

## $g\text{-C}_3\text{N}_4$ 光催化性能的研究进展

楚增勇, 原 博, 颜廷楠

(国防科学技术大学 理学院, 长沙 410073)

**摘 要:** 利用光催化剂将太阳能转化为人类可以直接利用的能量, 并用其解决地球资源的枯竭和生存环境的恶化是可再生能源研究的一个方向。 $g\text{-C}_3\text{N}_4$  的独特结构赋予其良好的光催化性能, 使之成为光催化领域的研究热点。目前在光催化领域,  $g\text{-C}_3\text{N}_4$  主要用于催化污染物分解、水解制氢制氧、有机合成及氧气还原。在实际应用中, 为进一步提高  $g\text{-C}_3\text{N}_4$  的光催化效果, 科研工作者开发了多种改进方法, 例如物理复合改性、化学掺杂改性、微观结构调整等。本文主要论述了  $g\text{-C}_3\text{N}_4$  在光催化领域的应用以及光催化性能的改进方法, 简要阐述了光催化和各种改进方法的机理, 分析了目前  $g\text{-C}_3\text{N}_4$  在光催化领域面临的问题和挑战, 展望了  $g\text{-C}_3\text{N}_4$  的应用前景。

**关 键 词:**  $g\text{-C}_3\text{N}_4$ ; 光催化; 改进方法; 综述

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## Recent Progress in Photocatalysis of $g\text{-C}_3\text{N}_4$

CHU Zeng-Yong, YUAN Bo, YAN Ting-Nan

(College of Science, National University of Defense Technology, Changsha 410073, China)

**Abstract:** Based on photocatalysts, solar energy can be converted into the energy that human can directly utilize, so as to solve the problems such as the depletion of the Earth's resources and the deterioration of living environments. The unique structure of  $g\text{-C}_3\text{N}_4$  gives it good photocatalytic performance. Its development and utilization have been a research hotspot recently. Generally,  $g\text{-C}_3\text{N}_4$  can be used in the degradation of pollutions, hydrolysis to generate hydrogen and oxygen, organic synthesis and oxygen reduction. However, in practical, its performance is not satisfactory. Researchers have tried many new methods to improve its photocatalysis, which include physical coupling modification, chemical bonding modification and microstructural modification. The review summarizes its photocatalysis and improving methods, briefly illustrates the catalysis mechanism, and presents detailed discussions and analysis on the existing problems as well as potential applications.

**Key words:**  $g\text{-C}_3\text{N}_4$ ; photocatalysis; improving methods; review

太阳能是取之不尽用之不竭的清洁能源, 人类正致力开发高效的光催化剂, 以实现太阳能的转化利用。目前, 已开发出的光催化剂大体可分为三种: 金属氧化物、硫化物(如  $\text{TiO}_2$ <sup>[1]</sup>、 $\text{ZnO}$ <sup>[2]</sup>、 $\text{CdS}$ <sup>[3]</sup>等), 贵金属半导体(如  $\text{Bi}_2\text{MoO}_6$ <sup>[4]</sup>、 $\text{BiOBr}$ <sup>[5]</sup>、 $\text{Ag}_3\text{PO}_4$ <sup>[6]</sup>等), 非金属半导体(如  $g\text{-C}_3\text{N}_4$ <sup>[7]</sup>、红磷<sup>[8]</sup>等)。 $\text{ZnO}$ (3.3 eV)和  $\text{TiO}_2$ (3.2 eV)带隙较宽, 仅能利用只占太阳能

4%的紫外光。 $\text{CdS}$ (2.4 eV)带隙较窄, 但稳定性较差。 $\text{Bi}_2\text{MoO}_6$ (2.9 eV)和  $\text{BiOBr}$ (2.8 eV)带隙适中, 但含有贵金属元素, 价格较高。 $g\text{-C}_3\text{N}_4$  是一种非金属半导体, 由地球上含量较多的 C、N 元素组成, 带隙约 2.7 eV, 对可见光有一定的吸收, 抗酸、碱、光的腐蚀, 稳定性好, 结构和性能易于调控, 具有较好的光催化性能, 因而成为光催化领域的研

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作者简介: 楚增勇(1974—), 男, 博士, 研究员. E-mail: chuzy@nudt.edu.cn

究热点。

$g\text{-C}_3\text{N}_4$ , 即石墨相的  $\text{C}_3\text{N}_4$ , 是五种  $\text{C}_3\text{N}_4$  中最稳定的一种, 其结构如图 1(a)所示。关于  $g\text{-C}_3\text{N}_4$  的单层结构, 人们主要有两种不同的看法: 一种认为单层  $g\text{-C}_3\text{N}_4$  以三嗪环( $\text{C}_3\text{N}_3$  环)为结构单元(如图 1(b))<sup>[9-12]</sup>, 另一种认为单层  $g\text{-C}_3\text{N}_4$  的基本结构单元是 3-s-三嗪环( $\text{C}_6\text{N}_7$  环)(如图 1(c))<sup>[13-15]</sup>。通过密度泛函(DFT)计算, 基于 3-s-三嗪环的  $g\text{-C}_3\text{N}_4$  结构比基于三嗪环的  $g\text{-C}_3\text{N}_4$  结构稳定<sup>[16]</sup>, 近年来, 大多数对  $g\text{-C}_3\text{N}_4$  的研究都以 3-s-三嗪环结构为理论模型。

