Light-driven directional ion transport for enhanced osmotic energy harvesting

Kai Xiao*,1, Paolo Giusto1, Fengxiang Chen*,2,5, Ruotian Chen3, Tobias Heil1, Shaowen Cao1,4, Lu Chen1,2, Fengtao Fan5, and Lei Jiang2

1Max Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, D-14476 Potsdam, Germany.

2Key Laboratory of Bio-inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry, Beihang University, 100191 Beijing, P.R. China.

3State Key Laboratory of Catalysis, 2011-iChEM, Dalian National Laboratory for Clean Energy (DNL) Dalian Institute of Chemical Physic (DICP) Zhongshan Road 457, 116023, Dalian, China.

4State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 430070 Wuhan, P. R. China

5State Key Laboratory of New Textile Materials and Advanced Processing Technologies, Wuhan Textile University, 430200 Wuhan, P. R. China

Corresponding authors*: xiaokai@iccas.ac.cn; fxchen_czx@buaa.edu.cn

ABSTRACT
Light-driven ion (proton) transport is a crucial process both for photosynthesis of green plants and solar energy harvesting of some archaea. Here, we describe that TiO$_2$/C$_3$N$_4$ semiconductor heterojunction nanotube membrane can realize a similar light-driven directional ion transport performance as biological systems. This heterojunction system can be fabricated by two simple deposition steps. Under unilateral illumination, TiO$_2$/C$_3$N$_4$ heterojunction nanotube membrane can generate a photocurrent of about 9 μA/cm$^2$, corresponding to a pumping stream of ~5500 ions per second per nanotube. By changing the position of TiO$_2$ and C$_3$N$_4$, a reverse equivalent ionic current can also be realized. Directional transport of photo generated electrons and holes results in a transmembrane potential, which is the basis of the light-driven ion transport phenomenon. As a proof of concept, we also show that this system can be used for enhanced osmotic energy generation. The artificial light-driven ion transport system proposed here offers a further step forward on the roadmap for the development of ionic photoelectric conversion and their integration in other applications, e.g. water desalination.

Keywords: ion pump; ion transport; nanofluidic; porous membrane; carbon nitride

INTRODUCTION
Nature’s biochemical machinery has been a source of inspiration in the development of artificial molecular devices or ion transport systems designed to emulate the form and function of their biological counterparts. A typical example is that the cellular metabolism in living organisms depends on the compartmentalization of ions, small molecules and macromolecules being maintained and managed by means of transmembrane active transport. Inspired by this, artificial systems were developed that are capable of transporting molecules against concentration gradients, such as molecular motors 1,2 and...
molecular pumps \(^3\). Photosynthesis by green plants or archebacter is the most important biochemical process in nature, which provides most of the energy we need and a comfortable environment suitable for biological survival. With the development of modern science, photosynthesis-inspired light-driven physical and chemical processes attract extraordinary attentions. We mention for instance photocatalytic chemical reactions\(^4\) or the photovoltaic cell,\(^5\) both of which occupy thousands of research group all over the world and already created tremendous economic value. Until now, artificial photosynthesis involving complex physical and chemical processes is still one of the most tough, but also promising missions in the field of bionics.\(^6\)–\(^9\).

In view of energy harvesting, artificial light-driven ion transport is a very attractive step, because the different photosynthetic processes of both green plants and halobacteria involve a step during which protons/ions are pumped from low concentration to high concentration to create an electrochemical potential, which is then used for ATPase to produce ATP. Consequently, the realization of artificial light-driven ion transport is the key point for a new “ionic” mode of solar energy harvesting and storage.\(^10\)

Remarkable progress has also been achieved toward the realization of permselectivity of protons or alkaline earth metal ions across membranes by light-induced charge separation,\(^11\)–\(^13\) photoisomerization,\(^14\)–\(^15\) and solid-state nanochannels.\(^16\)–\(^17\) This ability raises a pertinent question of artificial light-driven ion transport system: Is there a way to drive ion transport by light in an easy and universal manner, and then realize an efficient “ionic” energy harvesting as nature? Herein, we report the development of artificial light-driven ion transport system via semiconductor heterojunction nanotube membrane that drives ion transport in a specific direction under unidirectional illumination for photocurrent generation (Fig. 1a). We demonstrate that such semiconductor heterojunction nanotubes consisting of titanium oxide (TiO\(_2\)) and polymeric carbon nitride (C\(_3\)N\(_4\)) enable efficient light-driven ion transport and tunable ion transport direction by controlling the heterojunction structure.

