The Loading of Coordination Complex Modified Polyoxometalate Nanobelts on Activated Carbon Fiber: a Feasible Strategy to Obtain Visible Light Active and High Efficient Polyoxometalate Based Photocatalyst

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<th>Journal:</th>
<th>Dalton Transactions</th>
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<tr>
<td>Manuscript ID:</td>
<td>DT-ART-10-2014-003092.R2</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Paper</td>
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<tr>
<td>Date Submitted by the Author:</td>
<td>19-Nov-2014</td>
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<td>Complete List of Authors:</td>
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Tingting Lu\textsuperscript{a}, Xinxin Xu\textsuperscript{*a}, Huili Li\textsuperscript{b}, Zhenyu Li\textsuperscript{a}, Xia Zhang\textsuperscript{*a}, Jinzhao Ou\textsuperscript{a}, Mingliang Mei\textsuperscript{a}

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\textbf{NCC/POM/ACF} was fabricated successfully, which displays very excellent photocatalytic activity in visible light. Furthermore, the effect of mass ration between \textbf{NCC/POM} and \textbf{ACF} on photocatalytic activity was discussed.
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Abstract

To enhance the photocatalytic property of coordination complex modified polyoxometalate (CC/POM) in the visible light region, its nanobelts (CC/POMNBs) were loaded on activated carbon fiber (ACF) through a simple colloidal blending process. The resulted coordination complex modified polyoxometalate nanobelts loaded activated carbon fiber composite materials (CC/POMNBs/ACF) exhibited dramatic photocatalytic activity for the degradation of the rhodamine B (RhB) under visible light irradiation. Optical and electrochemical methods illustrated the enhanced photocatalytic activity of CC/POMNBs/ACF originated from high separation efficiency of photogenerated electron and hole on the interface of CC/POMNBs and ACF, which resulted from the synergy effect between them. In the composite material, the role of ACF could be described as photosensitizer and good electron transporter. Furthermore, the influence of mass ratio between CC/POMNBs and ACF on photocatalytic performance of the resulting composite material was discussed and an ideal value to obtain high efficient photocatalyst had been obtained. The results suggested the loading of CC/POMNBs on surface of ACF would be a feasible strategy to enhance its photocatalytic activity.
Introduction

Nowadays, critical pollution of organic dyes urges researchers to develop more efficient methods for their treatment.\textsuperscript{1, 2} In this field, photocatalysis has received much attention for its ambient operation condition and economic consumption during decomposition of recalcitrant contaminants.\textsuperscript{3, 4} As a kind of green and cheap photocatalyst, which possesses similar valence band position and band gap ($E_g$) with TiO$_2$, CC/POM, especially nanoscale coordination complex modified polyoxometalate (NCC/POM) has caught great interests from chemists and is employed to remove organic dyes from waste water.\textsuperscript{5, 6} Compared with other POM based photocatalysts, the solubility of NCC/POM is much lower, which makes it more convenient in recovering and recycling.\textsuperscript{7} Furthermore, NCC/POM also exhibits excellent chemical stability during the decomposition of pollutants.\textsuperscript{8} Up to now, although some ultraviolet light active CC/POM and NCC/POM photocatalysts have been explored, the design and fabrication of visible light active NCC/POM photocatalysts with high efficiency still remains as a challenge, which impede their further application in waste water treatment.\textsuperscript{9} For NCC/POM photocatalysts, these drawbacks originate from the wide band gap and the quick recombination rate of photogenerated electron-hole pair during photocatalytic process. Now, the enhancement of photocatalytic activity and efficiency in visible light region become urgent problems in research of NCC/POM photocatalyst. To resolve these problems, a feasible strategy is to load NCC/POM on a visible light active material, which also possesses excellent photogenerated electron-hole pair separation property.

