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Enhanced visible-light photocatalytic performance of a monolithic tungsten oxide/graphene oxide aerogel for nitric oxide oxidation

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ABSTRACT

Photocatalysis is considered a promising technique for removal of pollutants from indoor air. However, the low selectivity and limited recyclability of photocatalysts in powder form currently limit their practical application. In this work, we reported the successful preparation of a monolithic tungsten oxide (WO₃)/graphene oxide (GO) aerogel photocatalyst through a cost-effective freeze-drying method. GO not only acts as a macroscopic support, but also increases the catalyst surface area from 46 to 57 m²/g, enhances the light absorption in the visible-light region, and raises the separation efficiency of photogenerated electron-hole pairs. The Obtained WO₃/GO aerogel exhibited an outstanding visible-light photocatalytic degradation rate of nitric oxide of 51%, which was 3.3 times that of pristine WO₃ powder. In addition, the aerogel displayed excellent selectivity, with a generation fraction of toxic nitrogen dioxide of as low as 0.5%. This work presents a facile synthesis route to fabricate a monolithic WO₃/GO aerogel photocatalyst with great promise for air purification.

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1. Introduction

With the widespread use of fossil fuels and the rapid development of modern industry, gas pollution is becoming a serious issue that we face today. Nitrogen oxides [consisting of mainly nitric oxide (NO) and nitrogen dioxide (NO₂)] are common air pollutants that can lead to not only acid rain, tropospheric ozone depletion, and the greenhouse effect, but also respiratory disease and skin allergies [1–6]. Therefore, various techniques have been developed for NO removal, including physical adsorption [7–9], biofiltration [10,11], and thermal catalytic reduction [12,13]. However, the above-mentioned methods are

usually complex, expensive, and unsuitable to remove low concentrations of NO (ppb level). Recently, photocatalysis has been considered as a promising technique to achieve low-concentration NO removal. Various photocatalysts such as metals and metal oxides (Bi, TiO₂, BiOX: X = Cl, Br, I, or CO₃) [14–20], perovskite-type oxides (ATiO₃, where A = Ba, Sr or Pb) [21–23], and metal-free compounds (C₃N₄) with high NO photodegradation activity have been reported [24,25]. However, most reported photocatalysts generate a high fraction of NO₂, which is more poisonous than NO, leading to secondary pollution. Therefore, the development of photocatalysts with high selectivity for NO removal is still a great challenge.

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Tungsten oxide (WO_3) is a typical n-type semiconductor that has attracted great attention because of its nontoxicity, stable physicochemical properties, and good resistance to photocorrosion [26–34]. Importantly, both theory and experiments have proved that WO_3 possesses a relatively low valence-band edge, which endows it with strong oxidation ability and makes it a promising candidate for NO removal [35,36]. However, the inherent deficiencies of WO_3 , including its low specific surface area, wide bandgap, and high recombination rate of photogenerated electron-hole pairs, severely lower its photocatalytic performance. In addition, most of the reported WO_3 photocatalysts are in powder form, so they have a strong tendency to agglomerate and are difficult to recycle.

To overcome these typical limitations of photocatalysts, a three-dimensional (3D) macroscopic graphene aerogel and its derivatives (reduced graphene oxide (RGO) aerogel and graphene oxide (GO) aerogel) with large surface area, low density, and high porosity have been developed. For example, Li and co-workers synthesized BiOBr/RGO , TiO_2/RGO , and $\text{Cu}_2\text{O/RGO}$ nanocomposite aerogels via a freeze-drying method [37–40]. These nanocomposite aerogels exhibited high activity for the degradation of pollutants and were easily separated from the aqueous reaction systems to allow easy recycling, opening a new avenue for the development of integrated photocatalysts. In these systems, the graphene aerogel acts as not only the substrate but also has a positive effect on photocatalytic performance because it increases light absorption and slows the recombination of electron-hole pairs [41–44]. Moreover, the monolithic structure of photocatalyst aerogels makes them easy to recycle.

In this work, we report the fabrication of a monolithic WO_3/GO aerogel photocatalyst via a cost-effective freeze-drying process. GO acts as a scaffold to support WO_3 and also enhances the photocatalytic NO degradation activity of WO_3 . Moreover, the obtained WO_3/GO aerogel exhibits excellent selectivity, with NO_2 generation fraction as low as 0.5%. Our results demonstrate that WO_3/GO aerogels show great potential for use in indoor air purification.

2. Experimental

2.1. Materials

All chemical reagents were purchased from Chengdu Kelong Co. Ltd. in analytical grade and used without any further purification treatment.

