which is friendly to environment. Besides, TiO$_2$ nanoarrays/graphene on flexible substrates could provide potential opportunities for flexible-device fabrication with optimal performance in energy conversion/storage devices.

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TiO₂纳米阵列/石墨烯复合材料在水处理和能量转换与储存中的研究进展

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摘要 虽然TiO₂基纳米材料具有独特的化学物理特性, 在水处理和能量转换与储存中展现出广阔的前景, 但仍然存在一些局限性. 为了进一步提高其光化学特性, 基于各种合成技术在基体表面制备一维的TiO₂纳米阵列通常与石墨烯进行复合. 这种复合涂层具有优异的光催化性能以及优异的杀菌和吸附性能. 尤其是这种复合材料经过光催化处理后, 很容易回收再利用. 另外, 基体(尤其是柔性基体)表面的TiO₂纳米阵列/石墨烯复合涂层可以制备具有优异光电转化效率和光化学特性的柔性设备, 在能量转化和存储中具有潜在的应用价值.