In this aspect, carbon fiber (CF) is an ideal option, which meets all above mentioned requirements perfectly: at first, as a photosensitizer, CF can improve the photoresponse of NCC/POM in visible light region; secondly, CF possesses high
conductivity, which can transport photogenerated electron in time and prevent its recombination with photogenerated hole again; thirdly, its large surface area and excellent absorption capability make it an wonderful carrier for the preparation of composite materials.\(^{10, 11}\) Although these merits make CF a potential choice to improve photocatalytic property of NCC/POM, the shortage of active groups (such as -OH and -COOH) on its surface may reduce effective interactions between them and decrease stability of the resulting composite material. To overcome this shortcoming of CF, ACF is selected as its alternative, because of the existence of a large number of active groups on its surface. Based on these points, ACF can not only inherit the advantages of CF, but also can form stable composite material with NCC/POM.\(^{12-15}\) Hence we speculate the loading of NCC/POM on ACF is a feasible strategy to improve the photocatalytic property of NCC/POM.

Our imagination was confirmed to be reasonable by a visible light active photocatalyst ZnSiW\(_{11}\)NB/ACF, which was synthesized by loading the nanobelts of a new CC/POM, \([\text{Zn(HPyBim)}(\text{SiW}\(_{11}\)O\(_{39}\))](\text{H}_{2}\text{PyBim)})_{2}[(\text{HPyBim})\cdot(\text{H}_{2}\text{O})]_{7} (\text{ZnSiW}\(_{11}\), PyBim = 2-(4-pyridyl)benzimidazole) on surface of ACF. Photocatalytic degradation of RhB was investigated and results indicated the loading of ZnSiW\(_{11}\)NB on surface of ACF could enhance its photocatalytic activity effectively. To our knowledge, during the fabrication of composite materials, the mass ratio between ZnSiW\(_{11}\)NB and ACF (abbreviated as ZnSiW\(_{11}\)NB:ACF) had great effects on optical, electrochemical and photocatalytic property of the resulting composite material. To study the influence of ZnSiW\(_{11}\)NB:ACF value, the fabrication of composite material was conducted under different conditions and an ideal ZnSiW\(_{11}\)NB:ACF value to achieve ZnSiW\(_{11}\)NB/ACF with excellent photocatalytic activity was obtained.

**Experimental section**
**Materials and synthesis**

Zinc acetate dehydrate (Zn(OAc)$_2$$\cdot$2H$_2$O) and tungstosilicic acid hydrate (H$_4$SiW$_{12}$O$_{40}$) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 2-(4-pyridyl)benzimidazole (PyBim) was supplied by Alfa Aesar China Co., Ltd (Tianjin, China). Carbon fiber (CF) was purchased from SGL (Germany). All purchased chemicals were of reagent grade and used without further purification. The morphology was observed on an ultra plus field emission scanning electron microscope (ZEISS, Germany). PXRD patterns were recorded on D8 X-ray diffractometer, employing monochromatized Cu Kα incident radiation. FTIR spectra were recorded in the range 4000-400 cm$^{-1}$ on an Alpha Centaur FTIR spectrophotometer using KBr pellets. Diffuse reflectance spectra (DRS) were recorded on a Shimadzu-2501PC spectrometer using BaSO$_4$ as a standard. Electrochemical experiments were conducted on CHI 660B electrochemical workstation. The UV-visible adsorption spectrum was recorded using a Hitachi U-3010 UV-visible spectrometer.

**Synthesis of [Zn(HPyBim)(SiW$_{11}$O$_{39}$)]·(H$_2$PyBim)$_2$(HPyBim)·(H$_2$O)$_7$ (ZnSiW$_{11}$)**

ZnSiW$_{11}$ was prepared from the mixture of Zn(OAc)$_2$$\cdot$2H$_2$O (0.022 g, 0.1 mmol), PyBim (0.019 g, 0.1 mmol), H$_4$SiW$_{12}$O$_{40}$ (0.288 g, 0.1 mmol), and 6 mL H$_2$O. The mixture was stirred for 20 minutes and then transferred to a 23 mL Teflon-lined stainless steel bomb and kept at 180°C under autogenously pressure for 4 days. The reaction system was cooled to room temperature during 24 hours. A large amount of plate yellow crystals of ZnSiW$_{11}$ were obtained. Yield: 79% (based on Zn).