2.2. Synthesis of WO_3 and GO

Hexagonal WO_3 powder was prepared via a hydrothermal route according to our previous work [45,46]. In a typical procedure, ammonium metatungstate (248 mg) and acetic acid (2 mL, 25 vol %) were placed in a 25-mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 180 °C for 48 h and then cooled to room temperature. The solid residue was washed with deionized water and then dried at 70 °C to obtain WO_3 powder.

GO was synthesized through a modified Hummers method [40]. The final GO solution was diluted to a concentration of 4 mg/mL for use in further experiments.

2.3. Synthesis of monolithic WO_3/GO aerogel

The prepared WO_3 powder (360 mg) was dispersed in deionized water (90 mL) by ultrasonication at 300 W and 40 kHz for 1 h. GO solution (10 mL, 4 mg/mL) was added dropwise to the above suspension. The mixture was stirred for 24 h to achieve a uniform suspension and then frozen at –80 °C for 2 h. After freeze-drying for 48 h, 90 wt% WO_3/GO aerogel was obtained. For comparison, WO_3/GO aerogels with different contents of WO_3 (70 and 80 wt%) were prepared via a similar synthesis process, and are denoted as 70 wt% WO_3/GO and 80 wt% WO_3/GO , respectively. Unless otherwise stated, the WO_3/GO aerogel referred to is the 90 wt% WO_3/GO sample.

2.4. Characterization

Powder X-ray diffraction (XRD) was performed with a PANalytical X'pert diffractometer operated at 40 kV and 40 mA using $\text{Cu K}\alpha$ radiation. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on an FEI Tecnai G2 20 microscope operated at 200 kV. Ultraviolet-visible (UV-Vis) diffuse reflection spectra (DRS) were measured on a Shimadzu UV-2600 spectrophotometer. Fourier transform infrared (FTIR) spectra were collected on a Nicolet 6700 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250Xi spectrometer with $\text{Al K}\alpha$ radiation at 1486.6 eV. Brunauer-Emmett-Teller (BET) surface area measurements were performed using the nitrogen adsorption-desorption technique on a Quantachrome ASAP 2020 HD88 surface analyzer. Photoluminescence spectra (PL) were measured using Hitachi F-7000 with the light source of MVL-210 (Mejiro Genossen Inc.).

2.5. Photocatalytic measurements

Photocatalytic removal of NO at ppb level was measured using a custom-made testing system [19]. In this experiment, photocatalyst (400 mg) was split equally between two petri dishes that were used in the activity testing. The flow rates of air and NO were 2.0 and 12.0 mL/min, respectively. The removal ratio (η) of NO was calculated by Eq. (1):

$$\eta (\%) = (1 - C/C_0) \times 100\%, \quad (1)$$

where C is the concentration of NO during the reaction and C_0 is the initial concentration of NO. In addition, the generation ratio (ω) of NO_2 during the photocatalytic reaction was calculated by:

$$\omega (\%) = [C(\text{NO}_2) - C_0(\text{NO}_2)]/C_0(\text{NO}_x) \times 100\%, \quad (2)$$

where $C(\text{NO}_x)$ is the total concentration of nitrogen oxides (NO_2 and NO; $C(\text{NO}_x) = C(\text{NO}) + C(\text{NO}_2)$) and $C_0(\text{NO}_2)$ is the initial concentration of NO_2 before the photocatalytic reaction.

3. Results and discussion

3.1. Fabrication of monolithic WO₃/GO aerogels

Fig. 1 shows a schematic illustration of the fabrication process of the WO₃/GO aerogel. Firstly, the green WO₃ powder was dispersed in deionized water by ultrasonication for 1 h (Fig. 1(b)) to obtain a homogeneous suspension. Secondly, GO suspension was added dropwise under continuous stirring to achieve a homogeneous mixture in which WO₃ powder was uniformly attached on the surface of the GO nanosheets (Fig. 1(a), (c), and (d)). The obtained brown mixture was then freeze-dried to remove water to provide the low-density WO₃/GO aerogel, which can stably rest on a leaf (Fig. 1(e)).

3.2. Structure, morphology, and chemical composition

Fig. 2 presents the XRD patterns of GO, WO₃, and WO₃/GO aerogel. GO exhibited one peak at 9.9°, whereas WO₃ displayed four peaks located at 13.95°, 22.71°, 28.17°, and 37.63° that were assigned to the (100), (001), (200), and (210) facets of hexagonal WO₃ (JCPDS 33-1387), respectively [40–44]. The XRD pattern of the WO₃/GO aerogel contained all the peaks from WO₃, indicating that GO did not change the structure of WO₃. The (001)/(200) and (100)/(200) peak intensity ratios of 0.61 and 0.35, respectively, for the WO₃/GO aerogel were lower than those for WO₃ (0.95 and 0.63, respectively). This influence of the GO nanosheets confirmed their successful introduction to WO₃.