在自然界中, 至今还没有发现存在天然的  $g\text{-C}_3\text{N}_4$  晶体。所以,  $g\text{-C}_3\text{N}_4$  的研究依赖于实验合成。合适的碳源和氮源在一定条件下反应可得到  $g\text{-C}_3\text{N}_4$ , 常用的反应物有三聚氰胺、三聚氰氯、氰胺、二氰二胺、尿素等。目前,  $g\text{-C}_3\text{N}_4$  的主要合成方法有: 高温高压法<sup>[17]</sup>、溶剂热法<sup>[18]</sup>、沉积法<sup>[9, 19]</sup>、热聚合法<sup>[15, 20]</sup>等。热聚合法可以方便地通过加入其他物质或改变反应条件来调节  $g\text{-C}_3\text{N}_4$  的结构, 从而提高  $g\text{-C}_3\text{N}_4$  的光催化性能, 是目前  $g\text{-C}_3\text{N}_4$  研究中常用的合成方法。

## 1 $g\text{-C}_3\text{N}_4$ 光催化的类型

$g\text{-C}_3\text{N}_4$  独特的结构决定了其独特的性质, 并赋予了其在光催化领域的广泛应用。目前,  $g\text{-C}_3\text{N}_4$  主要应用于光催化污染物分解<sup>[21-22]</sup>、光解水制氢制氧<sup>[23-24]</sup>、光催化有机合成<sup>[15, 25]</sup>和光催化氧气还原<sup>[26]</sup>等。

### 1.1 光催化污染物分解

应用于  $g\text{-C}_3\text{N}_4$  光催化性能研究的主要污染物有两类, 即有机染料(亚甲基蓝(MB)<sup>[21]</sup>、甲基橙(MO)<sup>[27]</sup>和罗丹明 B(RhB)<sup>[28]</sup>等)和小分子化合物(苯酚<sup>[29-31]</sup>、2,4-二氯苯酚(2,4-DCP)<sup>[32]</sup>、2,4,6-三氯苯酚(2,4,6-TCP)<sup>[22]</sup>、十溴联苯醚<sup>[33]</sup>、乙醛<sup>[34-35]</sup>、 $\text{NO}$ <sup>[20]</sup>和  $\text{Cr(VI)}$ <sup>[36-37]</sup>等)。光照下,  $g\text{-C}_3\text{N}_4$  价带电子激发至导带形成电子-空穴对, 电子与氧气分子结合, 并进一步与水分子反应。上述三个过程促使三种活性粒子的生成, 即  $h^+$ 、 $\cdot\text{O}_2^-$  和  $\cdot\text{OH}$ <sup>[21]</sup>(图 2(a))。这些活性粒子可促使有机染料(图 2(b))和某些有机物分解。 $\text{NO}$  与活性粒子经一系列的反应可生成  $\text{HNO}_3$ 、 $\text{HNO}_2$ (如图 2(c)), 从而实现含  $\text{NO}$  气体的净化<sup>[20, 38]</sup>。

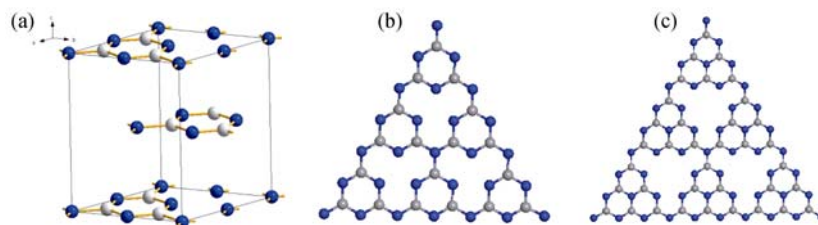


图 1  $g\text{-C}_3\text{N}_4$  的结构模型

Fig. 1 Structure models of  $g\text{-C}_3\text{N}_4$

(a) Crystal model<sup>[17]</sup>; (b) S-triazine model<sup>[7]</sup>; (c) 3-s-triazine model<sup>[7]</sup>

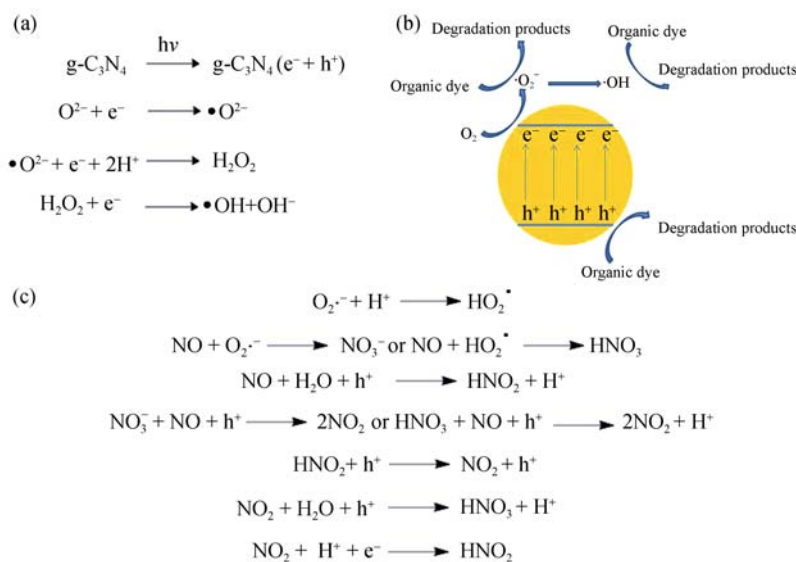


图 2 活性粒子的产生(a)<sup>[21]</sup>与其催化有机染料降解(b)<sup>[27-28]</sup>和含  $\text{NO}$  气体净化的机理(c)<sup>[38]</sup>