**Synthesis of ZnSiW$_{11}$NB**

The crystals of ZnSiW$_{11}$ were grinded for 3 hours with an agate mortar and pestle. The resulted powder was dissolved in methanol and placed in a Teflon autoclave,
which was heated in a microwave oven at 300 W for 3 hours. The resulted \( \text{ZnSiW}_{11}\text{NB} \) were separated by centrifugation, rinsed with water and then dried in a vacuum at 80 °C for 24 hours.

**Synthesis of ACF**

\( \text{CF} \) (1.0 g) was dissolved in 3 M H\(_2\)SO\(_4\) aqueous solution (30 ml) at room temperature and dispersed with sonication. After 40 minutes, 3M (NH\(_4\))\(_2\)S\(_2\)O\(_8\) aqueous solution (30 mL) was added slowly to above mixture at room temperature. Then the mixture was sonicated for 2 hours and stirred for 12 hours. The resulted ACF was separated and rinsed with water, alcohol and finally dried at 70°C for 24 hours in a vacuum.

**Synthesis of ZnSiW\(_{11}\)NB/ACF Composite Material**

The composite materials were prepared by one-step colloidal blending with \( \text{ZnSiW}_{11}\text{NB} \) and ACF in H\(_2\)O. At first, ACF was dissolved in 50 mL water. Then, \( \text{ZnSiW}_{11}\text{NB} \) (4.0 g) was dispersed in water and dropped into the solution of ACF. The resulted mixture was sonicated for 2 hours and further stirred for 10 hours at room temperature to obtain a homogeneous solution. The product was separated and dried in a vacuum at 70 °C for 10 hours. In the experiment, composite materials were prepared with mass ratio between \( \text{ZnSiW}_{11}\text{NB} \) and ACF equal to 400:1, 200:1, 100:1 and 50:1. These products were labeled as \( \text{ZnSiW}_{11}\text{NB/ACF(A)}, \text{ZnSiW}_{11}\text{NB/ACF(B)}, \text{ZnSiW}_{11}\text{NB/ACF(C)} \) and \( \text{ZnSiW}_{11}\text{NB/ACF(D)} \) respectively.

**Synthesis of ZnSiW\(_{11}\)NB/ACFM**

The mixture of \( \text{ZnSiW}_{11}\text{NB} \) and ACF was grinded for 30 minutes with an agate mortar and pestle. The product was separated and rinsed with water, alcohol and finally dried in a vacuum.

**X-ray crystallography**
Suitable single crystal of ZnSiW$_{11}$ was carefully selected under an optical microscope and glued on glass fibers. Structural measurements were performed on a Bruker AXS SMART APEX II CCD diffractometer at 293 K. The structures were solved by the direct method and refined by the full-matrix least-squares method on $F^2$ using the SHELXTL 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Carbon-bound hydrogen atoms were placed in geometrically calculated positions; Oxygen-bound hydrogen atoms were located in the difference Fourier maps, kept in that position and refined with isotropic temperature factors. PLATON/SQUEEZE program estimated the solvent-accessible region void to occupy 708.9 Å$^3$ and contain 176.1 electrons. The electron density was modeled as ten water molecules (two water molecules per asymmetric unit) which accounts for 180 electrons. The final chemical formula of ZnSiW$_{11}$ was calculated from the SQUEEZE results combined with the TGA results. The X-ray structural analysis is given in Table S1. Further details of the crystal structure have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication, which can be obtain free of charge (CCDC 955862). The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

**Wetting behavior test of CF and ACF**

A droplet of the sample suspension (CF or ACF) in ethanol was placed on a cleaned glass substrate fixed on a spin coater at a rotating speed of 1000 rpm for 2 minutes, and a film would be formed after drying. The wettability of the as-prepared films was characterized by measuring the water contact angle (CA) with a contact angle meter. A 2 µL water droplet was placed on this particle array film for water CA measurement. CA values were obtained by averaging five measurements on different areas of the sample surface.
**Electrochemical measurements**