The microstructure of WO₃ and the WO₃/GO aerogel was studied by TEM. As shown in Fig. 3(a) and (b), the WO₃ powder has a plate-like morphology that did not change after the formation of the WO₃/GO aerogel. In addition, two crystal facets with lattice spacings of 0.312 and 0.382 nm consistent with the (200) and (001) facets of WO₃, respectively, with a crossing angle of 90° were observed in the HRTEM images of both WO₃ and the WO₃/GO aerogel (Fig. 3(b) and (d)). The introduction of GO markedly increased the dispersity of WO₃, which is beneficial for enlarging surface area [46].

The BET analysis of WO₃ and the WO₃/GO aerogel was performed. Fig. 4 shows the N₂ adsorption-desorption isotherms for WO₃ and the WO₃/GO aerogel. WO₃ exhibited a type-IV iso-

Fig. 1. (a) Schematic showing the aerogel synthesis steps, including mixing of WO₃ and GO solutions and self-assembly of WO₃ on GO sheets. Photographs of the WO₃ powder (b), GO solution (c), mixed suspension of WO₃ and GO (d), and WO₃/GO aerogel (e).

Fig. 2. XRD patterns of GO, WO₃, and WO₃/GO along with the PDF card for WO₃.

therm pattern with H₁ hysteresis loop, which is associated with the straight pore structure caused by the random accumulation of WO₃ plates. In contrast, the WO₃/GO aerogel displayed H₃ hysteresis loop, which is attributed to a slit-like pore structure, indicating the favorable dispersion of WO₃ on the GO surface, in accordance with the TEM analysis. The increased dispersity of WO₃ in the aerogel enlarges the surface area from 46 to 57 m²/g, which should improve photocatalytic performance [47].

XPS measurements were used to investigate the chemical states, binding energies, and interactions in the aerogel. Fig. 5 depicts the high-resolution W 4f, O 1s, C 1s, and N 1s spectra. Binding energies were referenced to C 1s at 284.8 eV. The peaks for WO₃ at 35.5 and 37.6 eV corresponding to W 4f_{5/2} and W 4f_{7/2}, respectively, can be ascribed to the chemical state of W⁶⁺ in WO₃. These peaks shifted to higher binding energies of 35.7 and 37.8 eV after the introduction of GO [48]. The two peaks in the O 1s spectrum of WO₃ at 530.3 and 531.3 eV are related to W–O and C=O bonds, respectively. After coupling with GO, two new peaks appear at 532.1 and 532.6 eV that are attributed to the C–O–C and –COOH bonds of GO, respectively.

Fig. 3. TEM (a, c) and HRTEM (b, d) images of WO₃ (a, b) and the WO₃/GO aerogel (c, d).

Fig. 4. N_2 adsorption-desorption isotherms of WO_3 (a) and WO_3/GO (b) photocatalysts.

Fig. 5. High-resolution XPS analysis of WO_3 and WO_3/GO . (a) W 4f; (b) O 1s; (c) C 1s; (d) N 1s.

In the C 1s spectra, the peak at 286.0 eV is assigned to the C–O bonds on the surface of WO_3 , while a new peak at 286.8 eV corresponding to the C=O bond of GO is observed after the introduction of GO [49,50]. In the N 1s spectra, the peaks located at 399.8 and 401.7 eV are ascribed to the N–H bond in NH_2^- and nitrogen atom of NH_4^+ , respectively. After the formation of the WO_3/GO aerogel, the intensities of the N 1s peaks weaken because of the decrease of the surface content of nitrogen atoms. In addition, the binding energy shifts from 399.8 to 400.3 eV,

which indicates the decreased electron density on the N atoms in the aerogel. Fig. 6 shows FTIR spectrum of GO, WO_3 and WO_3/GO aerogel. The characteristic peaks located at 784 cm^{-1} , 1041 cm^{-1} , 1637 cm^{-1} and 3230 cm^{-1} can be ascribed to the O–W–O, C–O, C=O and N–H bonds [46,51]. Importantly, the peak located at 3230 cm^{-1} from N–H bonds disappeared after coupling with GO, indicating the release of NH_4^+ ions or NH_3 molecules from the channels of WO_3 during the ultrasonication treatment, consistent with the XPS analysis results.