Fig. 2 Generation of reactive species (a)<sup>[21]</sup> and action mechanism for degradation of organic dye (b)<sup>[27-28]</sup> and purification of gas containing  $\text{NO}$  (c)<sup>[38]</sup>

Cr(VI)/Cr(III)的还原电势为 1.33 V, 而 g-C<sub>3</sub>N<sub>4</sub> 的价带(1.5 V)和导带(-1.2 V)跨立在其两端, 故 g-C<sub>3</sub>N<sub>4</sub> 在光激发产生的电子可将剧毒的 Cr(VI)还原为低毒的 Cr(III)<sup>[36-37]</sup>。

## 1.2 光催化水解制氢制氧

g-C<sub>3</sub>N<sub>4</sub> 的导带和价带跨立在 H<sup>+</sup>/H<sub>2</sub> 和 H<sub>2</sub>O/O<sub>2</sub> 还原电势的两侧, 所以 g-C<sub>3</sub>N<sub>4</sub> 可用来催化水的分解。在 g-C<sub>3</sub>N<sub>4</sub> 光催化水解制氢时, 激发至导带的电子与氢离子结合, 留下的空穴由催化体系中加入的三乙醇胺<sup>[39]</sup>、维 C<sup>[40]</sup>或甲醇<sup>[41]</sup>及时移除。由于超电势的存在, g-C<sub>3</sub>N<sub>4</sub> 光激发产生的电子不能快速地转移给氢离子, 影响了光解制氢的速率。在 g-C<sub>3</sub>N<sub>4</sub> 表面沉积一定量的 Pt 可以有效解决这个问题, 这是由于 Pt 可以和 H 形成 Pt-H 键, 有利于电子的迅速转移使 H<sup>+</sup>转化为 H<sub>2</sub><sup>[42]</sup>。金属 Pt 的使用增加了水解制氢的成本, Hong 等<sup>[43]</sup>使用 NiS 作为共催化剂, 取得了与使用 Pt 作为共催化剂相当的催化速率。

在光解水制氧时, H<sub>2</sub>O 分子与光激发产生的空穴结合, 释放出氧气, 电子则需要加入 AgNO<sub>3</sub><sup>[42, 44]</sup>等试剂去除。为了防止 H<sup>+</sup>的积累导致 pH 的下降, 可使用缓冲试剂维持 pH 在 8~9 之间, 如 La<sub>2</sub>O<sub>3</sub><sup>[44]</sup>等。由于 N 原子相对于 O 易被氧化, 光解水制氧可能会生成 N<sub>2</sub><sup>[42]</sup>, 所有光解制氧时需要加入 RuO<sub>2</sub> 等试剂及时将空穴从 g-C<sub>3</sub>N<sub>4</sub> 中导出。g-C<sub>3</sub>N<sub>4</sub> 光解水制氧的能力较弱, 这可能是由于 g-C<sub>3</sub>N<sub>4</sub> 的价带(1.5V)与 H<sub>2</sub>O/O<sub>2</sub> 的电势(1.2V)较为接近, 热力学氧化驱动力不足造成的<sup>[42]</sup>, 因此可以通过降低价带的位置来提高水解制氧的速率<sup>[23]</sup>。

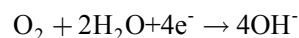
## 1.3 光催化有机合成

在有机合成中, 利用 O<sub>2</sub> 作为氧化剂制备某些有机物时, 由于 O<sub>2</sub> 氧化能力较强, 不可避免地会产生大量的过度氧化产物, g-C<sub>3</sub>N<sub>4</sub> 的加入可有效地解决这一问题, 实现精确性氧化<sup>[45-46]</sup>。在反应体系中, 氧气在 g-C<sub>3</sub>N<sub>4</sub> 表面与光激发产生的电子结合形成·O<sub>2</sub><sup>-</sup>, 由于空穴静电作用, ·O<sub>2</sub><sup>-</sup>吸附在 g-C<sub>3</sub>N<sub>4</sub> 表面。附着在 g-C<sub>3</sub>N<sub>4</sub> 上的反应物经·O<sub>2</sub><sup>-</sup>氧化后吸附能力减弱, 发生脱附, 因催化体系中没有游离的·O<sub>2</sub><sup>-</sup>而避免了被过度氧化<sup>[47]</sup>。在羟胺化合物的帮助下, g-C<sub>3</sub>N<sub>4</sub> 能很好地活化丙烯基位的碳氢键, 用于相应醛酮的合成<sup>[48]</sup>。CO<sub>2</sub> 的活化利用是有机合成的一个发展方向, Huang 等<sup>[15]</sup>在 SBA-15 的孔道中合成了 g-C<sub>3</sub>N<sub>4</sub>, 经金属离子修饰后能够很好地活化 CO<sub>2</sub> 用于环氧化合物和烯类化合物的合成。g-C<sub>3</sub>N<sub>4</sub> 还能催化 CO<sub>2</sub> 转化为 CH<sub>4</sub><sup>[49]</sup>, 这将在燃料动力设备中发挥重要作用。g-C<sub>3</sub>N<sub>4</sub> 中起桥连作用的 N 原子是 Lewis 碱