To prepare the electrodes, 10 mg of the as-prepared samples were dispersed into 5 mL ethanol to give homogeneous suspension upon bath sonication. A 10 µL of the suspension was dip-coated onto ITO and the electrode was then dried at room temperature. Photoelectrochemical tests were carried out with a conventional three-electrode system in quartz cell filled with 0.1 M Na$_2$SO$_4$ electrolyte (100 mL) with the ZnSiW$_{11}$NB/ITO or ZnSiW$_{11}$NB/ACF/ITO electrodes serving as the working electrode, a Pt plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Before experiment, the oxygen was excluded completely by N$_2$. A 300 W xenon lamp were used as the excitation light source for visible irradiation. For incident photon-to-electron conversion efficiency (IPCE) measurements, a mixture solution of 0.05 M I$_2$ and 0.5 M LiI in propylene carbonate was used as an electrolyte. The monochromatic light was from a 300 W xenon lamp, which passed through a grating monochromator and the wavelength was selected at 5 nm intervals between 280 and 600 nm. Electrochemical impedance spectra (EIS) were recorded in potentiostatic mode. The amplitude of the sinusoidal wave was 10 mV, and the frequency range of the sinusoidal wave was from 100 kHz to 0.05 Hz. The Mott-Schotty plot was measured at a frequency of 100 HZ in the dark.

**Photocatalytic property study**

The photocatalytic activities of samples were evaluated by the degradation of RhB in the aqueous solution. 80 ml RhB aqueous solution with concentration of $10^{-5}$ M was mixed with 20 mg catalysts, which was exposed to illumination. Before turning on the lamp, the suspension containing RhB and photocatalyst were magnetically stirred in a dark condition for 40 min till an adsorption-desorption equilibrium was established. Samples were then taken out regularly from the reactor and centrifuged...
immediately for separation of any suspended solid. The transparent solution was analyzed by a UV–vis spectrometer. A 300 W medium pressure mercury lamp served as an ultraviolet light source and a 300 W Xe lamp with a cutoff filter (λ ≥ 420 nm) served as a visible light source. Degradation efficiency of RhB was obtained from the following equation: (C₀ - C)/C₀ (C₀ is the original concentration of RhB, C is the concentration of RhB after degradation).

**Results and discussion**

**Structure, morphologies and characterization**

Single crystal X-ray analysis shows in the fundamental unit of ZnSiW₁₁, there are three free PyBim ligands, two lattice water molecules and one substituted α-SiW₁₋₂O₄₀ unit (Fig. 1a). As other substituted α-Keggin type POM, in ZnSiW₁₁ one WO₆ octahedron is substituted by ZnNO₄ pyramid, in which Zn–N bond distance is 2.107(13) Å and Zn–O bond distances range from 2.030(12) to 2.049(11) Å [18]. The central SiO₄ tetrahedron shares its oxygen atoms with one {ZnW₂} and three {W₃} groups. These {ZnW₂} and {W₃} subunits are joined to each other by corner-sharing mode. The Si–O bond distances vary from 1.490(13) to 1.546(15) Å and O–Si–O bond angles are in the range of 107.3(8) to 112.6(8)°. The W–O distances can be divided into three groups: The W–Oₐ bond distances range from 1.672(11) to 1.728(16) Å, W–Oₕ/c bond distances are in the range of 1.736(12) to 2.077(13) Å and W–Oₐ bond distance vary from 2.350(14) to 2.500(14) Å. The morphology of ZnSiW₁₁NB was studied with SEM. It could be seen the thickness of ZnSiW₁₁NB range from 40 to 60 nm, while its length and width vary from 8 to 12 µm and 1 to 2 µm respectively (Fig. 1b). At low and high magnifications, the surface of ZnSiW₁₁NB seems very smooth. Thermogravimetric analysis (TGA) of ZnSiW₁₁NB was carried out in nitrogen gas from 30 to 800 °C (Fig. S1). The first weight loss in the range from 91 to 148 °C is
due to the loss of guest water molecules. The second weight loss from 323 to 452 °C can be ascribed to the decomposition of organic ligands.