RESULTS AND DISCUSSION

Fabrication and characterizations of TiO\(_2\)/C\(_3\)N\(_4\) heterojunction nanotube

The heterojunction of the semiconductor nanotubes used here is TiO\(_2\)/C\(_3\)N\(_4\) heterojunction, which was fabricated by two deposition steps (Fig. 1b and Supplementary Figure 1). In the first step, TiO\(_2\) nanotubes with various wall thicknesses were fabricated by the atom layer deposition (ALD) method using porous anodic aluminum oxide (AAO) membrane with pore diameter about 100 nm as the substrate (Supplementary Figure 2). Then, the amorphous TiO\(_2\) nanotubes were crystallized by thermal annealing at 500 °C for 2 h. In the second step, the anatase TiO\(_2\) nanotubes (Supplementary Figure 3) were coated with a 10 nm layer C\(_3\)N\(_4\) (Supplementary Figure 4) by chemical vapor deposition (CVD).\(^18\) By this way, a TiO\(_2\)/C\(_3\)N\(_4\) heterojunction nanotube was fabricated (Fig. 1c). For analytical reasons, the carbon nitride nanotube can be released by chemical etching of the AAO substrate by 5 wt% phosphoric acid. Fig. 1d shows a typical TEM image of a TiO\(_2\)/C\(_3\)N\(_4\) heterojunction nanotube, the enlarged wall section shows that the wall is composed of an inner TiO\(_2\) layer and outer C\(_3\)N\(_4\) layer. High-resolution EDX measurements of the partial wall section in Fig. 1e and Supplementary Figure 5 show the inner TiO\(_2\) layer is about 5 nm thick, while the outer C\(_3\)N\(_4\) layer is about 10 nm thick (The pixels intensity represent the concentration of the related elements, respectively. Each pixel covers 1 nm\(^2\)). This is a representative of samples used in this
work, while the thickness of C$_3$N$_4$ and TiO$_2$ layer can be well controlled (see below). The length of all samples is the same, about 60 µm. The obtained heterojunction nanotubes were investigated by X-Ray Diffraction (XRD) measurements, FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS) (Supplementary Figures 6-8). All of the results indicate the formation of TiO$_2$/C$_3$N$_4$ heterojunction nanotubes.

**Light-driven ion transport phenomenon**

The light-driven ion transport properties were measured in a home-made electrolyte cell as we reported before. The TiO$_2$/C$_3$N$_4$ heterojunction nanotube membrane was symmetrically placed in contact with a 0.1 M KCl solutions and initially illuminated from one side. **Fig. 2a** shows the cycle-constant zero-volt current across the nanotube membrane by simulated solar illumination of 300 mW/cm$^2$. Without illumination, the zero-volt current is almost zero, while it increased to about 9 µA/cm$^2$ with illumination, indicating that light provides an external force to drive ions to move. By calculation, the changed current translates into the fact that a single nanotube actively transports ~5500 ions per second, an unprecedented breakthrough for artificial light-driven ion transport systems and much closer to the bacteriorhodopsin sodium pump or halorhodopsin Cl ion pump. The directional photo-driven ion transport phenomenon can be directly confirmed by the change of ion concentration in the two cells (Supplementary Figure 9), which can be monitored in real-time by scanning ion-selective electrode technique (SIET). In addition, the membrane shows an instantaneous stable and fully repeatable response to illumination. The ionic current is still stable even at longer illumination (Supplementary Figure 10). Further measurements show that the ion transport is closely connected to the illumination power density. The dependence can be confirmed by the ionic current in **Fig. 2b**. With the decrease of power density from 300 mW/cm$^2$ to 54 mW/cm$^2$, the ionic current decreases gradually from 9 µA/cm$^2$ to 0.8 µA/cm$^2$. It worth mentioning that the photo-induced voltage is also positively correlated with light power density (Supplementary Figure 9), while it is only dozens of millivolt and much smaller than pure C$_3$N$_4$ nanotube membrane.

