

Artificial Inorganic Leafs for Efficient Photochemical Hydrogen Production Inspired by Natural Photosynthesis

By Han Zhou, Xufan Li, Tongxiang Fan,* Frank E. Osterloh, Jian Ding, Erwin M. Sabio, Di Zhang,* and Qixin Guo

Using sunlight to split water molecules and produce hydrogen fuel is one of the most promising tactics for controlling our carbon-based energy “habit”.^[1–3] Of the various possible methods, nature provides a blueprint for converting solar energy in the form of chemical fuels.^[4] A natural leaf is a synergy of elaborated structures and functional components in order to produce a highly complex machinery for photosynthesis in which light harvesting, photoinduced charge separation, and catalysis modules combine to capture solar energy and split water into oxygen and “hydrogen” (in the form of reducing equivalents) efficiently.^[5] Thus, the design of efficient, cost-effective artificial systems by the coupling of leaflike hierarchical structures and analogous functional modules under the guidance of the key steps of natural photosynthesis—capture of sunlight photons, electron–hole separation with long lifetimes,^[6] and energy transduction into hydrogen—would be a major advance in the development of materials for energy conversion. Here, we present a general strategy to assemble man-made catalysts (Pt/N-doped TiO₂) into leaf-shaped hierarchical structures, named artificial inorganic leaf (AIL), for efficient harvesting of light energy and photochemical hydrogen production. This concept may broaden the horizon for the design of artificial photosynthetic systems based on biological paradigms and provides a working prototype to exploit solar energy for sustainable energy resources.

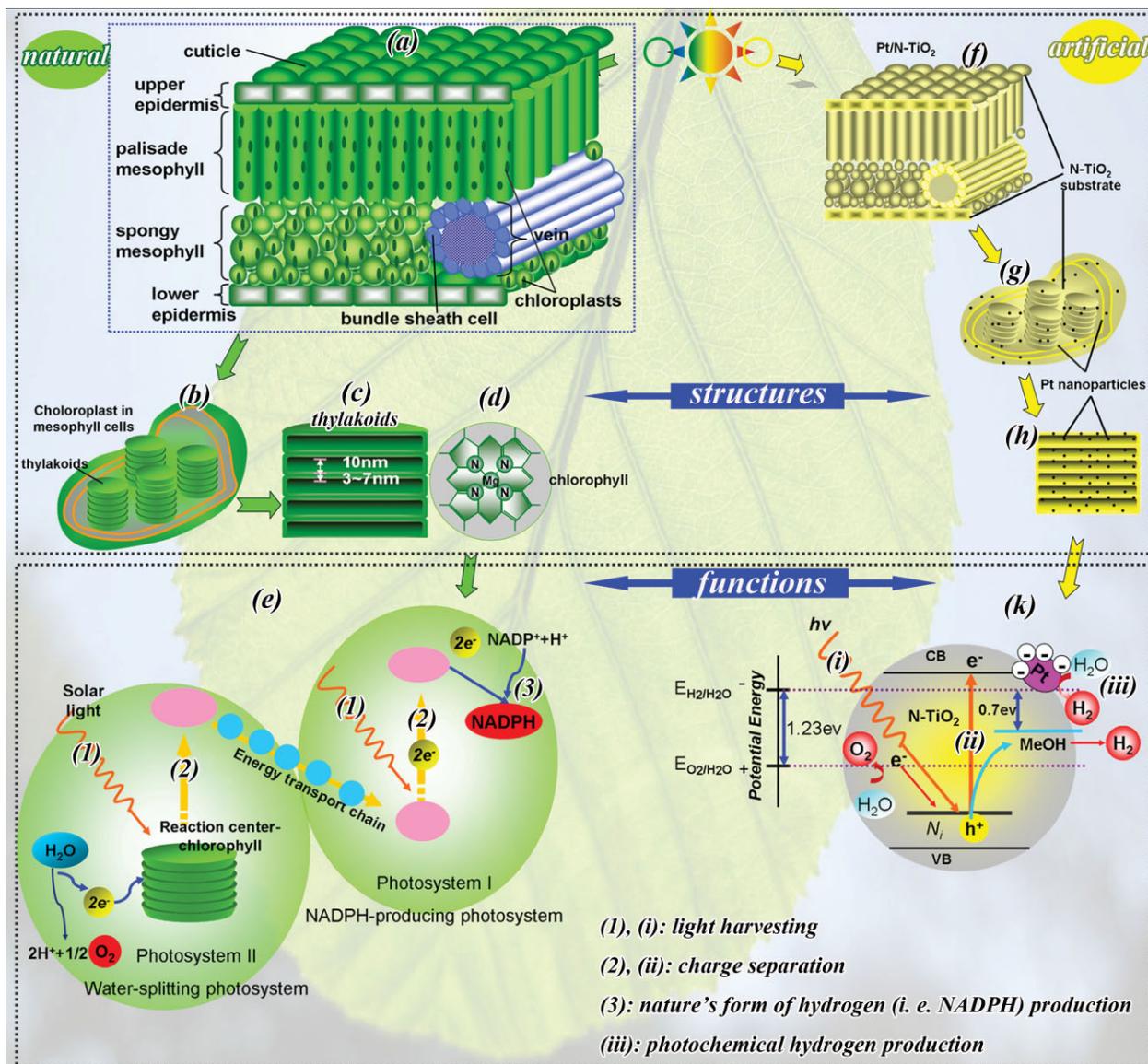
Many research efforts have been carried out to develop artificial photosynthetic systems by constructing a variety of analogous molecular systems consisting of electron donors and acceptors to mimic light-driven charge separation, which occur in photosynthetic reaction centers,^[7–9] or by assembling semiconductor photocatalysts into various nanostructures.^[10,11] Though signifi-

