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Biomimetic polymeric semiconductor based hybrid nanosystems for artificial photosynthesis towards solar fuels generation *via* CO_2 reduction

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ABSTRACT

In photosynthesis, an intricate polymeric system is constructed by connecting a light-harvesting antenna network, a molecular water oxidation center, and CO_2 or proton-reduction machinery in a nanolayered architecture as a basic photosynthetic unit for solar-to-fuels conversion. Herein, we present a prototype basic artificial photosynthetic unit by connecting a typical CO_2/proton reduction catalyst, a cocatalyst and an electron mediator as well as CO_2 activator into a polymer based nano-architectured system for artificial photosynthesis with water and CO_2. Here, g-C_3N_4 nanosheets, mimicking the nanolayered thylakoids stacks are demonstrated as promising photocatalytic elements with planar configuration and high surface area, which provide an excellent platform for the assembly of other analogous elements. Au NPs are served as a suitable cocatalyst. ZIF-9, as a typical cofactor to illustrate this concept here, is used as a CO_2 concentrator and an electron mediator to promote the redox reaction. In artificial photosynthesis, driven by light energy, water and CO_2 are served electron donor and carbon source respectively for the generation of H_2 and CO. The artificial unit described here as a simple model, provides an important biomimetic step down a path aligned with the low-cost artificial photosynthetic systems manufacturing.

1. Introduction

Artificial photosynthesis, the solar conversion process that is combining water splitting and CO_2 reduction without sacrificial electron donors is a great challenge for the generation of sustainable green energy [1–4]. Compared with water splitting, "CO_2 reduction" is more urgent but also more challenging [5–7] because of rather low efficiency, limited catalysts and sacrificial agents usually needed. Biomimetics, emulating or duplicating biosystems from the molecular to the nano- and macroscales, is a promising approach for novel artificial systems [8–10]. A natural leaf is a three-dimensional polymeric system [11] with abundant non-metallic elements at the most fundamental (molecular) level (Fig. 1(a)). At the nanoscale level, photosynthesis occurs in the nanolayered thylakoids stacks (granum) where photosynthetic pigments, functional proteins, electron carriers and cofactors are precisely arranged, serving as the most basic photosynthetic unit (Fig. 1(b),(c)) for the further integration into a 3D hierarchical biomachinery [12]. Therefore, to realize artificial photosynthesis applicable, we are motivated to design a model system by the construction of a basic artificial photosynthetic unit consisting of (a) inexpensive and widely available earth-abundant materials as a stable water splitting and CO_2 reduction system, combined with cofactors for light harvesting, charge-separation, CO_2 activation and so forth. (b) Linkage of typical artificial elements together into an architectural and functional analogous working assembly.

Molecular biomimetic is a fundamental approach for the design of biomimetic catalysts from molecular principles. The functions of some enzymes in photosynthesis rely on the N–C=N groups (e.g. histidine shown in Fig. 1(a), which is used for CO_2 fixation). Motivated thus, graphitic carbon nitride (g-C_3N_4), a metal-free polymeric semiconductor with abundant N–C=N bonds composed of N-bridged tri-s-triazine units [13] has emerged as a promising material. Such molecular structure endows g-C_3N_4 a super electronic structure with 2.7 eV bandgap as well as surface basicity

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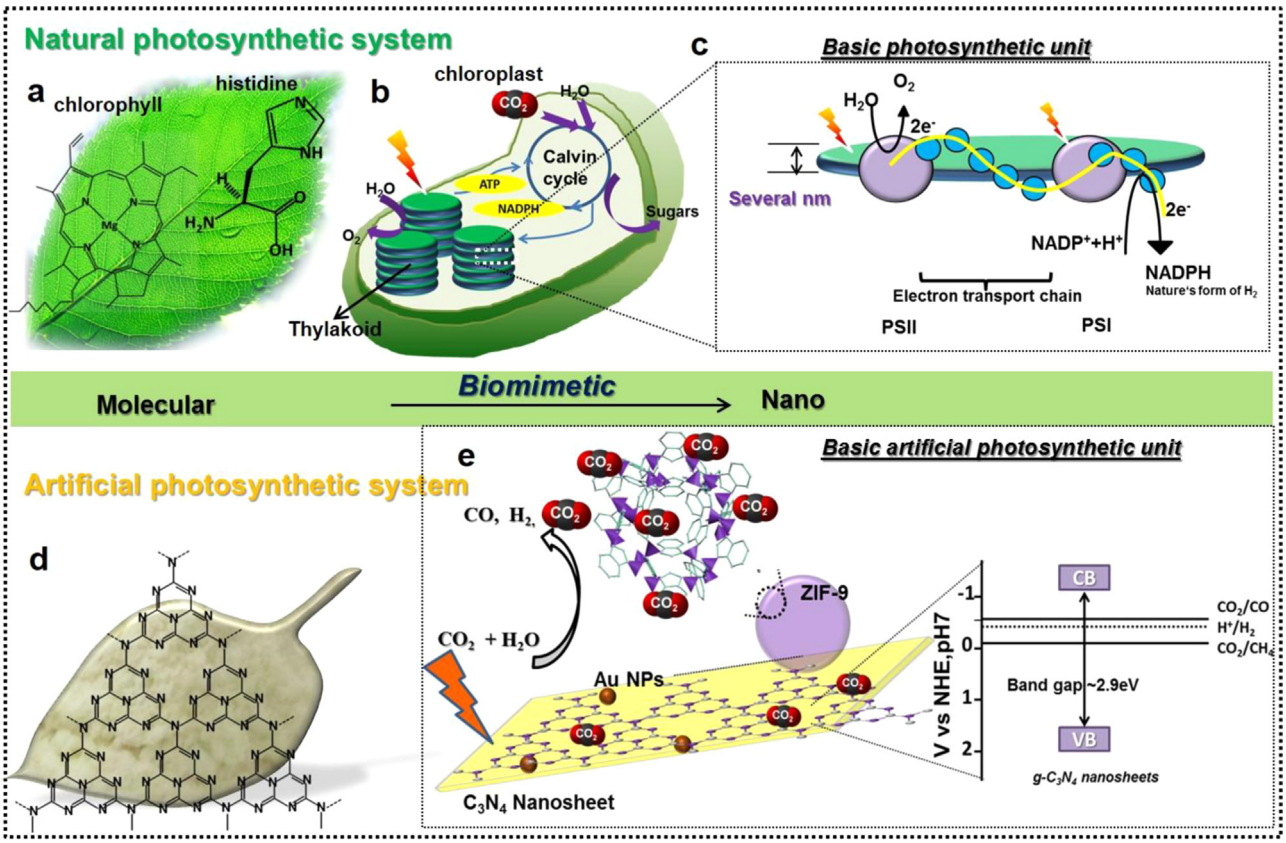

