Tungsten oxide nanowire-reduced graphene oxide aerogel for high-efficiency visible light photocatalysis

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ABSTRACT

A light, 3-D, porous aerogel was fabricated by way of a simple approach from 1-D tungsten oxide nanowires and 2-D reduced graphene oxide sheets. The as-prepared graphene oxide, tungsten oxide nanowires, and tungsten oxide-reduced graphene oxide (W18O49-RGO) aerogel were characterised. The photocatalytic activities of as-prepared aerogel under visible light irradiation were investigated through the degradation of six different organic dyes including Rhodamine B, reactive black 39, reactive yellow 145, weak acid black BR, methyl orange, and weak acid yellow G. In comparison with the pure W18O49 nanowires, the prepared W18O49-RGO aerogel had significantly improved photocatalytic efficiency. Also, the photocatalysis of W18O49-RGO aerogel maintained its efficiency after 30 cycles for each of the six dyes. The photocatalytic mechanism was studied by adding hole and radical scavengers: the results confirmed that the holes generated in W18O49-RGO aerogel played a key role in the visible light photocatalytic process.

1. Introduction

A variety of organic dyes has been widely used for a long time in many industries, such as: tanneries, paper manufacture and processing, and textile production. During the dyeing process, surplus organic dyes are wasted and released into water courses, with the concomitant harmful effects on the environment and to human health [1,2]. Therefore, removal of these organic dye pollutants from waste water has attracted much attention in recent years. For this reason, a wide range of techniques, such as: solvent extraction, chemical oxidation, catalytic degradation, biodegradation, and adsorption, have been developed to remove organic dyes from waste water [2–8]. Among these methods, photocatalytic degradation of organic dyes on the surface of semiconductors has been widely studied for water purification [9,10]. To date, titanium dioxide (TiO2) has been the most widely investigated photocatalyst for water purification under ultraviolet (UV) irradiation due to its wide band gap energy of 3.2 eV [11]. However, UV radiation only comprises 4–5% of the solar light spectrum, which limits UV light activating photocatalysts in practical applications. As a result, the development of novel visible-light-driven photocatalysts with high photocatalytic activity is currently a hot research topic [12–14]. In recent years, tungsten oxides (WO3−x, 0 ≤ x ≤ 1), a relatively narrow-band-gap semiconductor (band-gap 2.4–3.0 eV), have attracted much attention due to their unique physical, chemical, and optical properties [15,16]. In particular,
non-stoichiometric $W_{18}O_{49}$ has been reported as a promising visible-light-driven photocatalyst owing to its unusual defect structure and intense near-infrared photo-absorption [17–21].

Graphene, a two-dimensional (2-D) monolayer of sp$^2$ hybridised carbon atoms with an unprecedentedly large specific surface area, flexible structure, excellent mobility of charge carriers, and good electrical and thermal conductivities [22–24], has attracted much attention since few-layer graphene flakes were first prepared by a micro-mechanical cleavage of graphite in 2004 [25]. Graphene oxide (GO), a precursor for graphene preparation is prepared through the strong oxidation/intercalation of graphite, and the oxidation introduces many oxide-containing groups, such as: epoxy, hydroxyl, carboxyl, and carbonyl groups on the carbon basal plane [26]. Therefore, hydrophilic GO can be stably dispersed in water to form hydrogels by ultrasoundization [27]. Based on these advantages of GO, various hybrid materials have been synthesised by compositing graphene with other functional nanomaterials to realise unprecedented properties arising from either the components themselves or synergistic effects. Graphene-based hybrid materials have been studied for their potential applications in electronics, optoelectronics, as photocatalysts, and as energy-storage devices [28,29].