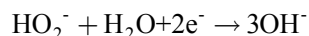
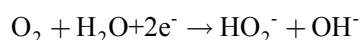
活性位点, 可催化 Knoevenagel 缩合反应<sup>[50]</sup>。除此之外, g-C<sub>3</sub>N<sub>4</sub> 可催化对苯二甲酸转化生成 2-羟基对苯二甲酸<sup>[29, 51]</sup>、β-酮酯的酯交换反应<sup>[52]</sup>、苯的傅-克酰基化反应<sup>[53]</sup>、苯甲醛与醇的酯化反应<sup>[54]</sup>和胺类的二聚反应<sup>[55]</sup>等。

## 1.4 光催化氧气还原

氧气的还原反应(ORR)是燃料电池的一个重要半反应。碳材料中共轭的 N 原子可以有效地催化 ORR<sup>[56]</sup>, 故对 ORR 的催化已成为 g-C<sub>3</sub>N<sub>4</sub> 应用研究的一个方向<sup>[57]</sup>。O<sub>2</sub> 的最低空轨道(LUMO)与 g-C<sub>3</sub>N<sub>4</sub> 中的共轭氮原子相互作用, 发生电荷的转移, 从而促进氧气的还原<sup>[58]</sup>。研究表明, g-C<sub>3</sub>N<sub>4</sub> 对 ORR 的光催化是一个较为复杂的过程, 其可分为四电子还原



和双电子还原



两种<sup>[59]</sup>。经石墨烯/CoO<sup>[60]</sup>、石墨烯/Co<sup>[61]</sup>、C<sup>[62]</sup>、Fe<sup>[63]</sup>修饰的 g-C<sub>3</sub>N<sub>4</sub> 对 ORR 具有较好的催化活性, 具有较好的应用前景。

除了上面几种在光催化领域的应用外, 科研人员还开发了 g-C<sub>3</sub>N<sub>4</sub> 的其他用途, 例如对钢材的电化学保护<sup>[64]</sup>、合成石墨烯的模板<sup>[65]</sup>、光生电<sup>[66]</sup>、超级电容器<sup>[67]</sup>、荧光探测和成像<sup>[12, 68-69]</sup>等。

## 2 g-C<sub>3</sub>N<sub>4</sub> 光催化性能的改进方法

g-C<sub>3</sub>N<sub>4</sub> 有着广泛的应用, 但由于电子空穴复合快和比表面积不够大等原因, 实际应用效果并不理想。为此, 科研人员开发了多种方法改进 g-C<sub>3</sub>N<sub>4</sub>, 例如物理复合改性、化学掺杂改性、微观结构调整等。

### 2.1 物理复合改性

物理复合改性是最方便的改进方法。目前, 选用的复合物主要有金属化合物(如 CdS<sup>[40]</sup>、Fe<sub>3</sub>O<sub>4</sub><sup>[27]</sup>、ZnO<sup>[28]</sup>、AgX<sup>[70]</sup>(X= Br, I)、TiO<sub>2</sub><sup>[30, 71]</sup>、SmVO<sub>4</sub><sup>[72]</sup>、MoS<sub>2</sub><sup>[41]</sup>、Bi<sub>2</sub>WO<sub>6</sub><sup>[73]</sup>等)、类石墨烯材料(如石墨烯<sup>[74]</sup>、氧化石墨烯<sup>[32]</sup>、碳纳米管<sup>[75]</sup>等)、高分子化合物(如 P3HT<sup>[76]</sup>、PANI<sup>[77]</sup>等)和贵金属(如金<sup>[77]</sup>)等, 复合后 g-C<sub>3</sub>N<sub>4</sub> 的光催化性能都有一定提高(如表 1)。g-C<sub>3</sub>N<sub>4</sub> 与复合物之间并非简单的物理混合, 而是充分接触并形成异质结。由于二者导带和价带位置的差异, g-C<sub>3</sub>N<sub>4</sub> 光激发产生的电子或空穴转移至复合物的导带或价带中, 电子空穴分离(如图 3), 复合率降低, 从而可以更高效地利用光激发产生的活性粒子。经

表 1 g-C<sub>3</sub>N<sub>4</sub> 与物质复合后光催化性能的提高

Table 1 Improvement of photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub> physically coupled with other materials