Fig. 1. Schematic illustration of natural and artificial photosynthetic systems. (a) A natural leaf with abundant nonmetallic elements at the most fundamental (molecular) level, left part: molecular structure of chlorophyll, the main photosynthetic pigment. Right part: molecular structure of histidine, an important enzyme for photosynthesis, with abundant N–C=N bonds. (b) A simplified scheme of the light-driven reactions of photosynthesis in a chloroplast. (c) basic photosynthetic unit: a single thylakoid embedded photosynthetic pigments, protein complexes to carry out the light reactions of photosynthesis. (d) molecular structure of polymeric g-C_3N_4. (e) artificial photosynthesis on the basic artificial photosynthetic unit composed of CNS as the catalytic element, Au NPs as a cocatalyst and ZIF-9 as electron mediator and CO_2 activator. Indicating the process is using CO_2 and H_2O as the inputs and CO, H_2 as the outputs under light irradiation.

[14]. Thus g-C_3N_4 has wide applications in photocatalytic water splitting and photoelectrochemical energy conversion [15,16], oxygen-reduction reactions [17], NADH regeneration [18], CO_2 activation thermally [19] or catalytically with sacrificial agents [20], catalysis [21,22] and pollutants control [23]. Therefore, thanks to its earth-abundant elements and biomimetic molecular configuration, g-C_3N_4 has shown great promise for artificial photosynthesis. In particular, nanostructured g-C_3N_4 with biomimetic super structures is appealing. However, the design, selection and assembly of other artificial elements suitably onto g-C_3N_4 nanoarchitectures to construct an architectural and functional analogous device are the key questions.

Natural photosynthesis takes place in the nanolayered thylakoid membrane where photosystems are connected with an electron transfer chain. These processes ensure that the charge separation quantum efficiency is close to unity. While for the CO_2 fixation process, carbon dioxide concentrating mechanisms exist, sharing the common feature of concentrating CO_2 around the carbon-fixing enzyme, such that RuBisCO operating at a higher efficiency [24]. Inspired by photosynthesis, the constructions of some cofactors such as electron mediator, CO_2 concentrator/activator are particularly important. Metal-organic frameworks (MOFs) are microporous 3D materials with ultrahigh surface areas, adjustable cavities and controllable chemistry [25]. Zeolitic imidazolate frameworks (ZIFs), as a subclass of MOFs are constructed from transition-metal ions together with organic ligands. Both of the two building units function synergistically for the efficient transfer of the excited electrons for redox reaction. Furthermore, ZIFs show exceptionally high capacity for CO_2 uptake [26,27]. This gives some opportunities for MOFs/ZIFs to play a significant role in artificial photosynthesis [25,28].

To this end, we present a prototype basic artificial photosynthetic unit by connecting a typical CO_2/proton reduction catalyst, a cocatalyst and an electron mediator as well as CO_2 activator into a polymer based nano-architectured system for artificial photosynthesis with water and CO_2. Here, g-C_3N_4 nanosheets, mimicking the nanolayered thylakoids stacks (Fig. 1(c) and Fig. 2 (a)) are demonstrated as a promising photocatalytic element with planar configuration and high surface area which provide an excellent platform for the assembly of other analogous elements. Au nanoparticles (NPs) are served as a suitable cocatalyst. ZIF-9, as a typical cofactor to illustrate this concept here, is used as a CO_2 concentrator and an electron mediator to promote the redox reaction. In artificial photosynthesis, driven by light energy, H_2O and CO_2 are served electron donor and carbon source respectively for the generation of H_2 and CO. This work demonstrates a conceptual strategy for the versatile design of highly efficient systems *via* integration of multiple functional components onto g-C_3N_4 nanoarchitectures.

2. Experimental

2.1. Synthesis of Au loaded C_3N_4 nanosheets

Firstly, C_3N_4 nanosheets were first synthesized *via* a thermal oxidation etching process according to a procedure described previously. Typically, dicyandiamide was calcined at 550 °C for 4 h