cant progress has been achieved, most research only focused on the functional imitation of photosynthesis and neglected the structural effect. Actually, the whole structure of natural leaves strongly favors light harvesting:^[12–14] the focusing of light by the lenslike epidermal cells,^[15,16] the multiple scattering and absorbance of light within the veins’ porous architectures,^[12,17] the light propagation in the columnar cells in palisade parenchyma acting as light guides,^[18] the enhanced effective light pathlength and light scattering by the less regularly arranged spongy mesophyll cells,^[19] and the efficient light-harvesting and fast charge separation in the high surface area three-dimensional constructions of interconnected nanolayered thylakoid cylindrical stacks (granum) in chloroplast.^[13] Meanwhile, the photosynthetic pigments in chloroplast successfully perform electron transfer and energy transduction.^[20] Thus, in order to mimic a photosynthetic system, it may be necessary for an artificial system to both have similar hierarchical structures for efficient light-harvesting and charge-separation-analogous functional modules, which could i) absorb incident photons, generating excited states, ii) transfer this excitation energy to a donor/acceptor interface, where photochemical charge separation takes place. Meanwhile, such a system should be able to transfer charge away from the interface in order to limit the rate of wasteful recombination reactions, and iii) it should couple the photochemically generated charges to appropriate catalysts for the production of hydrogen. So our approach for artificial photosynthesis is to construct an artificial leaf by copying the complex architecture of leaves, replace the natural photosynthetic pigments with man-made catalysts, and realize efficient light-harvesting and photochemical hydrogen production.

We first demonstrate this new concept with N-doped TiO₂, a widely used visible-light-responsive photocatalyst for hydrogen production.^[21] Recently, there has been a strong interest in doping TiO₂ with anions such as N, S, B, P, C, and halogens.^[22–25] N was claimed to be the best dopant for TiO₂ activated under visible light.^[21] Since N is contained in different forms in natural leaves, such as in cytoplasm, karyons, chlorophyll, enzymes, and lecithin among others, N is expected to be self-doped into TiO₂ from the natural leaves during synthesis in our experiment. We chose *Anemone vitifolia* Buch. leaf, a typical dicotyledon leaf as a model for biomimicry. Firstly, we explore aspects of natural leaf that may enable attainment of the high efficiency of solar energy transduction. We begin with a brief introduction of the elaborate architectures of the natural leaf ranging from macro-, micro-, to nanoscales (Scheme 1a–d). The organization of structural elements within the leaf and the unique architecture of each

[*] Prof. T. Fan, Prof. D. Zhang, Dr. H. Zhou, X. Li, Prof. J. Ding
State Key Laboratory of Metal Matrix Composites
Shanghai Jiaotong University
Shanghai 200240 (China)
E-mail: txfan@sjtu.edu.cn; zhangdi@sjtu.edu.cn
Prof. F. E. Osterloh, Dr. E. M. Sabio
Department of Chemistry
University of California
Davis, 1 Shields Ave, Davis, California 95616 (USA)
Prof. Q. Guo
Department of Electrical and Electronic Engineering
Saga University
Saga 840-8502 (Japan)

DOI: 10.1002/adma.200902039



Scheme 1. Comparison of natural and artificial leaves from their structures and functions. Natural and artificial leaves have similar hierarchical structures. They use some key steps for energy transduction.

element play a significant role in the promotion of the light harvesting efficiency.^[12]

Many plant species possess lenslike epidermal cells (Fig. 1a and Fig. S1b of the Supporting Information). These cells act as lenses that focus the light in the leaf interior via refraction^[15] (Fig. 1a). Light that is incident upon the adaxial leaf surface is concentrated within the palisade, whereas light that is incident upon the abaxial leaf surface is concentrated within the spongy layers.^[15] Such convexly shaped epidermal cells would also facilitate the capture of light that strikes the leaf from oblique directions.^[15] So, refraction of light through the epidermis of leaves can create local irradiances within the leaf that are significantly higher than that present within the ambient light environment. Theoretically maximal focal intensification can approach 20 times the irradiance of incident light^[26] when that

light is collimated. Furthermore, internal light-scattering can trap light so that internal fluence rates can exceed that of incident light. As a result, epidermal focusing and the distribution of light within the leaf enhance light-harvesting for photosynthesis.

