Review

Solar energy conversion on g-C$_3$N$_4$ photocatalyst: Light harvesting, charge separation, and surface kinetics

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A B S T R A C T

Photocatalysis, which utilizes solar energy to trigger chemical reactions, is one of the most desirable solar-energy-conversion approaches. Graphitic carbon nitride (g-C$_3$N$_4$), as an attractive metal-free photocatalyst, has drawn worldwide research interest in the area of solar energy conversion due to its easy synthesis, earth-abundant nature, physicochemical stability and visible-light-responsive properties. Over the past ten years, g-C$_3$N$_4$ based photocatalysts have experienced intensive exploration, and great progress has been achieved. However, the solar conversion efficiency is still far from industrial applications due to the wide bandgap, severe charge recombination, and lack of surface active sites. Many strategies have been proposed to enhance the light absorption, reduce the recombination of charge carriers and accelerate the surface kinetics. This work makes a crucial review about the main contributions of various strategies to the light harvesting, charge separation and surface kinetics of g-C$_3$N$_4$ photocatalyst. Furthermore, the evaluation measurements for the enhanced light harvesting, reduced charge recombination and accelerated surface kinetics will be discussed. In addition, this review proposes future trends to enhance the photocatalytic performance of g-C$_3$N$_4$ photocatalyst for the solar energy conversion.

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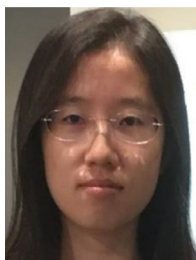
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1. Introduction

Due to the explosion of population and industrialization, humans are currently facing the global energy shortage and environmental problems. It is necessary to explore and develop sustainable and green energy system. Solar energy, which is a type of free, clean, abundant, and renewable energy on earth, is a fascinating gift from nature. However, the solar energy cannot be used as industrial and domestic energy supply directly due to its discontinuity and instability. Thus, tremendous attention have been focused on the area of solar energy conversion [1–4]. Photocatalysis, which stores solar energy into chemical bonds, exhibits high potential for solar energy conversion. Since the pioneering work from Fujishima and Honda in 1970s [5], the whole world shows dramatically increasing interest in the photocatalysis [6–8], which can be confirmed by the exponential increase of annual publications in this area [9].

Photocatalysis mainly includes water splitting for hydrogen (H_2) generation [10], reduction of carbon dioxide (CO_2) for solar energy generation [11], degradation of pollutant [12] and organic synthesis [13], of which the basic mechanism is the same. Taking semiconducting photocatalyst as an example, the electrons jump up to the conduction band (CB) while holes generate in the valence band (VB) under light irradiation, and then they transfer to the surface of photocatalyst for redox reaction (Fig. 1a). During the charge transfer, photo-excited electron-hole pairs easily recombine and lower the solar energy conversion efficiency. The whole photocatalytic reaction is a six-step process, including absorption of photon, separation of exciton, diffusion of carrier, transport of carrier, catalytic reaction and transfer of mass. The six processes are in different time scales, varying from femtosecond to microsecond (Fig. 1b) [14]. The photocatalytic reaction is the synergistic effect of the six processes. Apparently, the six processes can be briefly divided into three main steps: light absorption, charge separation and transport, and surface reaction. To achieve high solar energy conversion efficiency, the photocatalyst should meet three requirements. First, the photocatalyst should be visible-light responsive, because more than 45% of sunlight is visible light [14]. Second, the photocatalyst should show good electric conductivity, otherwise the photo-excited electron-hole pairs may recombine during the transport process (Fig. 1a). Third, the surface of the photocatalyst should be active for the redox reaction. Thus, the development of efficient photocatalysts is mainly focused on three aspects: enhancing light harvesting, reducing charge recombination, and accelerating surface kinetics.