The wall thickness of TiO$_2$ nanotube has an obvious effect on the light-driven ion transport properties (**Fig. 2c**). With the increase of wall thickness from 5 nm to 15 nm (Supplementary Figure 2), the ionic current decreases from about 9 µA/cm$^2$ to 2.5 µA/cm$^2$. This could be ascribed to a less efficient photochemical charge separation and more interfacial recombination of electrons and holes in thicker case. The light-driven ion transport system also shows an obvious relationship with the light wavelength (**Fig. 2d**). When applying various monochromatic light with the same power density (300 mW/cm$^2$), white light and high-energy blue light have a comparable high “power” to drive ion transport, while low-energy green and yellow light show a much weaker effect (Supplementary Figure 11). This is consistent with the light absorbance of the exposed C$_3$N$_4$ layer (Supplementary Figure 12). In general, isoelectric point of C$_3$N$_4$ fabricated by different precursor is in the range of 3.5 to 5. While the light-driven ion transport system is universal and works constantly in a wider pH value range from 1.9 to 9.5 (**Fig. 2e**). In strong alkali solution with a pH value of 12.5 it shows a different phenomenon since C$_3$N$_4$ is surface hydrolyzed under such conditions (Supplementary Figure 13). Meanwhile, the ionic current shows a positive correlation with electrolyte concentration (Supplementary Figure 14).
Mechanism of light-driven ion transport

The surface charge redistribution of heterojunction nanotube due to the photo-induced separation of electrons and holes is thought to be the key of the light-driven ion transport phenomenon. As illustrated in Fig. 3a, the initial TiO\textsubscript{2}/C\textsubscript{3}N\textsubscript{4} nanotube is symmetrically weakly negatively charged due of the acidity of the inner C\textsubscript{3}N\textsubscript{4} layer.\textsuperscript{28} In this condition, there is no ionic current in the external circuit. When illuminated from one side of the H-cell, the surface charge density in the irradiated side of the TiO\textsubscript{2}/C\textsubscript{3}N\textsubscript{4} nanotube increases because the built-in potential in the heterojunction resulting from band bending will drive photogenerated holes move from the C\textsubscript{3}N\textsubscript{4} layer to the TiO\textsubscript{2} layer (Fig. 3b). This results in a positive charged TiO\textsubscript{2} layer and a negative charged C\textsubscript{3}N\textsubscript{4} layer. As asymmetric negative surface charge is created, cations will move from the non-illuminated side to the illuminated side, while anions move oppositely (Fig. 3c). By this way, a light-driven ion transport system develops. Previous work has shown that already a single phase C\textsubscript{3}N\textsubscript{4} nanotube exhibits similar but weaker light-driven ion transport properties,\textsuperscript{20,29} which is because of a less efficient photocharge separation.\textsuperscript{30,31} In the present system the nanoscopic TiO\textsubscript{2}/C\textsubscript{3}N\textsubscript{4} heterojunction structure provides two different phases for each charge. The proposed mechanism is further confirmed by fluorescent mapping. As shown in Fig. 3d, the fluorescent mappings of C\textsubscript{3}N\textsubscript{4} nanotube system (left) exhibited fluorescence signals, which represent the recombination of photo-generated electrons and holes; while for the TiO\textsubscript{2}/C\textsubscript{3}N\textsubscript{4} heterojunction system (right), the fluorescence is negligible (Supplementary Figure 15), which means that radiative recombination is effectively suppressed in the heterojunction structure.