As shown in the cross-section (Scheme 1a), a leaf is mainly composed of veins, palisade mesophyll, and spongy mesophyll layers arranged between two layers of epidermal cells from a tissue scale. The optical (Fig. 1c) and field-emission scanning electron microscopy (FESEM) (Fig. 1d) images of the cross-section of the veins indicate highly porous architectures. Light that enters leaf venation architectures becomes highly scattered and increases light absorption. Bundle sheath extensions (Fig. 1b) cover up to 50% of the leaf surface area,^[17] which can transfer light into deeper layers,^[17] implying a potentially important linkage with light-harvesting capacity.

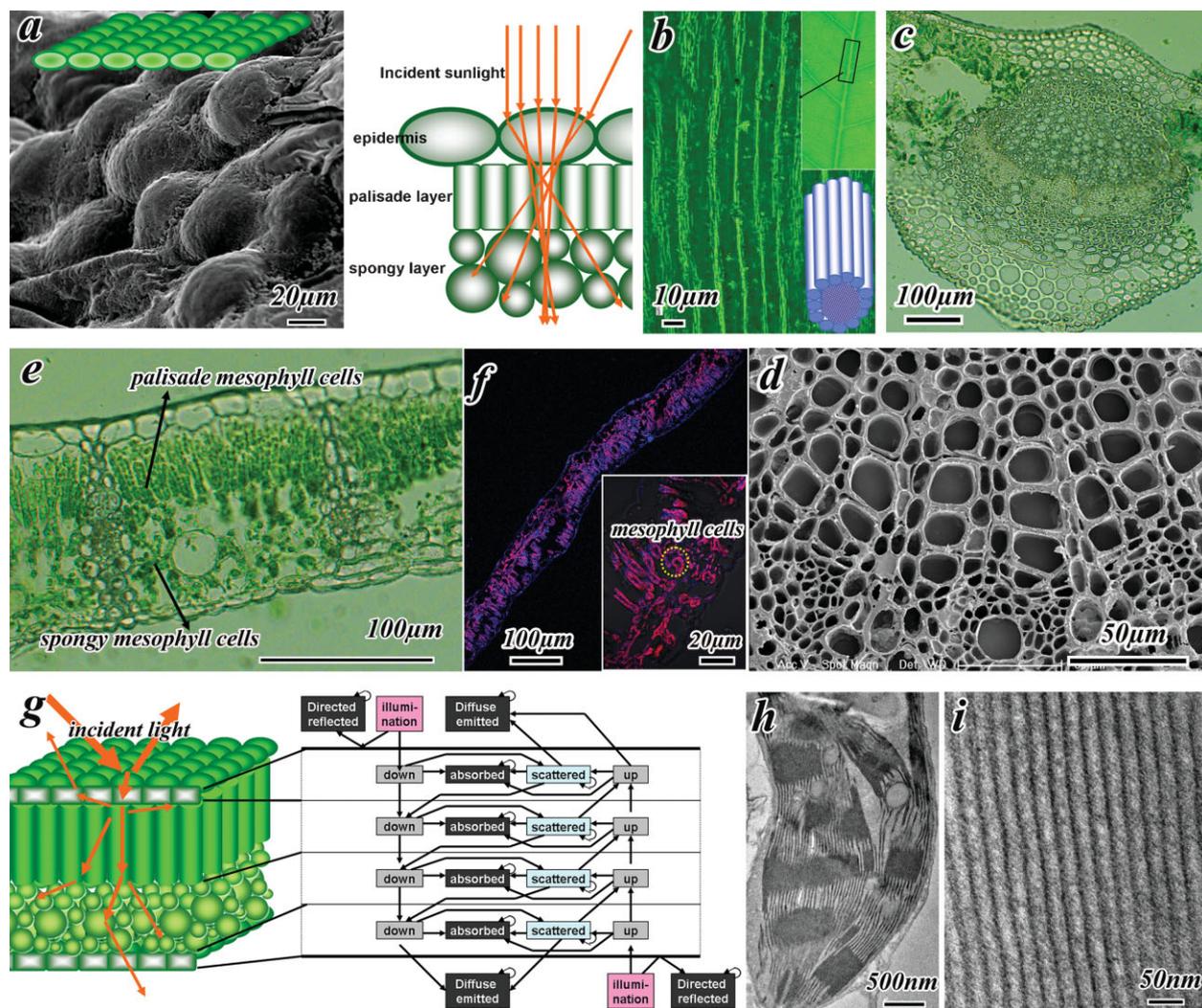


Figure 1. a) Left: FESEM image of the upper epidermis of *A. vitifolia* Buch. Leaf; the inset shows a 3D image of the same. Right part: illustration of epidermal focusing by a lens mechanism and light distribution within the leaf. b) Magnified surface image of bundle sheath extensions (top view) obtained by digital microscopy; the inset is 3D illustration of the same. c) Cross-section of the vein architecture observed with optical microscopy. d) FESEM image of the cross-section of the vein architecture. e) Optical microscopy image of the cross-section of *A. vitifolia* Buch. leaf, indicating the differentiation of leaf mesophyll into palisade and spongy layers. f) Cross-section observed under CLSM, with the inset of a magnified image. g) pathway of light through a dicotyledon leaf as envisioned by the stochastic theory. h) TEM image of a chloroplast in mesophyll cells and i) TEM image of a granum—the layered nanostructure of thylakoid membranes.

A further important factor that modifies the leaf light-harvesting efficiency is the differentiation of leaf mesophyll into palisade and spongy layers (Scheme 1a, Fig. 1e, and Fig. S2 of the Supporting Information). The columnar cells in palisade parenchyma are elongated and parallel to the direction of direct light, facilitating light channeling into the leaf.