Photocatalyt	Application	Photocatalytic performance of pure g-C <sub>3</sub> N <sub>4</sub> <sup>[a]</sup> / (min <sup>-1</sup> or μmol·g <sup>-1</sup> ·h <sup>-1</sup> )	photocatalytic performance of modified g-C <sub>3</sub> N <sub>4</sub> <sup>[a]</sup> / (min <sup>-1</sup> or μmol·g <sup>-1</sup> ·h <sup>-1</sup> )	Reference
Fe <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	Degradation of MO	0.0030	0.0163	[27]
AgX/g-C <sub>3</sub> N <sub>4</sub> (X=Br, I)	Degradation of MO	0.0006	0.1900 <sup>[b]</sup>	[70]
			0.0068 <sup>[c]</sup>	
ZnO/g-C <sub>3</sub> N <sub>4</sub>	Degradation of RhB	0.0078	0.0239	[28]
SmVO <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	Degradation of RhB	0.0143	0.0338	[72]
GdVO <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	Degradation of RhB	0.0142	0.0434	[80]
DyVO <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	Degradation of RhB	0.0142	0.0365	[81]
Formate anion/g-C <sub>3</sub> N <sub>4</sub>	Reduction of Cr(VI)	0.0010	0.0033	[37]
MoS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Hydrogen generation by hydrolysis	0.15	23.10	[41]
CdS QDs/g-C <sub>3</sub> N <sub>4</sub>	Hydrogen generation by hydrolysis	38	4494	[40]
Gr/g-C <sub>3</sub> N <sub>4</sub>	Hydrogen generation by hydrolysis	147	451	[74]
P3HT/g-C <sub>3</sub> N <sub>4</sub>	Hydrogen generation by hydrolysis	1.8	555.0	[76]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Degradation of phenol	0.022	0.053	[30]
	Degradation of MB	0.0054	0.0338	[82]
	Reduction of Cr(VI)	0.0028	0.0157	
g-C <sub>3</sub> N <sub>4</sub> /rGO/MoS <sub>2</sub>	Degradation of RhB	0.0041	0.0156	[32]
	Degradation of 2,4-DCP	0.0037	0.0077	

[a] min<sup>-1</sup> for degradation of pollution, μmol·g<sup>-1</sup>·h<sup>-1</sup> for hydrogen generation by hydrolysis; [b] degradation rate of MO by utilizing AgBr/g-C<sub>3</sub>N<sub>4</sub>; [c] degradation rate of MO by utilizing AgI/g-C<sub>3</sub>N<sub>4</sub>

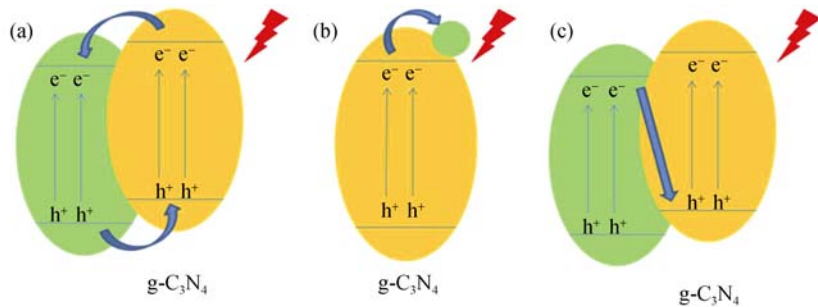


图 3 g-C<sub>3</sub>N<sub>4</sub> 与物质复合后电子和空穴的分离

Fig. 3 Separation of electrons and holes of g-C<sub>3</sub>N<sub>4</sub> physically coupled with other materials

(a) Convection-type charge transfer<sup>[30, 40]</sup> (such as TiO<sub>2</sub>, CdS); (b) Advection-type charge transfer<sup>[27, 74]</sup> (such as Fe<sub>3</sub>O<sub>4</sub>, graphene); (c) Z-type charge transfer<sup>[35, 71]</sup>

某些颜料(如曙红 Y<sup>[78]</sup>)光敏化的 g-C<sub>3</sub>N<sub>4</sub> 对可见光的吸收增强, 光催化能力明显提高。复合物的加入还可赋予催化剂一些独特的优点, 例如 g-C<sub>3</sub>N<sub>4</sub> 与 Fe<sub>3</sub>O<sub>4</sub><sup>[27]</sup>、Bi<sub>25</sub>FeO<sub>40</sub><sup>[79]</sup>复合后具有磁性, 方便了光催化剂的回收利用。