Recently, various tungsten oxide-graphene hybrid materials have been synthesised. Yang’s group reported a material consisting of highly-ordered, mesoporous WO$_3$ nanocrystals grown on RGO as a visible-light-driven photocatalyst for oxygen generation [30]. Akhavan et al. synthesised graphene-tungsten oxide composite thin films which showed excellent visible-light photocatalytic performance in the photo-inactivation of viruses [31]. Sun et al. synthesised ultrathin $W_{18}O_{49}$ nanowires on RGO sheets by a one-step solvothermal method as an improved photocatalyst for methyl orange [32]. However, to the best of the authors’ knowledge, no porous, low-density composite of $W_{18}O_{49}$ nanowire-RGO, especially in aerogel form, and thereby applicable to the efficient photocatalytic degradation of organic dyes has yet to, date, to be reported. Considering its high specific surface and ultralow density due to its porous structure, the composite aerogel of $W_{18}O_{49}$-RGO should have much better performance as a photocatalyst. Herein, a strategy to synthesise $W_{18}O_{49}$-RGO aerogel by a two-step method is reported. In the first step, $W_{18}O_{49}$ nanowire was prepared by hydrothermal treatment of WCl$_6$ in absolute alcohol. Subsequently, $W_{18}O_{49}$-RGO aerogel was fabricated by freeze-drying a $W_{18}O_{49}$-GO dispersion, followed by chemical reduction with hydrazine vapour. The $W_{18}O_{49}$-RGO aerogel has a porous morphology and good mechanical properties with a high specific surface area, and it exhibits highly efficient photocatalytic activity for the degradation of six different dyes under visible light.

2. Materials and methods

2.1. Materials

Graphite powder (2500 mesh, 99.8% purity) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Sulphuric acid (H$_2$SO$_4$, 98%), potassium permanganate (KMnO$_4$), sodium nitrate (NaNO$_3$), hydrogen peroxide (H$_2$O$_2$, 30%, w/w), reactive black 39 (RB), reactive yellow 145 (RY), weak acid black BR (AB), methyl orange (MO), weak acid yellow G (AY), and Rhodamine B (RhB) were of analytical reagent grade and were used without further purification. Deionised water (DI water) was used throughout.

2.2. Synthesis of GO sheets

Graphene oxide (GO) was synthesised using natural graphite powder as the starting material by a modified Hummers method [33]. Typically, 1 g of graphite powder was ground with NaNO$_3$ (1 g) for 15 min. Afterwards, the mixed solid was transferred to a 250 mL jacketed reactor. 25 mL of concentrated sulphuric acid was added and the mixture was stirred at 50 °C for 2 h. After cooling to 0 °C, 4 g of KMnO$_4$ was slowly added into the mixture at a temperature of below 5 °C and then the temperature was increased to 35 °C while the mixture was continuously stirred for a further 15 h. Thereafter, the mixture was diluted with distilled water under mechanical stirring and 5 mL of 30% H$_2$O$_2$ aqueous solution was slowly added until an earthen yellow suspension developed. Finally, the mixture was repeatedly centrifuged and washed with 1 M HCl solution twice, the washed with copious amounts of water, and centrifuged for collection.

2.3. Synthesis of $W_{18}O_{49}$ nanowire

Uniform hydrophilic $W_{18}O_{49}$ nanowire with a high aspect ratio, which was less than 15 nm in diameter and tens of microns in length was obtained by modified methods described previously [20]. In a typical procedure, 150 mg WCl$_6$ was dispersed in 50 mL absolute alcohol, and then the resultant solution was transferred into a 100 mL Teflon$^\circ$-lined autoclave and heated at 200 °C for 12 h. After the hydrothermal reaction, the autoclave was allowed to cool naturally to room temperature. The resulting product was collected by centrifugation and washed repeatedly with distilled water and absolute ethanol followed by vacuum drying at 60 °C overnight. The dispersion of nanowires in water was ivory coloured.

2.4. Synthesis of $W_{18}O_{49}$-RGO aerogel

Typically, 3 mL of 10 mg mL$^{-1}$ $W_{18}O_{49}$ dispersion was added to 2 mL of 1.5 mg mL$^{-1}$ GO aqueous solution and then the resulting mixture was sonicated for about 4 h to yield a homogenous suspension. Then the suspension was poured into a cylindrical crucible and freeze-dried for 2 days. The as-prepared $W_{18}O_{49}$-graphene oxide foam was chemically reduced by hydrazine vapour at 90 °C for 24 h, followed by vacuum-drying at 80 °C for 24 h [34]. RGO was obtained from GO by a similar process without the presence of $W_{18}O_{49}$.

