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Two-dimensional hierarchically porous C_3N_4 for photocatalysis: perspective and challenges

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Abstract

Owing to its unique structure, porosity and photoresponse properties, two-dimensional hierarchically porous (2D-HP) C_3N_4 has attracted wide attention in environmental remediation and sustainable energy evolution fields. Up to today, 2D-HP C_3N_4 has been developed as an efficient photocatalyst for various environmental/energy photocatalytic applications. Its advantages in promoting light harvesting, reactant diffusion and transportation, surface molecule activation and photoinduced carrier separation have been verified. In this perspective, we highlighted the advantages of 2D-HP C_3N_4 in various photocatalytic reactions such as water splitting and H_2O_2 production. The relevant mechanism was simultaneously discussed. Moreover, the prospects and obstacles for the industrial utilization of 2D-HP C_3N_4-based photocatalysts are outlined and summarized. Finally, we envision available approaches for the deployment of 2D-HP C_3N_4-based materials to promote its practical application.

Keywords: Two-dimensional materials, hierarchically porous, C_3N_4, photocatalysis

INTRODUCTION

Since Geim and Novoselov[1], for the first time, prepared two-dimensional (2D) graphene via the exfoliation of graphite by Scotch tape 20 years ago and revealed the fantastic performance of such innovative material[1,2]. A variety of outstanding characteristics of 2D graphene have been exploited, facilitating its applications in catalysis, biosensors, energy storage, optoelectronic devices, *etc.*[3]. In the past decade, a great deal of work has been conducted to investigate other 2D nanomaterials beyond graphene[4,5]. Furthermore, hierarchical pores are frequently produced on the 2D nanomaterials during the specific synthesis processes such as thermal-exfoliation and hydrothermal treatment, making 2D-hierarchically porous (HP) materials a research spot in current studies[6]. Owing to the large surface area, low density, tunable electronic bandgap configuration and good light response properties, 2D nanomaterials commonly present superior activity than the bulk counterpart in photocatalysis, thermocatalysis and electrocatalysis fields[7].

Furthermore, the HP structure is also favorable for improving the chemical and physical properties of nanomaterials[8]. To be specific, hierarchical pores could make materials with facile mass diffusion channels, lower density, and rich surface reaction sites, enabling them to be more proficient in light utilization, electron/ion migration, and reactant diffusion. Thus, hierarchically porous materials are deemed as a kind of important candidates in environmental protection and energy evolution/storage fields including environmental photocatalysis, gas detection, toxic substance elimination, waste decomposition, *etc.*[9]. The 2D-HP materials could couple the structure, morphology and electronic band gap merits from both 2D and HP materials, therefore showing extraordinary photocatalytic performance. Their light absorption ability is superior to other kinds of materials because of the multiple light scattering effect[10]. Meanwhile, the impassable channels could completely be penetrated, abundant edges and boundaries would be generated, and almost all the positions of 2D-HP materials could be contacted to the surrounding reaction media and the reactants, thus accelerating the diffusion of reactant molecules into the inner space of materials. Nevertheless, the fact that the nanosheets are prone to agglomeration in aqueous solution should be paid more attention in future studies.

In the past decade, 2D-HP C_3N_4, as an emerging class of nanomaterials, has appealed to extensive study, which usually exhibits a plate-like morphology and consists of ultrathin layers[11,12]. Because of its outstanding light response, abundant reactive sites, large surface area and tunable electronic characteristics, 2D-HP C_3N_4 is considered as a high-performance advanced functional material [Figure 1A and B]. Nowadays, environmental pollution and energy shortage issues have appealed to increasing concerns[13]. In this regard, 2D-HP C_3N_4 is extensively studied as a promising photocatalyst to convert solar energy into chemical energy to drive various photocatalytic reactions such as pollutant degradation, hydrogen evolution, H_2O_2 production, and CO_2 reduction.

UNIQUE PROPERTIES OF 2D-HP C_3N_4 IN PHOTOCATALYSIS

Migration kinetics of electron/ion

The electron/ion migration kinetics is highly important for the activity of photocatalysts in chemical reactions[14]. The 2D-HP material possesses apparent advantages for ion/charge carrier diffusion and shift via coupling the characteristics of 2D configuration, which displays outstanding electronic properties and abundant exposed atoms on the surface, and HP material, which has a large specific surface area, low density and excellent accessibility [Figure 1C and D]. In particular, 2D-HP C_3N_4 can offer a high exposed surface with rich channels for solution, electrolyte and gas, thus effectively improving their wetting and penetration ability. Meanwhile, the carrier shift, charge transport, and reactant diffusion between various phases and the surface reaction rates of C_3N_4 are significantly enhanced. For example, boron-doped 2D-HP C_3N_4 [Figure 1E] displayed much higher photocatalytic H_2O_2 evolution ability than other 2D C_3N_4 samples