^[18] These cells act as light guides, propagating light through the tube-shaped vacuoles and intercellular air spaces.^[18] The spongy mesophyll cells are less regularly arranged, leading to greater effective light path length and light scattering.^[19] Many optical models for leaves have predicted photon transport within the leaves.^[27–30] Figure 1g illustrates the pathway of light through a dicotyledon leaf derived from the stochastic theory.^[27] The boxes represent different photon states. Such complex structures bring about multiple

scattering and light absorption within the leaves, resulting in enhanced light-harvesting.

The internal structure of an individual mesophyll cell contains a number of chloroplasts, which occur in mesophyll cells that display a chlorophyll fluorescence (red), while the vascular bundles, cuticles, and mesophyll cell walls can be observed through their blue fluorescence emission with confocal laser-scan microscopy (CLSM) (Fig. 1f). Each chloroplast contains nano-layered (only several nanometers) thylakoids stacks (granum) (Scheme 1b and 1c), which are consistent with TEM findings (Fig. 1h and 1i). A series of photosynthetic pigments arrange in the thylakoid membrane of chloroplasts, among which chlorophyll is the most important one (Scheme 1d). Such stacked nanolayered three-dimensional lamellar structures with high

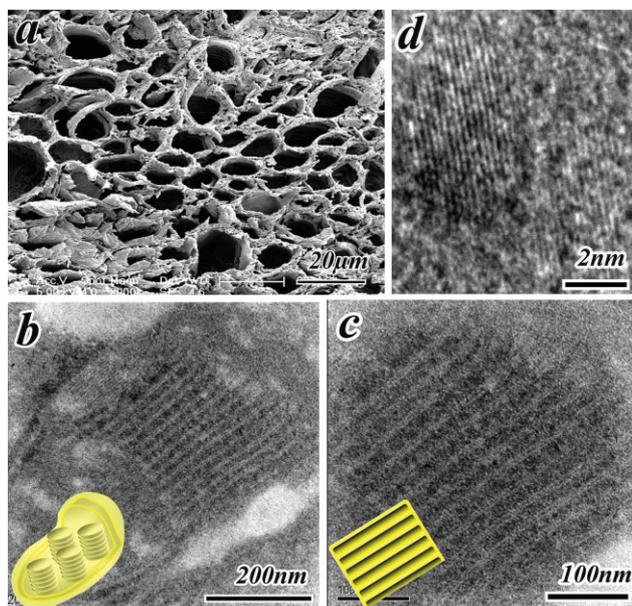


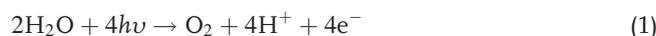
Figure 2. a) FESEM image of a cross-section of AIL-TiO₂ derived from *A. vitifolia* Buch. leaf. b) TEM image of a layered nanostructure in AIL1-TiO₂, with a corresponding illustration of the 3D structures. c) Magnified TEM image of layered nanostructures in AIL1-TiO₂; the inset is the corresponding illustration. d) HRTEM image of Pt nanoparticles deposited on TiO₂.

surface areas are favorable for the efficient interaction between photosynthetic pigments and sunlight.^[14] Moreover, the nano-layered architectures (Scheme 1c) on nanoscale are beneficial for the fast charge separation.