2.5. Characterisation

The phase compositions of the as-prepared products were determined by X-ray diffraction analysis (XRD, Rigaku D/max-2500) using graphite-monochromised Cu-K$_\alpha$ radiation. The structure and morphology were investigated by scanning electron microscope (SEM) (FEI Sirion-F250), transmission
electron microscope (TEM) (FEI Tecnai G2 20 STWIN), and atomic force microscope (AFM, SPM-9600). The X-ray photoelectron spectrum (XPS) was derived from measurements conducted on an X-ray photoelectron spectrometer using an Mg-Kα radiation excitation source (AXIS ULTRA DLD, Kratos). Thermo-gravimetric analyses (TGA Rigaku, TG8101D) were performed from room temperature to 800 °C at a heating rate of 5 °C min⁻¹ in flowing air. Raman spectra were recorded on a Thermo Fisher DXR using an Ar⁺ laser (wavelength 532 nm, 2 mW) with 1 μm laser spot equipped with optical microscopy. The specific surface area, pore size, and pore volume were determined by a Brunauer–Emmett–Teller (BET) apparatus, V-Sorb 2800P (Gold APP Instruments Corporation, China). The surface area was determined by evaluating the isotherm of the physical adsorption of nitrogen and the specific surface area was determined by the BET method. The surface area of the mesopores was calculated by applying the Battet–Joyner–Halenda adsorption (BJH) approach. The electrical properties were measured by a Hall measurement system (Accent HL5500). The sample was pressed into thin films under a pressure of 25 MPa. The total organic carbon (TOC) values at different irradiation times were determined with Shimadzu TOC Analyzer (TOC-5050-A, Japan).

2.6. Photocatalytic activity measurement

The photocatalytic activities of the as-prepared W₁₈O₄₉-RGO aerogel were evaluated by measuring the photo-degradation of RB, RY, AB, MO, AY, and RhB under visible-light irradiation. Before starting the illumination, the sample suspension was magnetically stirred for 120 min in the dark to ensure the establishment of an adsorption–desorption equilibrium between the dye and the catalyst. Photo-irradiation was carried out using a 500 W xenon lamp through UV cut-off filters (JB420) to completely remove any radiation below 420 nm and to ensure illumination by visible-light only. The experiments were performed at 25 °C as follows: 25 mg of W₁₈O₄₉-RGO aerogel was added to 100 mL of a 50 mg L⁻¹ dye aqueous solution. The concentration change of the dyes was monitored by measuring the UV–vis absorption of the suspensions at regular intervals. The suspension was centrifuged for 5 min to remove the photocatalysts before measurement. The photocatalyst was recycled by the filtration of the solutions after dye degradation and then used for the next cycle of dye degradation after sufficient drying. The photocatalyst was recycled 30 times. Adsorption experiments were carried out as follows: W₁₈O₄₉-RGO aerogel (20 mg) was added to 100 mL of each dye solution (0.02 mg mL⁻¹), and stirred at room temperature. After 2 h, the aerogel composite was removed from the solution by filtration. The dye concentrations were calibrated using the Beer–Lambert law at λ_max values of 596.0, 422.0, 581.0, 463.0, 407.0, and 550.0 nm for RB, RY, AB, MO, AY, and RhB, respectively.

3. Results and discussion

Fig. 1a shows the XRD patterns of the GO and as-prepared W₁₈O₄₉-RGO aerogel. The typical XRD pattern of the GO sheets exhibits a sharp (001) diffraction peak at around 12.1°, corresponding to a d-spacing of 0.73 nm. This interlayer distance of GO is much larger than that of pristine graphite (0.34 nm) due to the introduction of oxygen-containing groups on the carbon basal plane [35]. The diffraction peak of graphite was not observed due to the effective intercalation. All peaks up to 2θ = 23° (where θ is the angle of diffraction) of W₁₈O₄₉-RGO aerogel can be assigned to the phase of monoclinic W₁₈O₄₉ (CPDS 71-2540) [17,36,37] (Fig. 1a). The (001) diffraction peak of the GO sheets has almost disappeared, indicating an exfoliation of the ordered, stacked GO sheets, and also the reduction of GO to RGO after chemical reduction by hydrazine vapour.