In order to directly observe the charge distribution, we mapped the surface potential by Kelvin probe force microscopy (KPFM) under unilateral illumination. For the C\textsubscript{3}N\textsubscript{4} nanotube, the potential of the pore area is 40 mV lower than that of the wall area, indicating upward band bending and electrons capture by the C\textsubscript{3}N\textsubscript{4} nanotube surface. Meanwhile, light irradiation increased its surface potential in both areas, indicating the n-type semiconductor property of C\textsubscript{3}N\textsubscript{4} (Supplementary Figure 16). As for the TiO\textsubscript{2}/C\textsubscript{3}N\textsubscript{4} heterojunction structure, surface potential of the pore area exceeds that of the wall area by 10 mV (Fig. 3e and Supplementary Figure 17), indicating the band bending and generation of built-in electrical field in the heterojunction. After light irradiation, both the surface potential of pore area and wall area decreased obviously, giving direct evidence for the directional transport of photogenerated electrons (to the outer C\textsubscript{3}N\textsubscript{4} layer) and holes (to the inner TiO\textsubscript{2} layer) (Fig. 3f). The observed electron accumulations at the illuminated side both on the wall and in the pore coincides with the measured cations migration towards the illuminated surface (Fig. 3c), thus indicating that the light-induced charge redistribution is responsible for the driving force of ion migration.\textsuperscript{32}

Reverse ion transport by C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} heterojunction nanotubes

The light-driven ion transport can also be easily reversed by changing the position of C\textsubscript{3}N\textsubscript{4} and TiO\textsubscript{2}. We fabricated a second C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} nanotube membrane by the same deposition methods but with reverse order (Fig. 4a). Now, C\textsubscript{3}N\textsubscript{4} is placed in the inner layer and TiO\textsubscript{2} in the outer layer. Fig. 4b shows a typical TEM image of the C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} heterojunction nanotube and the enlarged wall section shows clearly that the wall is compositied by an inner C\textsubscript{3}N\textsubscript{4} layer and an outer TiO\textsubscript{2} layer, both of which have a thickness about 7 nm (a
representative sample). With the unilateral illumination, the outer TiO$_2$ layer should be positive charged due to the directional movement of photogenerated holes (Fig. 4c). By this way, the anions will move from non-illuminated side to the illuminated side (Fig. 4d). Fig. 4e shows the cyclic constant zero-volt current across the nanotube membrane under a simulated solar illumination of 300 mW/cm$^2$. Without illumination, the zero-volt current is almost zero, while it increased to about -9 μA/cm$^2$ under illumination, which indicates that light provides an opposite external force for ion pumping. Fig. 4f shows clearly that the reverse C$_3$N$_4$/TiO$_2$ combination yields an opposite transmembrane photovoltage compared to the TiO$_2$/C$_3$N$_4$ combination (Fig. 3f), in agreement with the reversed ion transport performance and further confirming the mechanism of light-driven ion transport. By this way, we can assume that not only the ion transport direction can be directly controlled using different semiconductor heterojunction combinations, but also that the photocurrent value can be adjusted by combining different semiconductor with suitable band gaps. It means that semiconductor heterojunction nanotubes are a universal way to realize light-driven ion transport.

**Photo-enhanced blue energy generation**

Beyond providing a novel way for photoelectrical energy conversion, this ion transport system can be potentially integrated into other energy harvesting approaches, e.g. to harvest salinity gradient energy, also called “blue energy”$^{33-35}$. Blue energy is discussed to be a sustainable, abundant and inexpensive source of clean energy that is mainly stored in the sheer amount of available fresh and salty water being mixed (for instance at the Yangtze river muzzle)$^{36}$. The recently developed nanofluidic reverse-electrodialysis (NRED) method provides a very appealing way to harvest this energy and works again by a charged nanochannel or porous nanochannel membranes.$^{10,37}$ In the NRED process, surface charge density plays a crucial role. Generally speaking, high surface charge density will boost the blue energy power density. The weakly charged TiO$_2$/C$_3$N$_4$ heterojunction nanotube membrane can be already used to harvest blue energy, but only creates an osmotic current of 21 μA/cm$^2$ employing a 100-fold (0.1 M-0.001M) concentration gradient (Fig. 5). With 300 mW/cm$^2$ light irradiation from the low concentration side, the osmotic current increased to about 28 μA/cm$^2$. This enhanced osmotic current is ascribed to the increased surface charge density induced by light irradiation, but also to the pumping flux being of the order of the current increase. The present light-driven ion transport system thereby provides a chance to integrate of solar energy and salinity gradient energy,$^{32}$ potentially even overcoming the disadvantages of low energy efficiency and poor power density that blue energy still meets so far.