Based on the prototype of the hierarchical structures of natural leaf, N-doped TiO₂ replicas are obtained via a two-step infiltration process with natural leaves as templates, as demonstrated by previous research in our group.^[31] The replicas inherit the hierarchical structures of the natural leaf at macro-, micro-, and nanoscales including convexly shaped epidermal leaf cells (Fig. S3a of the Supporting Information), tubelike parallel bundle sheath extensions (Fig. S3b of the Supporting Information), a porous framework of veins (Fig. 2a), the differentiation of columnar palisade mesophyll cells, and irregularly arranged spongy cells (Fig. S3c of the Supporting Information), and nanolayered lamellar structures of granums in chloroplast (Fig. 2b and 2c). Thus, we refer to the replica as AIL1-TiO₂. We deposited 2 wt.% Pt nanoparticles on the AIL1-TiO₂ by using photodeposition,^[32] this way we obtained N-TiO₂-Pt composites, termed as AIL1-Pt/TiO₂. The size of the Pt nanoparticles was estimated to be 3–5 nm (Fig. 2d). The corresponding illustrations of the artificial leaves are shown in Scheme 1f–h. Besides *A. vitifolia* Buch. leaf, *Zea Mays* Linn. and *Vigna sinensis* Linn. leaf were used as templates as well to produce AIL2-TiO₂ (Fig. S4 of the Supporting Information) and AIL3-TiO₂ (Fig. S5 of the Supporting Information), respectively. Such AILs has assembled the light-harvesting, photoconversion, and catalytic modules into an integrated system which is possible to realize artificial photosynthesis.

To this end, it is important to know the detailed knowledge of natural photosynthesis first. The basic principles of light

reactions in photosynthesis are illustrated in Scheme 1e. The primary two steps of natural photosynthesis involve the harvesting of sunlight (Scheme 1e-(1)) and its conversion into spatially separated electron/hole pairs (Scheme 1e-(2)). The essential roles of chlorophylls are to capture solar energy, transfer the excitation energy to special locations, the reaction centers, and bring about the charge separation for the subsequent electron-transfer processes. As depicted in Scheme 1e, which shows the “light reactions”, there are photosystem I (PS I) and photosystem II (PS II), which involve the production of nicotinamide adenine dinucleotide phosphate-oxidase (NADPH) (nature’s form of hydrogen) and water splitting, respectively.^[33] The essential steps of water splitting that take place in PS II can be summarized as:



In the subsequent light reaction of PS I, the hydrogen is formally transferred to oxidized nicotinamide adenine dinucleotide phosphate (NADP⁺) and thereby reaches almost the same reduction potential as free H₂.^[33] The reaction sequence of PS I can be summarized as:



Essentially, Equation (2) can be simplified to:



Photosynthesis combines the oxidative and reductive chemistry described by Equations (1) and (3) to perform the overall reaction given by Equation (4):



Similar photochemical processes can be imitated in our artificial photosynthetic systems (Scheme 1k). Since Fujishima and Honda discovered photocatalytic H₂ evolution over TiO₂ in 1972,^[34] the photocatalytic procedures in TiO₂ or Pt-TiO₂ systems are widely investigated.^[35] Three main steps are shown in Scheme 1k including harvesting of photons to form electron–hole pairs, charge separation and migration of photogenerated carriers, and surface photocatalytic reactions.

As depicted in Scheme 1, many parallels from structures and functions can be drawn between natural and artificial leaves. They not only possess similar hierarchical structures but also experience some key steps for energy transduction: light harvesting, charge separation, and photochemical hydrogen/nature’s form of hydrogen (i.e., NADPH) production.

Next the performances of artificial systems are investigated. Firstly, the light-harvesting properties are characterized by UV–vis spectroscopy (Fig. S6 of the Supporting Information). Compared with TiO₂ nanoparticles, AIL-TiO₂ samples show two prominent features: one is that the overall visible-light absorbance intensities are enhanced. The other one is that the band-gap-absorption onsets, at the edge of the UV and visible light, show a red-shift. Here we set the absorbance intensity of TiO₂ nanoparticles as the reference, by subtracting the reference