Representative Raman spectra of GO and W₁₈O₄₉-RGO aerogel are shown in Fig. 1b. As for the GO sheets, there are two broad peaks centered at 1349 and 1591 cm⁻¹, assigned to sp² (D band) and sp³ (G band) hybridisation carbon atoms, respectively [32]. The Raman spectrum of the aerogel also contains both peaks at about 1347 and 1591 cm⁻¹, which are attributed the D and G bands of RGO. The intensity ratio of the D band to the G band (I_D/I_G) of RGO (0.94) is lower than that of GO (1.04), which further confirms the reduction of GO [38]. Additionally, the bands at 245 and 302 cm⁻¹ can be assigned to W–O–W flexural vibrations, while the bands at 710 and 784 cm⁻¹ can be attributed to the W–O stretching modes (Fig. 1c) [39].

Qualitative XPS revealed the surface electronic structure and elemental valence of the GO sheets and the W₁₈O₄₉-RGO aerogel. The survey XPS spectrum for the GO sheets indicates that elemental C and O occurred, evidencing the oxidation of graphite; while for the W₁₈O₄₉-RGO aerogel, W could be detected (Fig. 2a). The core-level XPS spectrum of C 1s and the corresponding deconvoluted spectra for the GO sheets are shown in Fig. 2b. The peak with a binding energy centered on 284.6 eV could be attributed to the C–C bond. The deconvoluted peaks with binding energies of 286.6, 287.6, and 288.9 eV could be assigned to the C–O, C=O, and O=C=O bonds, respectively [40]. While for the W₁₈O₄₉-RGO aerogel, the C 1s spectrum becomes a major peak at 284.9 eV, and peaks corresponding to the C–O, C=O, and O=C=O bonds are significantly weakened, suggesting effective reduction of the GO sheets (Fig. 2c). The presence of the binding energy profile at 286.4 eV (C–O bond) indicates that there is small amount of oxygen-containing carbon groups in the final W₁₈O₄₉-RGO aerogel, which is commonly found for chemically RGO [41]. The core-level XPS spectrum of W 4f can be deconvoluted into two doublets, as shown in Fig. 2d. The main one consists of two peaks with binding energies of 36.5 and 38.6 eV, which belong to W 4f⁷/₂ and W 4f⁵/₂ of the W⁴⁺ formal oxidation state, respectively. The second doublet has binding energies of 35.5 and 37.2 eV, corresponding to the W⁶⁺ oxidation state. This is indicative of the non-stoichiometric characteristics of the as-synthesised W₁₈O₄₉ [39]. The photoelectrons from O 1s display a relatively wide, asymmetric peak, with the highest point at 531.2 eV, which could be assigned to the oxygen bond with W atoms in W₁₈O₄₉ (Fig. 2e). The other peak at higher photoelectron energy of 531.8 eV may be attributed to the residual water and/or C–O bond originating from the residual oxygen-containing groups [39].
The thermal properties and the composition of the RGO and W$_{18}$O$_{49}$-RGO aerogel were characterised by TGA in air as shown in Fig. 2f. A slight mass loss of RGO occurred in the low temperature region (<200°C), indicating that the oxygen functional groups were mostly removed due to the chemical reduction processing of GO. The majority of the mass loss was recorded above 400°C, which was attributed to the decomposition of carbon networks and those remaining oxygen functional groups [42]. As for the W$_{18}$O$_{49}$-RGO aerogel, about 17% of its mass was lost between 20 and 100°C, and this was attributable to the elimination of adsorbed/trapped water molecules [43]. The mass loss (5%) recorded in the temperature range 200–450°C can be assigned to the mass gained during the evolution of the W$_{18}$O$_{49}$ into WO$_3$ and the simultaneous mass loss caused by the removal of the physically adsorbed and chemically bound water [44]. This phenomenon was probably due to the porous nature of the aerogel, which was favourable for the adsorption of water molecules, which are commonly found in porous materials [45]. An abrupt mass loss occurred from 500°C to 700°C, which indicated the combustion of graphene. Above 700°C the mass did not change significantly, which indicated that the W$_{18}$O$_{49}$ had evolved to WO$_3$ and that the graphene had been removed. When the temperature reached 800°C, the mass of the hybrid remaining at 66.8% (w/w) should be attributed to WO$_3$: because the tungsten oxide nanowires in the composite undergo an oxidation process, the weight percentage of W$_{18}$O$_{49}$ was estimated to be 65.5% (w/w).