Fig. 6. FTIR spectrum of GO, WO₃ and WO₃/GO samples.

3.3. Optical properties and photocatalytic performance

Fig. 7(a) shows the UV-Vis DRS results for WO₃, GO, and the WO₃/GO aerogel. The absorption edge of WO₃ was around 360

nm, indicating a bandgap of 3.44 eV. After coupling with GO, a red shift of the absorption edge was observed, resulting in a narrow bandgap of 3.16 eV, which is attributed to the black-body and surface sensitization behavior of GO and demonstrates the broadened light response of the WO₃/GO aerogel compared with that of WO₃ [18].

Photooxidation of NO over WO₃ and the WO₃/GO aerogel was carried out under visible-light illumination. As illustrated in Fig. 7(b), all the aerogel samples exhibited enhanced NO removal compared with that of WO₃. The highest removal ratio of 51% was obtained for the 90 wt% WO₃/GO aerogel, which is 3.3 times higher than that of WO₃. It should be noted that the integrated structure of the aerogel collapsed when the mass ratio of WO₃ exceeded 90% and thus the 90 wt% WO₃/GO sample was chosen for the recycling test. Fig. 7(c) clearly reveals that the NO removal ratio decreased in first two cycles because the oxidation products (NO₂⁻ and NO₃⁻) blocked the active sites. After the desorption of these products through UV illumination, the catalyst reverted back to its original activity [19,52–54]. In addition, NO₂ is a photodegradation product of NO that is a poisonous gas and leads to secondary pollution [18]. The as-prepared WO₃ possesses a low NO₂ generation fraction of only 1.8% and after the introduction of GO, the NO₂

Fig. 7. (a) Absorption spectra of GO, WO₃, and WO₃/GO. (b) Photocatalytic removal of NO by various photocatalysts under visible-light irradiation ($\lambda > 420$ nm). (c) Photocatalytic recycling of WO₃/GO. (d) Generation of NO₂ in the presence of WO₃ and WO₃/GO photocatalysts.

Fig. 8. XPS valence-band spectra (a) and photoluminescence spectra (b) of WO_3 and WO_3/GO .

generation fraction further decreases as low as 0.5%, indicating the excellent selectivity of WO_3/GO aerogel. Compared with the previously reported works, the as-prepared WO_3/GO aerogel exhibited not only favorable photocatalytic performance but also outstanding selectivity with the lowest NO_2 generation fraction of 0.5%, which is more advantageous in practical application [14–21,24].

Based on the above XPS valence-band (Fig. 8(a)) and UV-Vis DRS (Fig. 7(a)) analyses, a possible band structure and photocatalytic mechanism for the WO_3/GO aerogel are illustrated in Fig. 9. Generally, a photocatalytic process includes three main steps [18]. Firstly, the pollutant is adsorbed on the surface of the photocatalyst. The WO_3/GO aerogel possesses a large surface area, which endows it with a higher adsorption capacity for Rhodamine B (RhB) of 32 mg/g than that of 2 mg/g for WO_3 . Secondly, the photocatalyst absorbs photons and excites electron-hole pairs. The WO_3/GO aerogel exhibited broadened light absorption compared with that of WO_3 . Finally, photogenerated carriers are transferred to the photocatalyst surface, where they oxidize NO and RhB [43,51]. The GO aerogel provides multidimensional electron pathways that hinder the recombination of electrons and holes. Fig. 8(b) shows the PL spectra of WO_3 and the WO_3/GO aerogel. After the introduction of GO, the PL intensity obviously decreases, indicating the decreased recombination of photogenerated carriers. All in all,

the large surface area, broadened light absorption, and fast electron transportation work together to result in the WO_3/GO aerogel displaying excellent photocatalytic performance and selectivity.

4. Conclusions

In conclusion, a WO_3/GO aerogel was prepared by a cost-effective freeze-drying process. The introduced GO not only acted as a support material for the formation of the aerogel but also increased the surface area, light absorption, and charge separation efficiency of the photocatalyst. The WO_3/GO aerogel showed a high NO removal ratio of 51%, which was 3.3 times that of WO_3 powder, and excellent selectivity, with the fraction of NO_2 generated as low as 0.5%. The outstanding photocatalytic NO degradation activity and excellent selectivity of the WO_3/GO aerogel mean it has great potential for use in indoor air purification.

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Fig. 9. Schematic illustration of photocatalysis by the WO_3/GO aerogel.