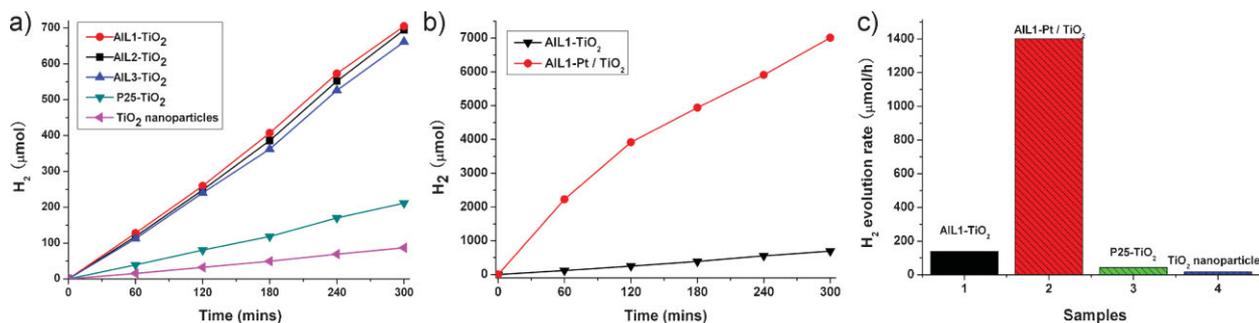


Figure 3. Hydrogen evolution from the samples in 20% aqueous methanol under UV- and visible-light irradiation. a) Comparison between AIL-TiO₂ series, commercial P25-TiO₂, and TiO₂ nanoparticles synthesized without templates. b) Comparison between AIL1-TiO₂ and AIL1-Pt/TiO₂. c) Hydrogen evolution rates of four typical samples.

from those of AIL-TiO₂, we found that the average absorbance intensities within visible range increased 234, 207, and 200% for AIL1-TiO₂, AIL2-TiO₂, and AIL3-TiO₂, respectively. We attribute the overall light-harvesting enhancements to the hierarchical structures of the AIL derived from natural leaves including the organization of structural elements and unique architectures of each element. When incident light falls on the lenslike artificial epidermal cells of AIL-TiO₂, one part is absorbed by the surfaces, the other part becomes concentrated and propagates within the artificial leaf with much higher intensity. Similarly, the pathway of light through the artificial leaf is complicated: light entering an artificial leaf becomes highly scattered, partially absorbed, partially by multiple reflections from the numerous interfaces encountered as light passes through the artificial leaf. The large proportion (i.e., accounts for 50% of the surface area) and rounded shape of the artificial veins' porous architectures and the less regularly arranged artificial spongy mesophyll cells increase multiple scattering and the mean path length of the light. The tubelike parallel artificial bundles' sheath extensions are favorable for the transfer of light into deeper layers. The three-dimensional interconnected nanolayered constructions of artificial thylakoid cylindrical stacks have high surface areas for further light-harvesting. Thus, the synergy of the above factors increases the overall light-harvesting. On the other hand, the bandgap-absorption onsets, at the edge of the UV and visible light, show red-shifts of 25–100 nm. This is caused by the self-doping of N with weight contents of about 0.9–1.5%, as demonstrated in our previous study.^[31] The nitrogen self-doping results in the formation of a localized state beyond the valence band.^[36] It is worth mentioning that in traditional nitrogen-doping methods large amounts of extra nitrogen sources are needed, such as Et₃N in a sol-gel procedure,^[37] NH₃ during calcinations, or N₂ gas during sputtering.^[38] However, our method does not depend on any extra nitrogen sources, which makes it a more straightforward approach. The AIL-TiO₂ successfully realizes the synergy of both the structure-introduced enhancement of the visible-light harvesting and the red-shift of the bandgap-absorption onsets induced by self-doping of nitrogen.

Photocatalytic studies for H₂ evolution (Fig. 3 and Table S1 of the Supporting Information) were also carried out. Apparent quantum efficiencies (QE = 2 · [H₂]/I) were calculated from the mean H₂ evolution rate (mol s⁻¹) and the quantum flux I (mol s⁻¹) of the irradiation system. The AIL1-TiO₂ evolves H₂ at a