The XRD, Raman, XPS and TGA data (above) confirm the formation of a W$_{18}$O$_{49}$-RGO composite. The following Figs. 3–5 will reveal the morphology and microstructure of this composite. Typical photographs of this W$_{18}$O$_{49}$-RGO aerogel (Fig. 3) show the columnar shape and its low density (6.7 mg cm$^{-3}$). The as-prepared W$_{18}$O$_{49}$-RGO aerogel exhibits excellent mechanical properties: 34.5 mg of W$_{18}$O$_{49}$-RGO aerogel could support a static load of at least 0.5 N and exhibited good resilience when released from compression. As shown in Fig. 3, when the compression was released, the sample almost recovered its original shape, indicating the sample was strong and resilient. The 3-D aerogel
Fig. 3 – Digital photos of $W_{18}O_{49}$-RGO aerogel under 50 g added mass (0.5 N load). (A colour version of this figure can be viewed online.)

Fig. 4 – (a) SEM and (b) TEM images of the $W_{18}O_{49}$ “flowers”. (c) TEM images of the ultra-thin $W_{18}O_{49}$ nanowires. (d) HRTEM image and (e) SAED pattern of a single $W_{18}O_{49}$ nanowire. Inset on (c): TEM image of $W_{18}O_{49}$ nanowires sonicating in aqueous solution.

Fig. 5 – AFM image (a) and height profile (b) of GO deposited on the mica substrate; TEM images of GO (c) and $W_{18}O_{49}$-RGO aerogel (d); (e) SEM images of $W_{18}O_{49}$-RGO aerogel. (A colour version of this figure can be viewed online.)
architectures have been prepared by way of an in situ self-assembly of graphene oxide aerogel obtained by a chemical reduction of graphene oxide nanowires. After the formation of the 3-D W18O49-RGO architecture, the W18O49 nanowires were captured by the graphene network and distributed homogeneously onto both sides of the graphene sheets in the network. We believed that the following factors should contribute the most to the structural integrity of the aerogel: (1) stacking between the hexagonal carbon rings of the graphene sheets, and (2) possible covalent bonding resulting from the reaction between the residual oxygen-functional groups [46]. The oxygen-containing functionalities in GO surface are partially removed during the reduction of GO and the residual oxygen-containing groups ensure the hydrophilicities of as-prepared aerogel. The hydrophilic W18O49 nanowires were coated onto the RGO sheets, which would enhance the hydrophilicities of the aerogel. The aerogel is readily dispersed in water under the action of the applied stirring, which is an important factor in the photocatalytic reaction.

An SEM image (Fig. 4a) shows that the as-prepared W18O49 exhibits a flower-like hierarchical structure with 1 μm “flowers” and numerous nanowires. As revealed by the TEM image (Fig. 4b), the W18O49 sample consisted of well-dispersed nanowires with typical lengths of 1–2 μm and W18O49 “flowers”. The W18O49 “flowers” were actually composed of numerous ultra-thin nanowire bundles with lengths of approximately several microns and diameters of 10–20 nm, respectively. The bundles were able to be broken down into individual nanowires by sonication and the length of the nanowires was shortened simultaneously (see inset on Fig. 4c). An HRTEM image of a single nanowire and its corresponding SAED pattern are shown in Fig. 4d and e, which exhibit uniform lattice fringes at a spacing of 0.378 nm, oriented in the (010) direction, indicating that the individual nanowire is a single crystal along the (010) direction [47].