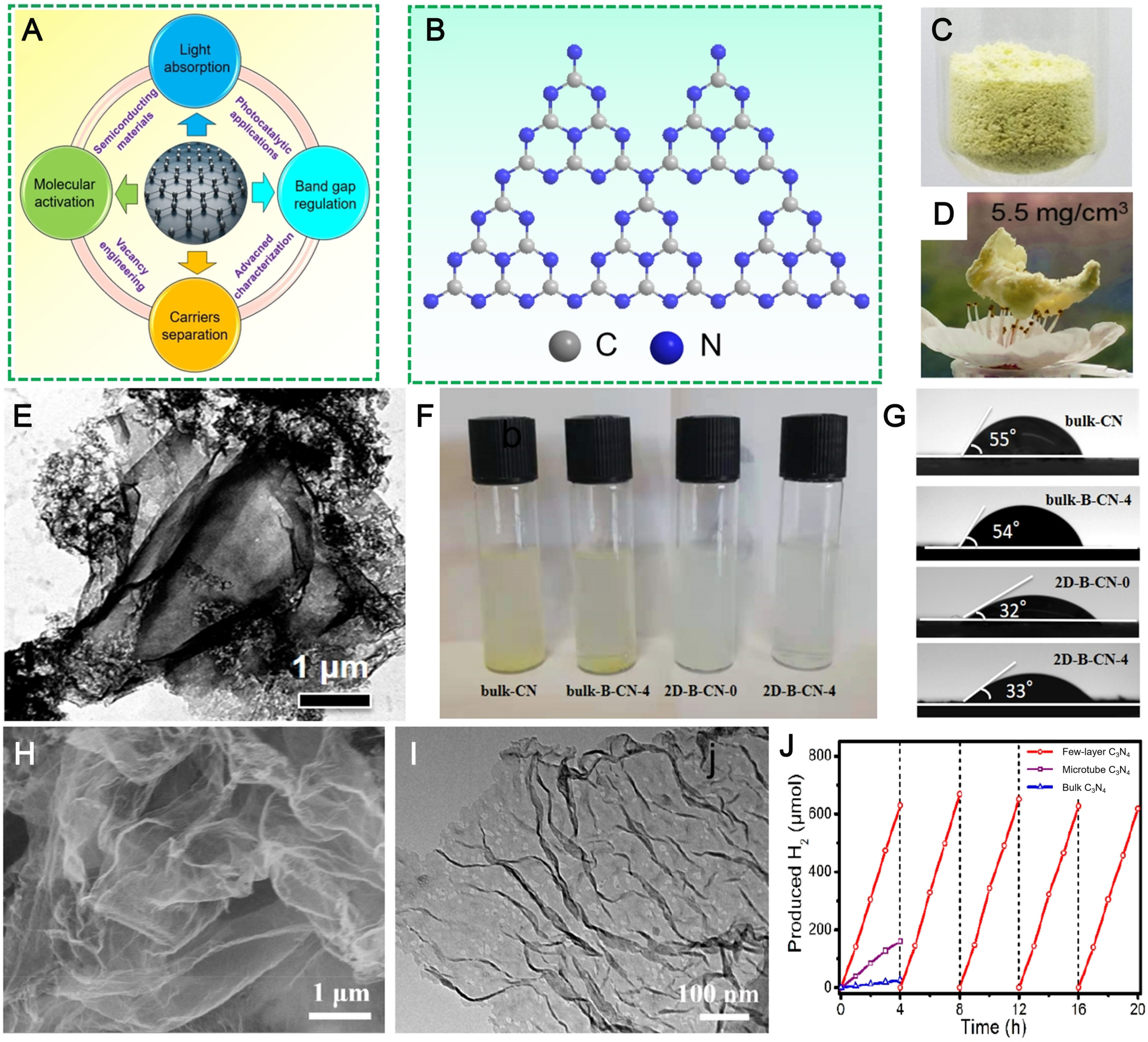

Figure 1. (A) Advantages of 2D-HP C_3N_4 materials in photocatalysis; (B) Schematic structure of C_3N_4 photocatalyst; (C and D) Photograph of C_3N_4 powder and the low density; (E) TEM image of boron-doped 2D-HP C_3N_4; (F) Photographs for the aqueous dispersion of the different C_3N_4 samples; (G) Images of water droplets on the C_3N_4 thin films; (H) SEM and (I) TEM images of 2D porous C_3N_4; (J) Photocatalytic H_2 evolution rate over various photocatalysts. 2D-HP: Two-dimensional hierarchically porous; TEM: transmission electron microscopy; SEM: scanning electron microscope.

without hierarchical porous configuration and other developed nonporous nanoplates[10]. The superior photocatalytic activity is attributed to the function of hierarchical pores on 2D nanosheets, which could reduce the shift way of O_2 via facile cross-plane movement of reactants to the reactive centers and make the migration of photoinduced electrons to the surface much easier. More importantly, the unique structure leads to good wetting ability and makes the reaction more efficient in aqueous solution [Figure 1F and G].