Since the first report about photocatalysis, many materials have been exploited as photocatalysts for solar energy conversion [6]. Among them, titanium dioxide (TiO_2) has been investigated mostly, because of its low-cost, long-term stability and environment friendly [15]. However, the bandgap of TiO_2 is around 3.2 eV, making it active only under UV light (4% of sunlight) illumination [16]. In order to achieve highly efficient solar energy conversion, many visible-light-responsive materials such as metal sulphide, metal (oxy)nitride, and solid solution have been developed as photocatalysts [6]. Some of them show high solar energy conversion efficiency, but they suffer from self-oxidation during the photocatalytic reaction and harm the long-term stability. In 2009, graphitic carbon nitride (g-C_3N_4) polymer was demonstrated as a non-metal photocatalyst for solar H_2 production under visible light [17]. Due to its easy synthesis, earth-abundant nature, physicochemical stability and visible-light-responsive property, this photocatalyst drew worldwide research interest immediately. Since the first report in 2009, the annual publications and citations about g-C_3N_4 photocatalyst increased dramatically [9]. Based on the indepth research, there has been a more comprehensive understanding about this photocatalyst over time. Although g-C_3N_4 is visible-light-responsive, the relative wide bandgap limits its light absorption to around 460 nm, which is only a small amount of visible light. In addition, the organic semiconductors usually produce Frenkel excitons under light irradiation. The Frenkel excitons possess high binding energy, which means low dissociation probabilities and leads to serious charge recombination [18,19]. The last but not the least, the surface of g-C_3N_4 lack active sites for redox reaction, which results in a low probability of surface reaction for the photogenerated charge carriers [17]. Around these issues, tremendous attention has been devoted into the development of g-C_3N_4 photocatalyst and great progress has been achieved. Many chemical strategies, including morphology control, doping, defects control, heterojunctions, and co-catalysts have explored to improve the photocatalytic activity [20–22].

Up to date, there have been some interesting reviews on g-C_3N_4, which described the history, property, synthesis techniques, possible applications and strategies of improving the photocatalytic performance [9,23–29]. However, considering the fast development of this area, a critical review focusing on the contributions of various chemical strategies to the photocatalytic process is lacking to provide the readers with a whole picture of the recent progress in this field. In order to better design the g-C_3N_4 photocatalyst for efficient solar energy conversion, it is of great importance to clarify the influence of those strategies to the photocatalytic activity. Herein, we make a critical review on the main contributions of those strategies to the light absorption, charge separation and transport, and surface kinetics. Furthermore, the evaluation measurements for the enhanced absorption of light, reduced recombination of charge carriers and accelerated surface kinetics have been
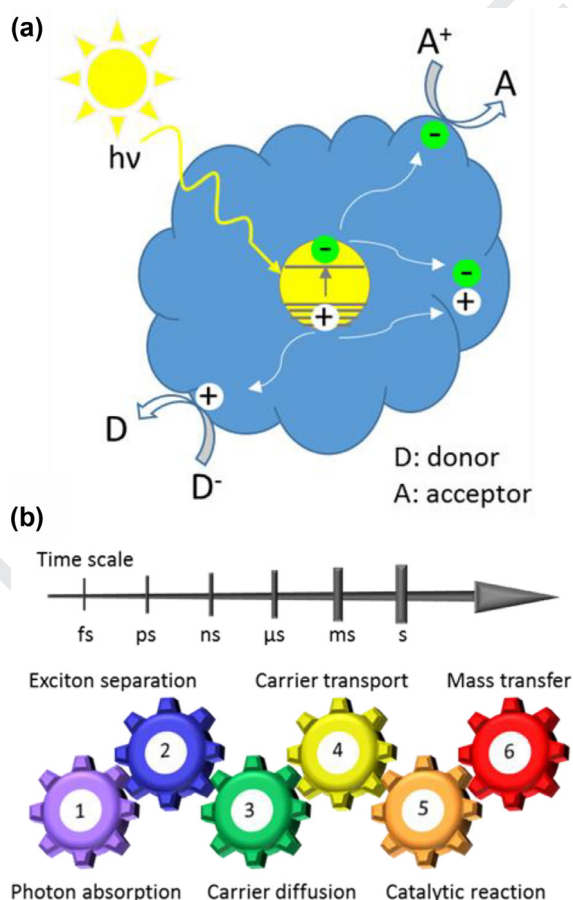

Fig. 1. (a) Scheme of photocatalytic reaction and (b) parameters required attention for efficient photocatalytic activity [14].