Fig. 5a shows the AFM image of the GO: the GO was lamellar and the average thickness of as-prepared GO measured from the height profile (Fig. 5b) of the AFM image was approximately 0.8 nm, which corresponded to a single-layer of GO indicating that the GO had been prepared successfully and completely exfoliated [48]. The TEM image (Fig. 5c) shows that the as-prepared GO sheets reunited, due to electrostatic attraction. As seen from a typical TEM image (Fig. 5d) of W18O49-RGO, the edges of the RGO sheets can be clearly recognised, and the W18O49 nanowires are uniformly distributed on the surfaces of the RGO sheets. The morphology of the as-prepared W18O49-RGO aerogel was also characterised by SEM, as shown in Fig. 5e. The SEM image shows that W18O49 nanowires were embedded in the RGO sheets and some W18O49 nanowires stretched out from the edges of the RGO sheets. The high surface area and porous structure, as well as the hydrophobic nature of the RGO surface, will be conducive to rapid dye absorption.

Reports on the preparation of graphene-based composite aerogels are sparse: chemical cross-linkers are generally used to prepare robust graphene-based composite aerogels, such as organic binders by the sol-gel polymerisation method [49], ion linkages [50], and ion coordination [51]. Although hydrothermal treatment of a GO solution can form a 3-D structure [46,52], and the freeze-drying approach by ice template-guided assembly also can produce 3-D porous graphene materials [53], it is hard to prepare graphene-functional nanomaterial composite aerogels since it is very hard to control the arrangement of nanowires or nanoparticles in the graphene network. In this method, the authors used the advantages of freeze-drying and hydrothermal processing without the need for chemical cross-linkers. The well dispersed W18O49-GO solution was frozen, and nanowire precipitation was avoided. During freeze-drying, the porous structure remains, and its collapse avoided. The composite was finally hydrothermally reduced by hydrazine vapour, but not in the hydrazine solution, which consolidates the porous structure to form a composite aerogel. There are some key factors influencing the success of the aerogel fabrication process in this method. Firstly, the GO sheets were thin enough (single layer sheets are preferred), secondly, the W18O49 nanowires should have smaller diameters to ensure high tenacity and softness. Thirdly, both W18O49 nanowires and GO sheets should be well dispersed, and the concentration should be as high as possible. Fourthly, after freeze-drying, the samples should be reduced by vapour. The composite will collapse in the hydrazine solution. With good control of these factors, one may fabricate many composite aerogels containing nanowires and graphene sheets, such as ZnO-RGO, TiO2-RGO, ZnS-RGO, Au-RGO, and Ag-RGO.

Electrical conductivity was used to determine whether or not the reduction process was complete. The free-standing W18O49-RGO aerogel had an electrical conductivity (3000 S/m) that was higher than the porous structures constructed by physically and randomly stacked graphene sheets [54]. The aerogel had much higher electrical conductivities because its constituent graphene sheets were chemically bonded, thus facilitating much faster charge transport across the graphene sheet junctions [55].

The N2 adsorption/desorption isotherms and corresponding pore size distribution curve for the as-prepared aerogel are presented in Fig. 6. The isotherms exhibited the characteristics of type IV isotherms with a hysteresis loop (Fig. 6a). It can be seen that the isotherms showed little uptake at low relative pressures (P/P0 < 0.1), indicating the existence of micropores. Significant hysteresis of the isotherms at high relative pressures (P/P0 > 0.1) can be seen which indicated that the aerogel was rich in mesopores. Subsequently, there was an upward trend at high relative pressures (P/P0 > 0.95), which may have originated from the presence of macropores, offering abundant channels for the solution of dyes [55,56].

The as-prepared aerogel exhibited a highly-developed, hierarchical porosity framework of macropores together with mesopores and micropores, which matched SEM observations (Fig. 5e). The pore size distribution data for the aerogel ranged from 2 to 266 nm (Fig. 6b), with the size of most of the pores being between 2 and 30 nm. The average pore size was 14.1 nm. The pore size distribution data were consistent with the previously reported graphene aerogel results [55].