**CONCLUSION**

In summary, we reported that semiconductor heterojunction nanotubes, here looking into TiO$_2$/C$_3$N$_4$ heterojunction nanotubes as an example, can be used for constructing artificial light-driven ion transport system, which then can be used for ionic energy generation. The light-driven ionic current can reach up to about 9 μA/cm$^2$, three times of C$_3$N$_4$ nanotubes. Meanwhile, the ionic transport direction can easily be reversed by modifying the semiconductor deposition sequence. The enhanced and flexible light-driven ionic current can be ascribed to the redistribution of surface charge across nanotubes. In addition, we may expect that other semiconductor or semiconductor heterojunction nanostructures, which are currently used...
for photocurrent generation, e.g. two-dimensional van der Waals semiconductors\(^{38}\) or 2D MOF\(^{39}\), also will exhibit similar light-driven ion transport performance. Most importantly, not only ions but also specific charged organic molecules up to small peptides are expected to be transported by the aid of this novel approach for directed molecular movement.

SUPPLEMENTARY DATA
Supplementary data are available at NSR online

ACKNOWLEDGEMENTS
This work was financially supported by Max Planck Society and National Key Research.

AUTHOR CONTRIBUTIONS
K.X. conceived, designed and performed the experiments. P.G. performed the CVD and fluorescent mapping. F.X.C performed the ALD and XPS. T.H. acquired the TEM measurements. R.T.C. helped measure the KPFM and discussed the mechanism. K.X. wrote the manuscript. All authors analysed the data and discussed the results.

REFERENCES
1. Ruangsupapichat N, Pollard MM and Harutyunyan SR \textit{et al.} Reversing the direction in a light-driven rotary molecular motor. \textit{Nat Chem} 2011; \textbf{3}: 53-60.
2. Li Q, Fuks G and Eoulin M \textit{et al.} Macromolecular contraction of a gel induced by the integrated motion of light-driven molecular motors. \textit{Nat Nanotechnol} 2015; \textbf{10}: 161-165.
3. Cheng C, McGonigal PR and Schneebeli ST \textit{et al.} An artificial molecular pump. \textit{Nat Nanotechnol} 2015; \textbf{10}: 547-553.
4. Chen G, Waterhouse GIN, and Shi R \textit{et al.} From Solar Energy to Fuels: Recent Advances in Light-Driven C1 Chemistry. \textit{Angew Chem Int Ed} 2019; \textbf{58}: 17528-17551.
5. Gratzel M. Photoelectrochemical cells. \textit{Nature} 2001; \textbf{414}: 338-344.
6. Kornienko N, Zhang J, and Sakimoto KK \textit{et al.} Interfacing nature’s catalytic machinery with synthetic materials for semi-artificial photosynthesis. \textit{Nat Nanotechnol} 2018; \textbf{13}: 890-899.
7. Zhang H, Liu H and Tian Z \textit{et al.} Bacteria photosensitized by intracellular gold nanoclusters for solar fuel production. \textit{Nat Nanotechnol} 2018; \textbf{13}: 900–905.
8. Ong WJ, Tan LL and Ng YH \textit{et al.} Interfacing nature’s catalytic machinery with synthetic materials for semi-artificial photosynthesis. \textit{Chem Rev} 2016; \textbf{116}: 7159-7329.
9. Steinberg-Yfrach G, Liddell P and Hung S-C \textit{et al.} Conversion of light energy to proton potential in liposomes by artificial photosynthetic reaction centres. \textit{Nature} 1997; \textbf{385}: 239-241.
10. Xie X, Crespo GA and Mistlberger G \textit{et al.} Photocurrent generation based on a light-driven proton pump in an artificial liquid membrane. \textit{Nat Chem} 2014; \textbf{6}: 202-207.
11. Xie X and Bakker E. Photoelectric conversion based on proton-coupled electron transfer reactions. \textit{J Am Chem Soc} 2014; \textbf{136}: 7857-7860.
12. Zhang Z, Li P and Kong X-Y \textit{et al.} Bioinspired Heterogeneous Ion Pump Membranes: Unidirectional Selective Pumping and Controllable Gating Properties Stemming from Asymmetric Ionic Group Distribution. \textit{J Am Chem Soc} 2018; \textbf{140}: 1083-1090.
13. Zhang Z, Kong X-Y and Xie G \textit{et al.} "Uphill" cation transport: A bioinspired photo-driven ion pump. \textit{Sci Adv} 2016; \textbf{2}: e1600689.
18. Giusto P, Cruz D and Heil T et al. Shine Bright Like a Diamond: New Light on an Old Polymeric Semiconductor. Adv Mater 2020; 32: 1908140.