The activation of CF is a very important process for the formation and stability of ZnSiW_{11}NB/ACF. Although the morphology of ACF is similar to that of CF, their surface element contents are of great difference (Fig. 2a). The XPS spectra of CF and ACF were employed to study this point. In CF, the peaks located at 284.8 eV and 532.4 eV can be attributed to C1s and O1s respectively. For ACF, the intensity of O1s peak increases to a great extent and implies the content of oxygen on its surface is much higher than CF (Fig. 2b). Furthermore, we also find C1s peaks appear at 286.1 and 288.6 eV, which can be attributed to C-O and C=O (Fig. S2). All these results imply there exist -OH and -COOH groups on surface of ACF, which are introduced during activation process of CF. This can also be illustrated by the differences between their surface wettabilities. For CF and ACF, their contact angles are 115.7° and 55.1° respectively, which further imply there exist many hydrophilic groups on the surface of ACF (Fig. 2e and 2f). These -OH and -COOH groups can form supramolecular interactions (such as hydrogen bonds) between ZnSiW_{11}NB and ACF, which will “catch” ZnSiW_{11}NB loaded on the surface of ACF and enhance the stability of ZnSiW_{11}NB/ACF.

The morphologies of ZnSiW_{11}NB/ACF were also studied with SEM. As for ZnSiW_{11}NB/ACF composite materials, it can be observed obviously there are different amounts of ZnSiW_{11}NB on the surface of ACF (Fig. 3a to 3d). In these composite materials, the ZnSiW_{11}NB loaded on ACF exhibit similar dimension with ZnSiW_{11}NB (Fig. 3e to 3f). PXRD was employed to study the structures of ZnSiW_{11}NB and ZnSiW_{11}NB/ACF (Fig. 4a). ZnSiW_{11}NB and ZnSiW_{11}NB/ACF took on similar diffraction patterns with ZnSiW_{11}, which illustrates in ZnSiW_{11}NB.
and ZnSiW₁₁NB/ACF the structures of ZnSiW₁₁ are still retained. Furthermore, no
peaks belonging to ACF are observed. This can be ascribed to the speculation that the
content of ACF might be too small to determine. FTIR spectra of ZnSiW₁₁NB/ACF
composite materials were studied to investigate the interactions between ZnSiW₁₁NB
and ACF (Fig. 4b). For ZnSiW₁₁NB the characteristic bands at 784, 921 and 972 cm⁻¹
can be attributed to stretching of W=O, W-O and Si-O respectively.¹⁹ Compared with
ZnSiW₁₁NB, in ACF/ZnSiW₁₁NB composite materials, the stretching of W=O, W-O
and Si-O shift to a higher wavenumber region. These reveal in ACF/ZnSiW₁₁NB,
there are effective interactions between ACF and ZnSiW₁₁NB, which can be
attributed to hydrogen bond.²⁰

Optical property study

The UV-vis diffuse reflectance spectra (DRS) of ZnSiW₁₁NB and
ZnSiW₁₁NB/ACF composite materials were studied (Fig. S3). Compared with visible
light inactive ZnSiW₁₁NB, ZnSiW₁₁NB/ACF composite materials exhibit strong
absorptions in ultraviolet and visible light region, which suggest ACF is a suitable
option to extend the photoresponse region of ZnSiW₁₁NB. To study the influences of
ZnSiW₁₁NB:ACF value on photoresponse region in detail, band gaps (E₉) of all the
ZnSiW₁₁NB/ACF composite materials were obtained from Tauc equation (Fig. 5a).
If the mass of ACF increased, E₉ became smaller at first. But as the mass increased
continuously, the value of E₉ began growing. In these composite materials,
ZnSiW₁₁NB/ACF(C) possesses the narrowest band gap, which illustrates
ZnSiW₁₁NB:ACF = 100:1 is an optical condition to fabricate composite material with
more excellent photoresponse under irradiation of visible light.