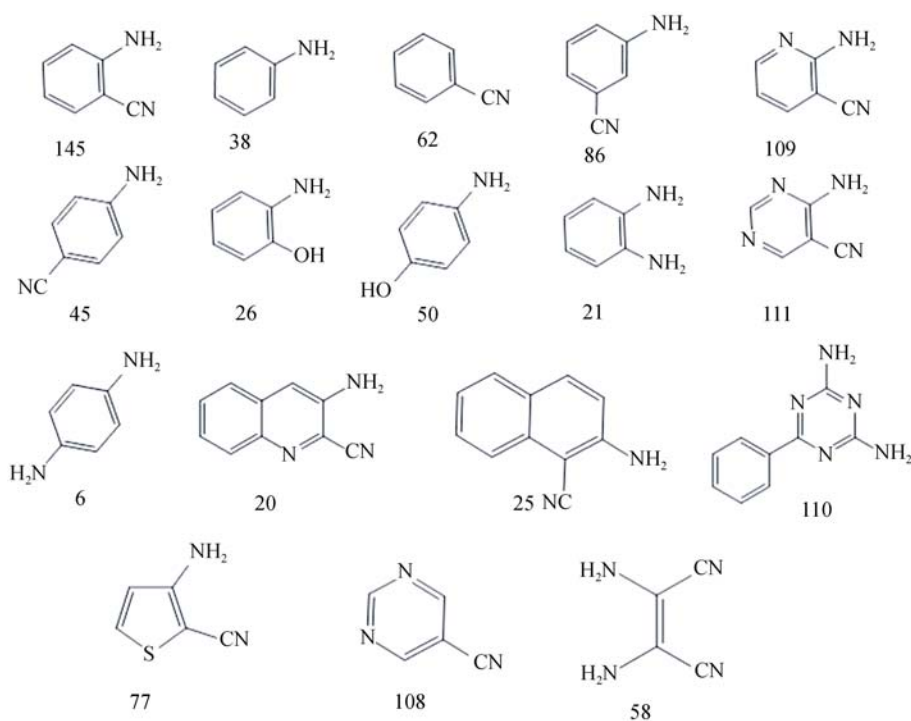
## 2.2 化学掺杂改性

化学掺杂改性能很好地改变 g-C<sub>3</sub>N<sub>4</sub> 的电子结构, 从而改善光催化性能。目前, 常采用杂环<sup>[44, 83-85]</sup>和杂原子(如 S<sup>[29]</sup>、P<sup>[66]</sup>、B<sup>[86]</sup>、F<sup>[87]</sup>等)进行掺杂。杂环的引入使 g-C<sub>3</sub>N<sub>4</sub> 的电子电势重新分配, 氧化还原位点分离<sup>[44]</sup>, 光催化性能提高(如图 4、表 2)。S、P、B、F 等杂原子与 C、N 原子的电负性不同, 它们的引入必然引起电子在整个网络中的不均匀, 导

致电子结构的改变<sup>[88-89]</sup>, 从而影响 g-C<sub>3</sub>N<sub>4</sub> 的光催化性能(如表 2)。异类元素的引入容易导致不对称掺杂或杂质, 这些都可以作为电子空穴的复合中心, 从而不利于光催化性能的提高, 故 Dong 等<sup>[90]</sup>研究了 C 的自掺杂对 g-C<sub>3</sub>N<sub>4</sub> 光催化性能的影响, 发现掺杂的 C 取代了 g-C<sub>3</sub>N<sub>4</sub> 网络中起桥连作用的 N, 扩大了电子的离域范围, 增加了电导率, 降低了带隙, 光催化性能得到了提高。

## 2.3 微观结构调整

在现有的 g-C<sub>3</sub>N<sub>4</sub> 光催化体系中, 都需要催化剂分散在溶剂中并与目标物充分接触, 活性粒子经催化剂表面作用于目标物, 所以 g-C<sub>3</sub>N<sub>4</sub> 的比表面积和微观形貌也影响了其光催化性能。因此, g-C<sub>3</sub>N<sub>4</sub> 光

图 4 引入不同的杂环对  $g\text{-C}_3\text{N}_4$  水解制氢速率的影响<sup>[83]</sup>Fig. 4 Influence of different heterocycles introduced into  $g\text{-C}_3\text{N}_4$  on the rate of hydrogen production<sup>[83]</sup>

Every figure ( $\mu\text{mol/h}$ ) below heterocycles means the rate of hydrogen production and the rate of hydrogen production of unmodified  $g\text{-C}_3\text{N}_4$  is  $18 \mu\text{mol/h}$

催化性能的提高也可通过  $g\text{-C}_3\text{N}_4$  微观结构的多孔化和低维化来实现。多孔、纳米颗粒、纳米棒、纳米薄层等结构的  $g\text{-C}_3\text{N}_4$ , 比表面积较大、结晶度较高, 光催化性能明显提高(如表 3)。

### 2.3.1 多孔结构

利用  $\text{SiO}_2$  作为硬模板, 可合成出多孔结构的  $g\text{-C}_3\text{N}_4$ <sup>[45, 52-53, 92-94]</sup>(如图 5(a)), 其光催化苯的傅-克酰基化反应、光解水制氢和对醇的选择性氧化的能力明显提高。多孔结构使  $g\text{-C}_3\text{N}_4$  比表面积增加, 电子的捕捉位点增多, 减缓了电子空穴对的复合, 使其能克服带隙略微增加带来的不利影响而提高光催化性能<sup>[94]</sup>。

多孔  $g\text{-C}_3\text{N}_4$  合成后, 需要去除硬模板, 这往往需要使用剧毒的  $\text{HF}$ <sup>[92]</sup>或  $\text{NH}_4\text{HF}_2$ <sup>[47]</sup>, 对人体的伤害较大。Xu 等<sup>[95]</sup>在前驱体中加入硫脲合成出多孔  $g\text{-C}_3\text{N}_4$ 。同样, Dong 等<sup>[94]</sup>用三聚氰胺的盐酸季铵盐作为前驱体, 也合成出多孔的  $g\text{-C}_3\text{N}_4$ 。硫脲和盐酸等软模板的加入, 不仅促使多孔结构的形成, 而且有效避免剧毒物质的使用。另外, 还可使用刻蚀液(如碱液<sup>[38]</sup>)将  $g\text{-C}_3\text{N}_4$  中不稳定的区域刻蚀掉, 得到多孔的  $g\text{-C}_3\text{N}_4$ 。

### 2.3.2 纳米颗粒和纳米棒

除了多孔结构外, 还可利用空间限制直接合成法<sup>[23, 96]</sup>或合成打碎法<sup>[97]</sup>将  $g\text{-C}_3\text{N}_4$  做成纳米颗粒<sup>[96]</sup>

(如图 5(b))和纳米棒结构<sup>[23]</sup>(如图 5(c))。这些纳米结构某些方向的尺寸较小, 减少了缺陷, 提高了结晶度, 缩短了光激发产生的电子和空穴转移至  $g\text{-C}_3\text{N}_4$  表面的距离, 使之较快地被利用, 降低了电子空穴的复合率。

