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Invited review

Enhancement of catalytic activity and oxidative ability for graphitic carbon nitride

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ABSTRACT

Growing awareness of energy conservation and pollutant elimination has been raised on graphitic carbon nitride (g-C_3N_4) recently thanks to the tunable electronic structure and excellent physicochemical stability of g-C_3N_4. This review summarizes the recent progress of g-C_3N_4 based materials regarding the catalytic activity improvement and oxidative ability enhancement. The former includes nanostructure design at different dimensions and fabrication of hybridized structure, core-shell structure or 3D hydrogel structure. The latter includes valence band modulation via conjugative effects of π-bond, copolymerization or doping, fabrication of Z-scheme heterojunction structure and synergetic effect of photoelectrocatalysis. The electronic structure and potential applications of g-C_3N_4 are also briefly discussed. This review provides new insights into the improvement of catalytic activity and oxidative ability for g-C_3N_4 materials and may help to facilitate their potential utilization in the field of energy transformation and environmental recovery.

Contents

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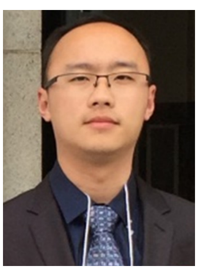

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1. Introduction

Nowadays, energy and environmental issues have become a realistic and urgent problem all over the world [1]. Photo-catalysis has been regarded to be the most appealing options for photovoltaic conversion and pollutant elimination [2,3]. The common use of photocatalytic reactions, along with rapid growth of the industry likely dated back to the 1970s when water splitting was discovered by Fujishima and Honda, which is caused by a TiO_2 electrode[4]. After that, other inorganic semiconductors including metal oxides, nitrides, sulfides, phosphides and so on are widely investigated as photo-catalysts. The research about photocatalysis mainly focus on metal-based complexes until 2009 when g-C_3N_4 was firstly regarded by Wang et al. as a metal-free photo-catalyst for producing hydrogen out of water with visible light [5]. As a photocatalyst under the drive of visible light, g-C_3N_4 attracted immense research interest on the global level resulting from its tunable electron configuration and excellent physical and chemical stability [6], which could serve as an excellent candidate for solar energy conversion and pollutant elimination. In addition, g-C_3N_4 is plentiful and can be made by one-step thermally condensing nitrogen-rich precursors such as cyanamide [5,7], dicyandiamide [8,9], melamine [10,11] and urea [12–14], thiourea [15,16]. Potential applications in hydrogen generation [5,17–25], oxygen evolution [20,21,26–28], carbon dioxide reduction [28–37], pollutant elimination[38–55], electrochemistry [56–59] and organic photosynthesis [60–63] have been widely investigated.

However, the pure g-C_3N_4 suffers from shortcomings such as too tiny surface area, inefficient use of visible light, low electric conductivity and fast recombination of photo-induced carriers [64], which results in low catalytic activity. On the other hand, the application of g-C_3N_4 in pollutant elimination, particularly benzene-based organisms, are severely confined by its lower ring opening together with oxidative capability as for its high valence band position [43,65]. What's worse, the intermediate products of some organics are more toxic than themselves if they are not completely mineralized. Therefore, pertinence measures are urgently needed to solve these two key problems.

The photo-catalysis of materials is usually determined by their structures. Nanostructures with proper morphologies not only determine the light harvest efficiency but also promote catalytic mass-transfer and foster photo-carriers to be separated and transported to facilitate relevant reactions [64]. Researchers have made great progress lately in designing g-C_3N_4 structure and investigating relations between morphology characteristics and photo-catalysis. A series of g-C_3N_4 materials with various structures have been developed, including 3D structure (porous structure and sphere structure) [38,39,66–69], 2D structure (nano-sheet structure) [40,56,70–76], 1D structure (nanorod structure, nanotube structure) [41,77–79], 0D structure (quantum dot structure) [19,80], hybridized structure [45–47,81–85], core-shell structure [45,81,82] and 3D hydrogel structure [86,87] et al. The structural design across the board will give novel ideas to produce high-powered g-C_3N_4 materials for the conversion of solar energy.

Compared with photocatalytic activity, the oxidative ability of a photo-catalyst plays an even more important role in the process of practical wastewater treatment [65]. Unfortunately, there are not so many efficient measures to enhance the oxidative ability of g-C_3N_4. Here, we summarize some progress achieved in recent years. One method is the valence band modulation of g-C_3N_4 including conjugative effects of π-bond, copolymerization and doping [42,43,65,88–92], which could lower the valence position and enhance the oxidizing ability of g-C_3N_4. Another way to improve the oxidizing ability is by fabricating Z-scheme heterojunction structure, which exhibits both highly efficient spatial charge-separation and outstanding redox ability [1,93,94]. Another way to enhance the oxidizing ability of g-C_3N_4 is synergetic removal