The specific surface area was determined, by use of the BET model, to be 228 m2/g, whereas the pore volume, determined from the BJH model, was 0.50 cm3/g. The BET value was reasonable according to the pores observed in the SEM image (Fig. 5e) and the digital photos of the porous aerogel (Fig. 3).
Combining the result with SEM measurements, the porous structure of macropores and mesopores may benefit the diffusion of dye molecules to active sites. These structural features and electrical properties were well-suited for applications in heterogeneous reactions involving charge transfer at the photocatalytic interface such as the degradation of organic dyes.

The photocatalytic activities of the as-prepared W18O49-RGO aerogel in the degradation of six selected dyes (RY, MO, AB, RB, AY, and RhB) have been performed under visible-light irradiation at room temperature (Fig. 7a). The photo-degradation experiments were conducted after adsorption equilibrium was attained. The photo-degradation performance of MO by RGO, pure W18O49 nanowire, and W18O49-RGO aerogel under visible-light irradiation is shown in Fig. 7b. The self-degradation of MO was not obvious, indicating the stabilisation of MO under visible-light irradiation. In the case of the RGO, slight photocatalytic performance is observed under visible light. When the bare W18O49 nanowire is used as a photocatalyst, about 68% of MO molecules are decomposed after being irradiated for 25 min. The good photocatalytic activity of pure W18O49 nanowire may arise from their large specific surface, low band-gap of 2.8 eV, and/or its defect structure as caused by the numerous oxygen vacancies [57–59]. It is interesting that RGO alone is a photocatalytically inactive compound under visible light, whereas the combination of W18O49 nanowire and RGO shows significant improvement of photocatalytic activity under visible-light irradiation and the MO solution is almost completely degraded within 25 min. The inset of Fig. 7b shows the rate constants obtained from the plots. This efficient photocatalytic activity may be attributed to the synergetic effects of W18O49 nanowire and RGO. The improvement mechanism of photocatalytic performance has been proposed in the literature [60,61], and will be further discussed here.

In addition to MO, the W18O49-RGO aerogel shows excellent catalytic activity on the other five dyes. As shown in Fig. 7c, it can be seen that all of the dyes were almost completely degraded within 25 min in the presence of W18O49-RGO aerogel, which indicates no selectivity of dyes and the potential for wide application of W18O49-RGO aerogel for dye degradation. To describe the photocatalytic performance of W18O49-RGO aerogel more intuitively, the photo-degradation process was expressed by pseudo-first-order kinetics:

\[ -\ln \frac{C}{C_0} = kt \]  

where \( k \) is a rate constant indicating photocatalytic efficiency, \( C_0 \) is the initial concentration of the dye and \( C \) is its concentration at the end of the reaction. The photocatalytic degradation rates of the dyes, in descending order were: RY, MO, AB, RB, AY, and RhB, as shown in Fig. 7d. The rate ranges from 4.3 to 22.9 min\(^{-1}\), which is superior to that previously reported [32]. The dyes: RY, MO, AB, and RB are totally decomposed in 25 min, while 150 min was needed for MO decomposition through an W18O49-RGO composite reported elsewhere [32]. As practical catalysts, the reusability, recoverability, and high catalytic activity in each cycle are necessary. The W18O49-RGO aerogel was successively used in the photocatalytic degradation of the six dyes over 30 cycles. The results are shown in Fig. 7e and it can be seen that there is a slight change in the photocatalytic activity of the catalyst over the first 30 cycles under visible-light irradiation, which is indicative of the recoverable catalytic activity of the W18O49-RGO aerogel. For photocatalytic activity of RGO-oxide composites, the addition of RGO has two effects. RGO acts as electron withdrawing agent and transport network, which is very important for improving the performance of the photocatalyst. On the other hand, RGO is black, and the light shielding effect caused by the RGO may have reduced the photocatalytic activity. However, according to the literatures and our results, the overall effect of RGO addition is very positive. For example, previous studies observed that the combination of RGO with TiO2 drastically increased the charge separation and transport in such composites [62]. Another paper reported that the addition of graphene increases the absorbance of visible light thus yielding a more efficient utilisation of incident solar energy [63].