rate of 1.30 μmol h⁻¹ in pure water (Fig. S7 of the Supporting Information). The activity of AIL1-TiO₂ in pure water is low, which might be attributed to high levels of recombination of the photogenerated electrons and holes as well as back reactions between the produced H₂ and O₂. When the reaction was performed in 20% aqueous methanol, which is a well-known sacrificial electron donor,^[39] the hydrogen evolution rate is about 108 times higher than in pure water, producing a total H₂ amount of 705.23 μmol after 5 h with an evolution rate of 141.05 μmol h⁻¹ (QE = 1.56%). The activity is about 8 times higher than that of TiO₂ nanoparticles synthesized without templates (QE = 0.193% in 20% aqueous methanol). AIL2-TiO₂ and AIL3-TiO₂ exhibit comparable activities with AIL1-TiO₂. Our AIL-TiO₂ samples also show much higher catalytic activity than P25, which is a commercial photocatalyst with high activity. The hydrogen evolution rate on average is about 3.3 times higher than P25. The enhanced catalytic activities of AIL-TiO₂ samples are a result of the synergy of their components and structures. The nitrogen doping could enlarge the bandgap absorption and enhance the visible light absorption in order to increase the photocatalytic activity. As emphasized above, the hierarchical structures derived from the natural leaves endow them with enhanced light-harvesting abilities, which could capture more photons for the photocatalytic reactions. A high surface area at macroscale, a porous framework at microscale, and an interconnected, nanolayered, 3D construction nanostructure at nanoscale endow them with high specific surface areas (e.g., 103.31 m² g⁻¹ for AIL1-TiO₂, Table S1 of the Supporting Information), which can offer more absorption and reaction sites for the photocatalytic reaction. Meanwhile, the focusing of incident light by the lenslike structures may increase the light intensity within the artificial leaf, and thus promote the photocatalytic reactions. The nanolayered, 3D nanostructures are beneficial for the effective charge separation at nanoscale.

When 2 wt % Pt nanoparticles are directly grown onto the artificial TiO₂ leaf, the hydrogen evolution rate of AIL1-Pt/TiO₂ increases to 1401.70 μmol h⁻¹ (QE = 15.54%) in 20% aqueous methanol, which is about 10 times higher than AIL1-TiO₂. It is known that the Pt co-catalyst promotes charge transfer and creates hydrogen desorption sites, leading to higher photocatalytic activity for H₂ production.^[40] The hydrogen evolution rates of four typical samples are compared in Fig. 3c. Furthermore, O₂ could also be detected (Fig. S8 of the Supporting Information)

when the reaction was performed in 0.05 M silver nitrate aqueous solution, a known sacrificial hole donor. The decrease in activity with reaction time is primarily attributable to the deposition of metallic silver on the catalyst surface, which blocks light absorption and obstructs active sites.^[41]

In summary, we have demonstrated here artificial inorganic leaves composed of Pt/N-doped TiO₂ for efficient water splitting under UV and visible light irradiation in the presence of sacrificial reagents by using natural leaves as biotemplates. The light-harvesting performance and photocatalytic activity of such systems are higher than those prepared with classic routes, which relate to the hierarchical structures derived from natural leaves and the effective nitrogen doping during synthesis. A systematic comparison of natural and artificial leaves from their structures and functions is presented. Though there are still many crucial differences between artificial and natural leaves, our results may represent an important first step towards the design of novel artificial solar-energy transduction systems based on natural concepts, particularly based on exploring and mimicking the structural design. Our means represents a versatile approach to multicomponent systems for the realization of the "Z scheme" derived from photosynthesis. It can also be extended to artificial polymeric or supermolecular leaves, whose appearances and components resemble much more than those found in nature. Our strategy also provides new perspectives for producing cost-effective leaf-shaped solar cells. Nature still has much to teach us, and human ingenuity can modify the principles of natural systems for enhanced utility.

Experimental

Experimental details are found in the Supporting Information.

Acknowledgements

This work is supported by National Natural Science Foundation of China (no.50972090), Program for New Century Excellent Talents in university (NCET-04-0387), National Basic Research Program of China (no.2006CB601200) and Major Fundamental Research Project of Shanghai Science Committee (no. 07D14001), and the Dawn program of Shanghai Education Commission (08SG15). Supporting Information is available online from Wiley InterScience or from the author.

Received: June 18, 2009

Revised: July 21, 2009

Published online: November 20, 2009

- [1] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729.
 [2] F. E. Osterloh, *Chem. Mater.* **2008**, *20*, 35.
 [3] M. Hambourger, G. F. Moore, D. M. Kramer, D. Gust, A. L. Moore, T. A. Moore, *Chem. Soc. Rev.* **2009**, *38*, 25.
 [4] N. Nelson, A. Ben-Shem, *Nat. Rev. Mol. Cell Biol.* **2004**, *5*, 971.
 [5] J. Barber, *Philos. Trans. R. Soc. Lond. Ser. A* **2007**, *365*, 1007.