Electrochemical analysis

The interface charge separation efficiency can be investigated by photocurrent
spectra, incident photon-to-electron conversion efficiency (IPCE) and electrochemical impedance spectroscopy (EIS). Photocurrent responses of ZnSiW_{11}NB/ITO and ZnSiW_{11}NB/ACF/ITO electrodes were studied under visible light irradiation (Fig. 5b). Results indicated the loading of ZnSiW_{11} on surface of ACF can enhance its photocurrent effectively. Furthermore, with the increasing of ZnSiW_{11}:ACF value, photocurrent of ZnSiW_{11}NB/ACF/ITO electrode increased at first and then decreased. In all these electrodes, ZnSiW_{11}NB/ACF(C)/ITO electrode exhibited the largest photocurrent. As photocurrent spectra, after the loading of ZnSiW_{11}NB on surface of ACF, IPCE also enhanced (Fig. 5c). The maximum IPCE value was observed on the ZnSiW_{11}NB/ACF(C)/ITO (26.78%), which was about 5.80 fold larger than that of ZnSiW_{11}NB/ITO electrode (4.62%). This further illustrates that a more effective charge separation and transfer process has occurred after ZnSiW_{11}NB is loaded on surface of ACF. To study the charge separation and transfer process in detail, electrochemical impedance spectra (EIS) was employed (Fig. 5d). In EIS, the radius of the arc on Nyquist plot reflects the reaction rate occurring at the surface of electrode.\(^{21}\) The arc radius of all ZnSiW_{11}NB/ACF/ITO electrodes were smaller than ZnSiW_{11}NB/ITO electrode, which illustrates a more effective separation of photogenerated electron-hole pair as well as a faster interfacial charge transfer have occurred. In all these electrodes, ZnSiW_{11}NB/ACF(C)/ITO electrode exhibited smallest arc radius. This illustrated it possesses the best photogenerated electron-hole pair separation efficiency. In summary, electrochemical tests are well matched with the optical property studies. All these results indicates the loading of ZnSiW_{11}NB on ACF leads to reduction in the recombination rate of photogenerated electron-hole pair and ZnSiW_{11}NB:ACF = 100:1 is an ideal condition to obtain composite material which possesses better electron-hole pair separation efficiency.
Photocatalytic property study

The photocatalytic activities of ZnSiW_{11}NB and ZnSiW_{11}NB/ACF composite materials were evaluated through the degradation of RhB in aqueous solution (Table 1). As an ultraviolet light active photocatalyst, ZnSiW_{11}NB exhibited no effect on RhB in visible light region (Fig. S4a and 4b). On the contrary, its composite materials with ACF showed more excellent photocatalytic activities in visible light region. The photocatalytic efficiency of ZnSiW_{11}NB/ACF is very close to a well-known POM-based visible light active photocatalyst, CuPW.⁹a We also observed as the mass of ACF increased, photocatalytic efficiency of ZnSiW_{11}NB/ACF composite materials did not raise monotonously (Fig. 6a and S5). At the beginning, photocatalytic performance enhanced with the increasing of ACF, but as ZnSiW_{11}NB:ACF < 100:1, photocatalytic efficiency began falling down. This can be attributed to the excess of ACF may encourage the recombination of photogenerated hole and electron, which may decrease photocatalytic efficiency of the composite materials. So, in ZnSiW_{11}NB/ACF(C), the photogenerated electron-hole pair can be separated more effectively and ZnSiW_{11}NB:ACF = 100:1 is an optical condition to obtain composite material with excellent photocatalytic activity. For ACF material based photocatalysts, the enhancement of photocatalytic activity originates from the synergy effect between ACF and the other component. As for ZnSiW_{11}NB/ACF, to illustrate this point clearly, ACF and ZnSiW_{11}NB/ACFM (the mechanically blended products of ZnSiW_{11}NB and ACF) were used as references to evaluate the photocatalytic efficiency (Fig. 6b, S6 and S7). It is notable their photocatalytic properties are weaker than ZnSiW_{11}NB/ACF, which implies the synergy effect between ZnSiW_{11}NB and ACF that play a crucial role in improving the photocatalytic activity of the ZnSiW_{11}NB.
In photocatalytic degradation reaction, the activity and stability of recycled catalyst are very important factors to determine the performance of a photocatalyst. Here, photocatalytic properties of ZnSiW₁₁NB/ACF composite materials were re-examined for five times and recycled photocatalysts still showed excellent catalytic properties (Fig. 6c). Furthermore, the recycled samples also exhibited similar PXRD patterns with original composite materials, which indicated their structures were not destroyed during the photocatalysis decomposition process of RhB (Fig. 6d).