### 2.3.3 纳米薄层

$g\text{-C}_3\text{N}_4$  具有类石墨烯的结构, 所以可以将  $g\text{-C}_3\text{N}_4$  做成纳米薄片甚至单层的结构(如图 5(d))。目前, 制备  $g\text{-C}_3\text{N}_4$  纳米薄层结构主要采用剥离法, 包括热剥离和溶剂剥离。热剥离是将  $g\text{-C}_3\text{N}_4$  在空气下进行热处理, 块状结构逐渐分解, 最后留下纳米薄层<sup>[20, 51]</sup>。对块状  $g\text{-C}_3\text{N}_4$  进行溶剂剥离常使用的溶剂为水<sup>[12, 68]</sup>和异丙醇(IPA)<sup>[39]</sup>等。Wu 等<sup>[14]</sup>经计算出, 双层  $g\text{-C}_3\text{N}_4$  具有很好的光吸收性能, 但目前难以精确控制  $g\text{-C}_3\text{N}_4$  的层数。

除了上述方法外, 还有一些其他的改性手段, 例如利用  $\text{NaNO}_3$  引入活性缺陷<sup>[98]</sup>等。单一的改性方法对光催化性能的提高都是有限的, 同时应用多种改性方法<sup>[83, 99]</sup>有望获得更好的效果。

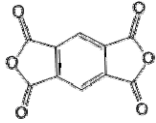
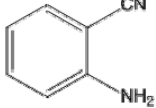
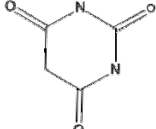
## 3 结语与展望

$g\text{-C}_3\text{N}_4$  是一种新型的非金属光催化剂, 仅由 C、N 组成, 价格便宜。其带隙约为  $2.7 \text{ eV}$ , 在太阳光照



表 2 化学掺杂对 g-C<sub>3</sub>N<sub>4</sub> 光催化性能的影响

Table 2 Influence of chemical binding modification on photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub>

Introduced component	Application	Photocatalytic performance of unmodified g-C <sub>3</sub> N <sub>4</sub> <sup>[a]</sup> / (μmol·h <sup>-1</sup> , min <sup>-1</sup> or %)	Photocatalytic performance of modified g-C <sub>3</sub> N <sub>4</sub> <sup>[a]</sup> / (μmol·h <sup>-1</sup> , min <sup>-1</sup> or %)	Reference
	Hydrogen generation by hydrolysis	7.0	20.6	[44]
	Oxygen generation by hydrolysis	0.8	7.7	
	Degradation of MO	0.0050	0.0557	
	Hydrogen generation by hydrolysis	18 <sup>[b]</sup>	147 <sup>[b]</sup>	[83]
		127 <sup>[c]</sup>	229 <sup>[c]</sup>	
	Hydrogen generation by hydrolysis	148.2 <sup>[d]</sup>	253.1 <sup>[d]</sup>	[84]
		6.5 <sup>[e]</sup>	29.4 <sup>[e]</sup>	
B, F	Oxidation of cyclohexane	1.6 <sup>[f]</sup>	5.3 <sup>[f]</sup>	[91]
F	Hydrogen generation by hydrolysis	4.9	13.0	[87]
	Oxidation of benzene	0.0001	0.0021	
S	Hydrogen generation by hydrolysis	20 <sup>[d]</sup>	160 <sup>[d]</sup>	[29]
		10 <sup>[e]</sup>	75 <sup>[e]</sup>	
B	Degradation of RhB	0.055	0.199	[86]
	Degradation of RhB	0.0081	0.0362	
C	Reduction of Cr(VI)	0.0010	0.0017	[90]
	Hydrogen generation by hydrolysis	17.8	25.3	

[a]: μmol/h for hydrogen and oxygen generation by hydrolysis, min<sup>-1</sup> for degradation of pollution, % for oxidation of cyclohexane; [b]: ABN was introduced into bulk g-C<sub>3</sub>N<sub>4</sub>; [c]: ABN was introduced into mg-C<sub>3</sub>N<sub>4</sub>; [d]: The catalytic system was irradiated in light of λ>300 nm; [e]: The catalytic system was irradiated in light of λ>420 nm; [f]: The Conversion rate of cyclohexane

射下, 价带电子跃迁, 形成电子-空穴对, 并进一步产生活性粒子, 催化污染物的分解、水解制氢制氧和氧气的还原, 另外还可实现有机物的精确合成。在这几种光催化反应类型中, g-C<sub>3</sub>N<sub>4</sub> 光解污染物和水的效果较好, 研究较多, 太多的改进方法也都是针对这两种光催化类型的。

由于电子空穴复合较快、比表面积小等原因, g-C<sub>3</sub>N<sub>4</sub> 的光催化性能不是很理想, 目前已开发出三种主要的改进方法, 即物理复合改性、化学掺杂改性和微观结构调整。物理复合改性可降低电子空穴的复合率, 提高电子或空穴的利用率; 化学掺杂改性可以很好地调整 g-C<sub>3</sub>N<sub>4</sub> 的电子结构; 微观结构调整可增大比表面积, 使活性位点增多。这三种改进方法中, 物理复合改性研究较多, 机理较为清楚, 光催化性能的提高也较为明显。

g-C<sub>3</sub>N<sub>4</sub> 的结构独特、光催化效果良好和改进方法简单, 使之成为光催化领域的研究热点, 对其的开发和利用必然引起未来环境治理与新能源开发