- [6] *Anoxygenic Photosynthetic Bacteria*, (Eds: R. E. Blankenship, M. T. Madigan, C. E. Bauer), Kluwer, Dordrecht **1995**.
 [7] S. Fukuzumi, *Eur. J. Inorg. Chem.* **2008**, 1351.
 [8] J. H. A. Acevedo, M. K. Brennaman, T. J. Mayer, *Inorg. Chem.* **2005**, *44*, 6802.
 [9] D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2001**, *34*, 40.
 [10] D. M. Kaschak, J. T. Lean, C. C. Waraksa, G. B. Saupe, H. Usami, T. E. Mallouk, *J. Am. Chem. Soc.* **1999**, *121*, 3435.
 [11] X. Wang, K. Maeda, X. Chen, L. Takanabe, K. Domen, Y. Hou, X. Fu, M. Antonietti, *J. Am. Chem. Soc.* **2009**, *131*, 1680.
 [12] U. Niinemets, L. Sack, *Prog. Bot.* **2006**, *67*, 385.
 [13] E. Shimon, O. Rav-Hon, I. Ohad, V. Brumfeld, Z. Reich, *Plant Cell* **2005**, *17*, 2580.
 [14] L. Mustardy, in: *Oxygenic Photosynthesis: The Light Reactions*, (Eds: D. R. Ort, C. F. Yocum), Kluwer Academic Publishers, Dordrecht, The Netherlands **1996**.
 [15] M. E. Poulson, T. C. Vogelmann, *Plant Cell Environ.* **1990**, *13*, 803.
 [16] W. K. Smith, T. C. Vogelmann, E. H. Delucia, D. T. Bell, K. A. Shepherd, *Bioscience* **1997**, *47*, 785.
 [17] D. Nikolopoulos, G. Liakopoulos, I. Drossopoulos, G. Karabourniotis, *Plant Physiol.* **2002**, *129*, 235.
 [18] T. C. Vogelmann, G. Martin, *Plant Cell Environ.* **1993**, *16*, 65.
 [19] E. H. Delucia, K. Nelson, T. C. Vogelmann, W. K. Smith, *Plant Cell Environ.* **1996**, *19*, 159.
 [20] H. Paulsen, *Photochem. Photobiol.* **1995**, *62*, 367.
 [21] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* **2001**, *293*, 269.
 [22] S. Yin, H. Yamaki, M. Komatsu, Q. W. Zhang, J. S. Wang, Q. Tang, F. Saito, T. Sato, *J. Mater. Chem.* **2003**, *13*, 2996.
 [23] W. K. Ho, J. C. Yu, S. C. Lee, *J. Solid State Chem.* **2006**, *179*, 1171.
 [24] W. Zhao, W. H. Ma, C. C. Chen, J. C. Zhao, Z. G. Shuai, *J. Am. Chem. Soc.* **2004**, *126*, 4782.
 [25] S. Sakthivel, H. Kisch, *Angew. Chem. Int. Ed.* **2003**, *42*, 4908.
 [26] R. A. Bone, D. W. Lee, J. M. Norman, *Appl. Opt.* **1985**, *24*, 1408.
 [27] S. W. Maier, W. Ludeker, K. P. Gunther, *Remote Sens. Environ.* **1999**, *68*, 273.
 [28] R. Kumar, L. Silva, *Appl. Opt.* **1973**, *12*, 2950.
 [29] S. L. Ustin, S. Jacquemoud, Y. Govaerts, *Plant Cell Environ.* **2001**, *24*, 1095.
 [30] Y. M. Govaerts, S. Jacquemoud, M. M. Verstraete, S. L. Ustin, *Appl. Opt.* **1996**, *35*, 6585.
 [31] X. Li, T. Fan, H. Zhou, S. K. Chow, W. Zhang, D. Zhang, Q. Guo, H. Ogawa, *Adv. Funct. Mater.* **2009**, *19*, 45.
 [32] B. Kraeutler, A. J. Bard, *J. Am. Chem. Soc.* **1978**, *100*, 4317.
 [33] G. Renger, *Angew. Chem. Int. Ed.* **1987**, *26*, 643.
 [34] A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37.
 [35] M. Ni, M. K. H. Leung, D. Y. C. Leung, K. Sumathy, *Renewable Sustain. Energy Rev.* **2007**, *11*, 401.
 [36] S. Livraghi, M. C. Paganini, E. Giamello, A. Selloni, C. D. Valentin, G. Pacchioni, *J. Am. Chem. Soc.* **2006**, *128*, 15666.
 [37] J. L. Gole, J. D. Stout, C. Burda, Y. B. Lou, X. B. Chen, *J. Phys. Chem. B* **2004**, *108*, 1230.
 [38] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* **2001**, *293*, 269.
 [39] K. Domen, A. Kudo, M. Shibata, A. Tanaka, K. Maruya, T. Onishi, *J. Chem. Soc., Chem. Commun.* **1986**, 1706.
 [40] G. R. Bamwenda, S. Tsubota, T. Nakamura, M. Haruta, *J. Photochem. Photobiol. A: Chem.* **1995**, *89*, 177.
 [41] A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, *J. Am. Chem. Soc.* **2002**, *124*, 13547.