Surface active sites

Generally, the photocatalytic activity is positively correlated with the amount of reactive centers in which the adsorption of reactant molecules and photogenerated carriers shift are carried out[15]. Typically, Xiao *et al.* adopted a facile bottom-up strategy to fabricate 2D few-layer C_3N_4 with rich pores on its surface [Figure 1H and I], which includes melamine molecule assembly into 2D precursors, alcohol molecules connection, and the final exfoliation process[11]. As expected, the synthesized 2D porous C_3N_4 nanosheets give rise to a specific surface area as high as 164.2 $m^2 \cdot g^{-1}$, being around 14 and 4 times higher than those of bulk C_3N_4 (11.3 $m^2 \cdot g^{-1}$) and C_3N_4 microtubes (42.6 $m^2 \cdot g^{-1}$) photocatalysts, respectively. Meanwhile, the pore size distribution characterization suggests that the 2D porous C_3N_4 nanosheets display hierarchically porous structure on their surface, which not only offer a high surface area for the accommodation of reactive centers, but also reduce shift distance for reactant molecules, intermediates and photoinduced charges. Notably, the nitrogen vacancies were also generated on the ultrathin 2D nanosheets, which could serve as reactive sites to facilely capture photoexcited electrons from the CB of C_3N_4 to effectively activate the reactant molecules. Finally, the 2D porous C_3N_4 nanosheets display efficient photocatalytic H_2 productivity of about 160 μmol·h^{-1}, being 26 folds larger than those of bulk C_3N_4 and microtube C_3N_4, respectively [Figure 1J].

Stability and corrosion resistance ability

Layered 2D materials are usually prone to aggregation and accumulation, generating a compact configuration that leads to decreased surface area, poor surface reactive center, restricted mass/charge transport, and, therefore, attenuated photocatalytic activity[16]. For instance, the van der Waals interaction and p-p stacking frequently result in serious aggregation of C_3N_4 nanosheets and prohibit the transfer of reactant molecules and intermediate species, hence damaging the activity of C_3N_4 during the reaction process[13]. The generation of abundant pores into nanosheets could effectively alleviate this issue by reducing the van der Waals force between the 2D nanosheets. Furthermore, it has been found that the creation of pores on 2D materials apparently stabilizes ultrathin 2D structure by reducing the surface energy[17,18]. From another perspective, the shortened mass transfer pathway and facile shift of photogenerated carriers from 2D-HP materials tightly attracted reactants between solution and photocatalyst[19-22], thus bringing out a low corrosion degree of photocatalyst and increased stability of 2D materials. Typically, Wu *et al.* prepared 2D porous C_3N_4 nanosheets via a solvothermal reaction with subsequent vacuum freezing-drying treatment[12]. The obtained 2D g-C_3N_4 exhibits outstanding recycling stability for H_2 evolution reaction for 100 h, being ascribed to the structure and porosity merits.

SUMMARY AND PERSPECTIVE

In short, 2D-HP C_3N_4, as an emerging advanced material, has displayed significant potential for pollutant elimination and sustainable energy production owing to its structure, morphology and electronic band gap merits. The photocatalytic activity and cycling stability of current 2D-HP C_3N_4-based materials have met the requirement of organic pollutant decomposition and H_2/H_2O_2 production to a certain extent in the laboratory. However, there is still a long road to achieve the demand of industrial application of 2D-HP C_3N_4-based materials. Nevertheless, 2D-HP C_3N_4, with the advantages of low cost, high surface area, abundant active sites, and tunable electronic structure, still holds great competitiveness in environmental and energy photocatalytic fields. We hope this perspective can stimulate several innovative concepts in the preparation of high-performance 2D-HP photocatalysts for achieving the ultimate industrial use.

DECLARATIONS

Authors' contributions

Prepared the manuscript: Ding Y, Wang C, Han N, Liu M, Zheng R, Chen LH, Zhong J
Performed manuscript editing: Su BL

Availability of data and materials

Not applicable.

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Conflicts of interest
Su BL, serving as Editor-in-Chief of *Chemical Synthesis*, was not involved in the editorial process of the work. The other authors have declared that they have no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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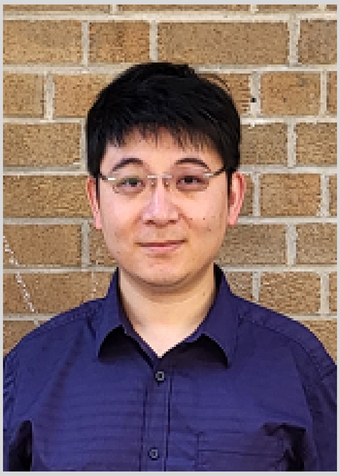

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