Mechanism study

Mott-Schotty measurement had been applied with impedance technique to study the intrinsic electronic property of ZnSiW₁₁NB/ACF composite material. We studied the capacitance measurement in the Mott-Schotty-type plot for ZnSiW₁₁NB (Fig. 7a). The positive slope of the obtained C^-2/E plot illustrates ZnSiW₁₁NB belongs to typical n-type semiconductors. The conductive band potential can also be obtained from this method, which is -0.18 V (vs SCE). Combined with band gap (E₉) estimated from DRS, the valence band (VB) of ZnSiW₁₁NB is calculated to be 3.00V (vs SCE) according to the formula: EᵥB = EᵥB + E₉.

Based on the positions of CB, VB and E₉ of ZnSiW₁₁NB and ACF, we speculate the mechanism of ZnSiW₁₁NB/ACF as follows (Fig. 7b). Under irradiation of visible light, ACF is excited. Electron is produces on VB orbital of ACF and transferred to its CB orbital. After that, electron moves to the CB of ZnSiW₁₁NB, at the same time, a hole is born on VB of ZnSiW₁₁NB and inject to VB of ACF. This process leads to the charge separation and stabilization, which hinders the recombination of electron and hole. Based on aforementioned points, in ZnSiW₁₁NB/ACF, the role of ACF can be described as photosensitizer and good transportation material of electron.

Conclusion
ZnSiW$_{11}$NB/ACF composite materials are successfully prepared through the loading of ZnSiW$_{11}$NB on surface of activated carbon fiber. We also discuss the influence of ZnSiW$_{11}$NB:ACF value on photocatalytic efficiency of the composite material and an optical ZnSiW$_{11}$NB:ACF value has been obtained. As expected, compared with ZnSiW$_{11}$NB, ACF and ZnSiW$_{11}$NB/ACFM, ZnSiW$_{11}$NB/ACF composite materials exhibit more excellent photocatalytic activity. This enhancement can be attributed to the synergy effect between ZnSiW$_{11}$ and ACF. After comparison of ZnSiW$_{11}$NB/ACF and other carbon based composite photocatalytic, such as graphene oxide (GO) or carbon nanotube (CNT) modified TiO$_2$, we find their degradation efficiency are very close. It can be concluded the preparation of ZnSiW$_{11}$NB/ACF enable us to establish a feasible approach to improve photocatalytic property of POM. Furthermore, ZnSiW$_{11}$NB/ACF composite material is a new kind of efficient photocatalyst for decontaminating colored wastewater for reuse in industries production.

Acknowledgements

This work was supported by National Natural Science Foundation of China (21303010 and 21103017); Research Foundation for the Doctoral Program of Higher Education of China (20120042110024); Fundamental Research Funds for the Central Universities (N120405005).