To understand the photocatalytic mechanism of this aerogel, the active oxidants generated in the photocatalytic process were trapped by disodium ethylenediaminetetraacetate dehydrate (EDTA-2Na, a hole scavenger) [64] and tert-butanol (a hydroxyl radical scavenger) [65] to identify...
The main active oxidant in the photocatalytic reaction process under visible-light irradiation. As shown in Fig. 7f, the catalytic activity of the $\text{W}_{18}\text{O}_{49}$-RGO photocatalyst was restrained by the addition of EDTA-2Na in the photo-degradation of MO and decreased slightly in the presence of tert-butanol, indicating that the hydroxyl radicals are not the main active species in the photocatalytic process and its progress [66]. EDTA anions can be absorbed on the surface of the photocatalyst and act as a hole trap or electron donor, resulting in the deactivation of the $\text{W}_{18}\text{O}_{49}$-RGO photocatalyst. The holes play a key role in the visible light photocatalytic process. The electron–hole combination in $\text{W}_{18}\text{O}_{49}$ is significantly suppressed since the generated electrons prefer to transfer onto graphene due to the high conductivity of RGO [67]. In addition, the large surface area of the aerogel, high absorption capacity, extended light absorption range, and the hydrophobic nature of RGO synergistically work to realise this high photocatalytic performance under visible light for six different dyes.

The adsorption capacity ($q_{eq}$ in mg g$^{-1}$) of the six dyes by the $\text{W}_{18}\text{O}_{49}$-RGO aerogel was calculated by the following expression:

$$q_{eq} = \frac{C_{0} - C_{eq}}{m} V$$  \hspace{1cm} (2)

where $C_{0}$ (mg L$^{-1}$) represents the initial dye concentration, $C_{eq}$ (mg L$^{-1}$) is the equilibrium concentration of the dye remaining in the solution, $V$ (L) is the volume of the aqueous solution, and $m$ (g) is the mass of the $\text{W}_{18}\text{O}_{49}$-RGO aerogel used in the experiment. Fig. 8 shows the variation of the adsorption capacity with time in the presence of the $\text{W}_{18}\text{O}_{49}$-RGO photocatalyst. Significant adsorption can be observed which could have been due to the large surface area and high adsorption ability of the aerogel. The rate of adsorption was initially rapid in all cases and the adsorption reached equilibrium after 100 min. Due to the significant adsorption capacity of the $\text{W}_{18}\text{O}_{49}$-RGO photocatalyst, it was necessary
to confirm that the dyes were photodegraded rather than adsorbed on the catalyst at the end of the reaction. Before starting the illumination, the photocatalytic systems were magnetically stirred for 2 h in the dark. The adsorption–desorption equilibrium of dyes on the photocatalyst surface was reached, as proved by the adsorption kinetics experiments (Fig. 8a). The dye concentration measured after equilibrium was used as the initial concentration, and it was reasonable to conclude that dye adsorption on the catalyst surface should have had little contribution to the variation of dye concentration during the photocatalytic process [68,69]. Therefore, the observed photobleaching in the photocatalysis process should have mainly been due to the oxidative photodegradation of the dye molecules rather than their adsorption. The mineralization of organic carbon was followed by TOC measurement, and the TOC amount decreased with time as shown in Fig. 8b. Therefore, it can be concluded that organic dyes may have been oxidized to carboxylic acids as a result of the photocatalytic reactions, and that inorganic forms may exist [70].

4. Conclusion

Through the successful assembly of nanowires inside a graphene network, the authors have developed an easy method for the preparation of a porous, lightweight W18O49-RGO aerogel. The method can be used to prepare other 3-D aerogels containing 1-D functional nanowires and 2-D graphene sheets. The W18O49-RGO aerogel thus obtained showed good photocatalytic activity and stability over 30 cycles, and six different dyes could be degraded completely within 25 min at room temperature under visible light irradiation. These findings provide insight into the potential use of well-defined functional nanomaterials/graphene aerogel for water purification as well as optoelectronic applications.

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