19. Xiao K, Giusto P and Wen L et al. Nanofluidic Ion Transport and Energy Conversion through Ultrathin Free-Standing Polymeric Carbon Nitride Membranes. Angew Chem Int Ed 2018; 57: 10123-10126.

20. Xiao K, Chen L and Chen R et al. Artificial light-driven ion pump for photoelectric energy conversion. Nat Commun 2019; 10: 74.

21. Inoue K, Ono H and Abe-Yoshizumi R et al. A light-driven sodium ion pump in marine bacteria. Nat Commun 2013; 4: 1678.

22. Bamberg E, Tittor J and Oesterhelt D. Light-driven proton or chloride pumping by halorhodopsin. Proc Natl Acad Sci U S A 1993; 90: 639-643.

23. Subila KB, Sandeep K and Thomas EM et al. CdSe-CdTe Heterojunction Nanorods: Role of CdTe Segment in Modulating the Charge Transfer Processes. ACS Omega 2017; 2: 5150-5158.

24. Wang X, Maeda K and Thomas A et al. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. Nat Mater 2009; 8: 76-80.

25. Zhu B, Xia P and Ho W et al. Isoelectric point and adsorption activity of porous g-C₃N₄. Appl Surf Sci 2015; 344: 188-195.

26. Sano T, Tsutsui S and Koike K et al. Activation of graphitic carbon nitride (g-C₃N₄) by alkaline hydrothermal treatment for photocatalytic NO oxidation in gas phase. J Mater Chem A 2013; 1: 6489-6496.

27. Tian J, Liu Q and Asiri AM et al. Ultrathin graphitic C₃N₄ nanofibers: Hydrolysis-driven top-down rapid synthesis and application as a novel fluorosensor for rapid, sensitive, and selective detection of Fe³⁺. Sens Actuators B Chem 2015; 216: 453-460.

28. Li X-H, Zhang J and Chen X et al. Condensed Graphitic Carbon Nitride Nanorods by Nanoconfinement: Promotion of Crystallinity on Photocatalytic Conversion. Chem Mater 2011; 23: 4344-4348.

29. Xiao K, Tu B and Chen L et al. Photo-Driven Ion Transport for a Photodetector Based on an Asymmetric Carbon Nitride Nanotube Membrane. Angew Chem Int Ed 2019; 58: 12574 – 12579.

30. Godin R, Wang Y and Zwijnenburg MA et al. Time-resolved spectroscopic investigation of charge trapping in carbon nitrides photocatalysts for hydrogen generation. J Am Chem Soc 2017; 139: 5216-5224.

31. Merschjann C, Tschierlei S and Tyborski T et al. Complementing Graphenes: 1D Interplanar Charge Transport in Polymeric Graphitic Carbon Nitrides. Adv Mater 2015; 27: 7993-7999.

32. Graf M, Lihter M and Unuchek D et al. Light-Enhanced Blue Energy Generation Using MoS₂ Nanopores. Joule 2019; 3: 1549-1564.

33. Chen C, Liu D and He L et al. Bio-inspired nanocomposite membranes for osmotic energy harvesting. Joule 2020; 4: 247-261.

34. Siria A, Poncharal P and Biance A-L et al. Giant osmotic energy conversion measured in a single transmembrane boron nitride nanotube. Nature 2013; 494: 455-458.

35. Siria A, and Bocauet M-L and Bocquet L. New avenues for the large-scale harvesting of blue energy. Nat Rev Chem 2017; 1: 0091.

36. Marbach S and Bocquet L. Osmosis, from molecular insights to large-scale applications. Chem Soc Rev 2019; 48: 3102-3144.

37. Macha M, Marion S and Nandigana VVR et al. 2D materials as an emerging platform for nanopore-based power generation. Nat Rev Mater 2019; 4: 588-605.