的重大革新, 但目前其还面临着以下几个困难和挑战:

(1) 虽然有许多改性方法, 但 g-C<sub>3</sub>N<sub>4</sub> 的可见光吸收主要集中在蓝紫光, 对可见光的利用有限, 因而光催化性能仍不高。

(2) 各种改性方法也有一定的缺陷, 选用的复合物质大都含有 Ti、Zn、Sm、Ag 等贵金属, 不仅价格昂贵, 且对水体有一定的污染。对 g-C<sub>3</sub>N<sub>4</sub> 进行化学掺杂时难以精确控制, 易引入杂质。微观结构也难以达到精确控制, 结构的控制方法较为单一, 且效果有限。

(3) 在催化某些有机合成物时, 虽然能够实现产物的精确化, 但反应进行的较慢, 反应物的转化率偏低。

(4) 实验室中合成的 g-C<sub>3</sub>N<sub>4</sub> 往往含有大量的缺陷, 结晶度不高, 且在水中的分散性较差, 制约了光催化性能的提高。

表 3 微观结构对 g-C<sub>3</sub>N<sub>4</sub> 光催化性能的影响

Table 3 Influence of microstructure on the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub>

Microstructure	Application	Photocatalytic performance of bulk g-C <sub>3</sub> N <sub>4</sub> <sup>[a]</sup> /( $\mu\text{mol}\cdot\text{h}^{-1}$ , $\text{min}^{-1}$ or %)	Photocatalytic performance of modified g-C <sub>3</sub> N <sub>4</sub> <sup>[a]</sup> / ( $\mu\text{mol}\cdot\text{h}^{-1}$ , $\text{min}^{-1}$ or %)	Reference
Porous structure	Degradation of RhB	0.014	0.131	[94]
Porous structure	Oxidation of toluene	24 <sup>[b]</sup>	>99 <sup>[b]</sup>	[47]
Porous structure	Friedel-Crafts reaction of benzene	0 <sup>[c]</sup>	90 <sup>[c]</sup>	[53]
Nanosheet	Degradation of RhB	0.0012	0.0163	[20]
Nanorod	Hydrogen generation by hydrolysis	28	84	[23]
	Hydrogen generation by hydrolysis	3.9	7	
Nanorod	Degradation of MB	0.0017 <sup>[d]</sup>	0.0025 <sup>[d]</sup>	[97]
		0.0021 <sup>[e]</sup>	0.0029 <sup>[e]</sup>	
Nanosheet	Hydrogen generation by hydrolysis	31.0 <sup>[f]</sup>	169.7 <sup>[f]</sup>	[51]
		10.7 <sup>[g]</sup>	31.8 <sup>[g]</sup>	
Nanosheet	Hydrogen generation by hydrolysis	10.4	93.1	[39]

[a]:  $\mu\text{mol}/\text{h}$  for hydrogen generation by hydrolysis,  $\text{min}^{-1}$  for degradation of pollution, % for oxidation of toluene and Friedel-Crafts reaction of benzene; [b]: Formaldehyde content in production; [c]: The conversion rate of benzene; [d]: The catalytic system was irradiated in light of  $\lambda>420\text{ nm}$ ; [e]: The catalytic system was irradiated in light of  $\lambda>290\text{ nm}$ ; [f]: The catalytic system was irradiated in ultraviolet light; [g]: The catalytic system was irradiated in visible light

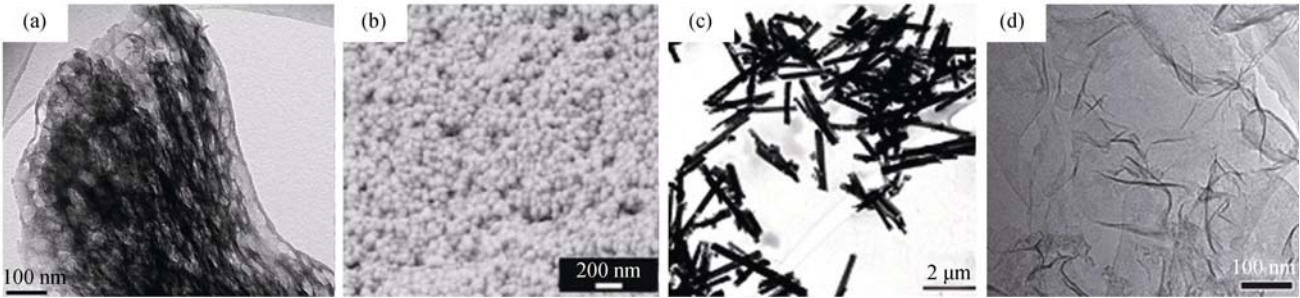


图 5 不同微观结构的 g-C<sub>3</sub>N<sub>4</sub>

Fig. 5 Different microstructures of g-C<sub>3</sub>N<sub>4</sub>

(a) Porous structure<sup>[94]</sup>; (b) Nanoparticle<sup>[96]</sup>; (c) Nanorod<sup>[23]</sup>; (d) Nanosheet<sup>[51]</sup>

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