Electronic supplementary information (ESI) available: TGA of ZnSiW$_{11}$NB; XPS spectrum of ACF (C1s peak of ACF); DRS of ZnSiW$_{11}$NB and ZnSiW$_{11}$NB/ACF composite materials; Absorption spectra of RhB degraded with ZnSiW$_{11}$NB under irradiation of ultraviolet and visible light; Absorption spectra of RhB degraded with ZnSiW$_{11}$NB/ACF, ACF and ZnSiW$_{11}$NB/ACFM under visible light irradiation.
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Table 1 Degradation efficiency of RhB with different photocatalysts

<table>
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<th>Photocatalyst</th>
<th>Condition</th>
<th>T (hours)</th>
<th>η (%)</th>
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<tr>
<td>ZnSiW_{11}NB</td>
<td>ultraviolet light irradiation</td>
<td>6</td>
<td>55.53</td>
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<tr>
<td>ZnSiW_{11}NB</td>
<td>visible light irradiation</td>
<td>6</td>
<td>2.51</td>
</tr>
<tr>
<td>ZnSiW_{11}NB/ACF (A)</td>
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<td>6</td>
<td>81.30</td>
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<td>ZnSiW_{11}NB/ACF (B)</td>
<td>visible light irradiation</td>
<td>4</td>
<td>83.37</td>
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<tr>
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<td>89.36</td>
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<td>ZnSiW_{11}NB/ACF (D)</td>
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<td>ACF</td>
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<tr>
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<tr>
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<td>ZnSiW_{11}NB/ACF (D)M</td>
<td>visible light irradiation</td>
<td>6</td>
<td>53.39</td>
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Figure Captions

Figure 1 (a) The fundamental unit of ZnSiW\textsubscript{11}; (b) SEM of ZnSiW\textsubscript{11}NB in high magnification.

Figure 2 (a) SEM of CF; (b) SEM of ACF; (c) XPS spectrum of CF; (d) XPS spectrum of ACF; (e) The shape of a water droplet on the surface of CF; (f) The shape of a water droplet on the surface of ACF.

Figure 3 (a) SEM of ZnSiW\textsubscript{11}NB/ACF(A); (b) SEM of ZnSiW\textsubscript{11}NB/ACF(B); (c) SEM of ZnSiW\textsubscript{11}NB/ACF(C); (d) SEM of ZnSiW\textsubscript{11}NB/ACF(D); (e) SEM of ZnSiW\textsubscript{11}NB/ACF(A) in high magnification image; (f) SEM of ZnSiW\textsubscript{11}NB/ACF(B) in high magnification image; (g) SEM of ZnSiW\textsubscript{11}NB/ACF(C) in high magnification image; (h) SEM of ZnSiW\textsubscript{11}NB/ACF(D) in high magnification image.

Figure 4 (a) PXRD patterns of ZnSiW\textsubscript{11}NB, ACF and ZnSiW\textsubscript{11}NB/ACF; (b) FTIR of ZnSiW\textsubscript{11}NB/ACF.

Figure 5 (a) Tauc plots ZnSiW\textsubscript{11}NB/ACF; (b) Photocurrent spectra of ZnSiW\textsubscript{11}NB and ZnSiW\textsubscript{11}NB/ACF under visible light irradiation; (c) IPCE of ZnSiW\textsubscript{11}NB and ZnSiW\textsubscript{11}NB/ACF; (d) EIS of ZnSiW\textsubscript{11}NB and ZnSiW\textsubscript{11}NB/ACF.

Figure 6 (a) Degradation rate for RhB by ZnSiW\textsubscript{11}NB and ZnSiW\textsubscript{11}NB/ACF under visible light; (b) Degradation rate for RhB by ZnSiW\textsubscript{11}NB/ACFM under visible light; (c) Cycling runs of the degradation of RhB in the presence of ZnSiW\textsubscript{11}NB/ACF; (d) PXRD of recycled ZnSiW\textsubscript{11}NB/ACF.

Figure 7 (a) Mott-Schottky plot of ZnSiW\textsubscript{11}NB. (b) Diagram of the photocatalytic mechanism for ZnSiW\textsubscript{11}NB/ACF under visible light irradiation.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7