38. Buscema M, Island JO and Groenendijk DJ et al. Photocurrent generation with two-dimensional van der Waals semiconductors. Chem Soc Rev 2015; 44: 3691-3718.

39. Song X, Wang X and Li Y et al. 2D Semiconducting Metal-Organiic Framework Thin Films for Organic Spin Valves. Angew Chem Int Ed 2020; 59: 1118 –1123.
Figure 1. Fabrication process and characterizations of TiO$_2$/C$_3$N$_4$ semiconductor heterojunction nanotubes. 

a, Simplified schematic of light-driven ion transport system. 
b, Fabrication process of TiO$_2$/C$_3$N$_4$ heterojunction nanotubes including two steps. Step 1: TiO$_2$ layer deposition by ALD; Step 2: C$_3$N$_4$ layer deposition by CVD, scale bar 0.5 cm. 
c, SEM images of TiO$_2$/C$_3$N$_4$ heterojunction nanotubes membrane from cross section and top view, scale bar 200 nm. 
d, TEM image of signal TiO$_2$/C$_3$N$_4$ nanotube (scale bar 100 nm) and enlarged wall surface (scale bar 10 nm). 
e, Elemental maps of TiO$_2$/C$_3$N$_4$ heterojunction nanotube wall. Each pixel covers 1 nm$^2$. 

Figure 2. Light-driven ion transport performance of TiO$_2$/C$_3$N$_4$ semiconductor heterojunction nanotube membrane. a, Measured cyclic constant zero-volt current with the alternating illumination at 0.1 M KCl concentration. b, Zero-volt current as a function of light density of 54 mW/cm$^2$, 128 mW/cm$^2$ and 300 mW/cm$^2$. c, Zero-volt current as a function of TiO$_2$ layer thickness. d, Zero-volt current as a function of monochromatic light (Blue: 405 nm; Green: 515 nm; Yellow: 590 nm) with same power density of 300 mW/cm$^2$. The ionic current is consistent with the light absorbance of outer C$_3$N$_4$ layer. e, Zero-volt current as a function of pH. Error bars in c-e represent the standard deviations of five independent experiments.
Figure 3. Mechanism of light-driven ion transport phenomenon. a, Schematic of the surface charge distribution on the nanotube before illumination, in which condition low density negative charge is homogeneous distributed over the nanotube. b, Light-induced separation of electrons and holes of C$_3$N$_4$. The holes will transfer from C$_3$N$_4$ to TiO$_2$. c, Schematic of the surface charge distribution on the nanotube after unilateral illumination, in which condition the separation of electrons and holes results in the heterogeneous negative charge distribution. d, Fluorescent mappings of C$_3$N$_4$ (left) and TiO$_2$/C$_3$N$_4$ (right) nanotube membranes. e, KPFM image of the TiO$_2$/C$_3$N$_4$ nanotube membranes. Scale bar, 200 nm. f, Surface potential (CPD) evolution with light on and off in pore area and wall area of the TiO$_2$/C$_3$N$_4$ nanotube.
Figure 4. Fabrication of C$_3$N$_4$/TiO$_2$ heterojunction nanotubes and their performance. a, Schematic fabrication process of the C$_3$N$_4$/TiO$_2$ heterojunction nanotube. Step 1: C$_3$N$_4$ layer deposition by CVD; Step 2: TiO$_2$ layer deposition by ALD. b, TEM image of signal C$_3$N$_4$/TiO$_2$ nanotube (scale bar 100 nm) and enlarged wall surface (scale bar 10 nm). c, Light-induced separation of electrons and holes of C$_3$N$_4$. The holes will transfer from C$_3$N$_4$ to TiO$_2$. d, Schematic of surface charge distribution and ion transport in the nanotube after unilateral illumination. e, Measured cyclic constant zero-volt current with alternating illumination. f, CPD evolution with light on and off in pore area and wall area of C$_3$N$_4$/TiO$_2$ nanotube.
Figure 5. Potential application of photo-driven ion transport for enhanced osmotic energy generation. The typical current-voltage curves before and after light (300 mW/cm$^2$) irradiation at 100-fold ($C_H=0.1$ M; $C_L=0.001$ M) KCl concentration gradient.