Graphical Abstract

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Enhanced visible-light photocatalytic performance of a monolithic tungsten oxide/graphene oxide aerogel for nitric oxide oxidation

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A monolithic tungsten oxide (WO_3)/graphene oxide aerogel photocatalyst displaying enhanced visible-light photocatalytic activity towards nitric oxide oxidation and inhibited generation of the harmful intermediate nitrogen dioxide compared with that of the powder WO_3 counterpart was developed.

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整体式三氧化钨/氧化石墨烯气凝胶增强可见光光催化氧化NO性能

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摘要: 近年来, 光催化技术在去除以NO为代表的诸多室内气体污染物方面展现出巨大的潜力. 单质铋和铋系氧化物, 非金属氧化物以及钙钛矿等众多半导体光催化材料均具有优异的NO降解效率, 但很难控制氧化产物. 因而会生成大量毒性更强的中间产物NO₂造成二次污染. 因此, 寻求一种清洁、高效, 且具有良好选择性的光催化材料成为了亟待解决的问题. 六方相三氧化钨(h-WO₃)的价带位置较正, 氧化电位较高, 具有很强的氧化能力, 是一种良好的氧化性光催化半导体材料. 然而, WO₃催化材料多为粉末状, 不仅容易团聚, 难以回收利用并且会堵塞检测气路. 同时, WO₃本身存在的电子-空穴复合率高, 弱的可见光响应性等问题使其光催化活性较低. 因而, 制备具有良好可见光响应, 高电子-空穴分离效率的一体化WO₃材料是其广泛应用前急需解决的问题. 而石墨烯气凝胶是理想的催化剂载体, 其较高的比表面积以及多孔状结构可有效地增加催化剂的暴露面积, 提升催化剂利用率; 更重要的是, 氧化石墨烯(GO)具有极高的导电率, 可作为电子受体加速电子-空穴对的分离而提升光催化活性. 因此, 以GO作为基体材料, 构建WO₃/GO气凝胶一体化材料有良好的应用前景. 然而, 现在还鲜见有关宏观WO₃/GO气凝胶光催化降解NO的报道.

本文以偏钨酸铵为钨源, 利用体积分数为25%的冰醋酸在180 °C条件下制备六方相三氧化钨. 通过机械搅拌以及冷冻干燥法制备WO₃/GO气凝胶. 经光催化氧化NO测试发现其可见光下降解率可达51%, 是WO₃粉末的3.3倍, 并且NO₂生成率仅为0.5%, 远远低于其他相关光催化材料. 采用了X射线衍射(XRD), 透射电镜(TEM), X射线光电子能谱(XPS), 紫外-漫反射分光光度计(UV-DRS), 傅里叶红外光谱(FTIR)和荧光光谱(PL)等手段研究了其光催化性能提高的原因.

XRD测试显示, 复合材料主体为h-WO₃, 说明GO的引入并未破坏材料晶体结构; TEM和BET测试发现, 在加入GO之后h-WO₃分散性变好, 比表面积变大, 从而可暴露更多的光催化活性位点. UV-DRS吸收光谱可以看到WO₃/GO气凝胶材料的吸收边发生了显著的红移, 其禁带宽度从3.44 eV减小到3.16 eV, 这可能是GO影响了WO₃的能带结构所致. 同时PL结果表明, 引入了GO之后, 气凝胶材料的非辐射跃迁程度明显减小表明其电子-空穴对的复合得到了显著抑制, 电子迁移显著加强.

综合以上结果, 可以得到WO₃/GO光催化性能提升以及良好的产物选择性的原因. 首先, 三维气凝胶材料的结构提升了催化剂的有效利用率, 较大的比表面积暴露了更多的活性位点. 其次, GO的引入减小了复合材料的禁带宽度, 并使其吸光性能有所改善, 产生了更多的光生电子和空穴. 最后, GO本身极高的导电性, 使光生电子-空穴对得以有效的分离, 一方面, 电子通过GO迅速转移到材料表面来参与光催化反应; 另一方面, 电子的快速转移抑制了电子-空穴对的复合, 进而提高光催化性能, 而且较正的价带位置保证了NO较为彻底的氧化为NO₃⁻. 因此, 相比传统粉末WO₃催化材料, 一体化的WO₃/GO气凝胶不仅显著提升了NO降解率, 同时严格抑制了毒副产物NO₂的生成, 同时更具有容易回收利用, 不存在二次污染的优点. 综上所述, WO₃/GO一体化气凝胶光催化材料有望在环境净化与能源领域表现出良好的应用前景.

关键词: 三氧化钨/氧化石墨烯气凝胶; 光催化剂; NO氧化; 选择性

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