A P25/(NH₄)ₓWO₃ hybrid photocatalyst with broad spectrum photocatalytic properties under UV, visible, and near-infrared irradiation

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In this study, a series of hybrid nanostructured photocatalysts P25/(NH₄)ₓWO₃ nanocomposites with the average crystallite size of P25 and (NH₄)ₓWO₃ of the sample was calculated to be about 30 nm and 130 nm, were successfully synthesized via a simple one-step hydrothermal method. The as-obtained samples was characterized by transmission electron microscopy (TEM), which implies that the P25/(NH₄)ₓWO₃ nanocomposites are fabricated with favourable nanosized interfacial. The XPS results confirmed that the obtained sample consists of mixed chemical valences of W⁵⁺ and W⁶⁺, the low-valence W⁵⁺ sites could be the origin of NIR absorption. As revealed by optical absorption results, P25/(NH₄)ₓWO₃ nanocomposites possess high optical absorption in the whole solar spectrum of 200–2500 nm. Benefiting from this unique photo-absorption property and the synergistic effect of P25 and (NH₄)ₓWO₃ broad spectrum response photocatalytic activities covering UV, visible and near infrared regions on degradation of Rhodamine B have been realized by P25/(NH₄)ₓWO₃ nanocomposites. Meanwhile, the stability of photocatalysts was examined by the XRD and XPS of the photocatalysts after the reaction. The results show that P25/(NH₄)ₓWO₃ photocatalysts has a brilliant application prospect in the energy utilization to solve deteriorating environmental issues.

Today, energy crisis and environment pollution are the grim challenge of human existence. As a free, inexhaustible and sustainable energy source, solar energy has long been considered one of the most promising renewable energy sources in the world, in order to solve those problems¹⁴–⁶. In view of solar energy utilization, the search for semiconductor photocatalysts that can harvest the wide spectrum of solar light, from ultraviolet (UV) to near-infrared (NIR) wavelength, and achieve efficient solar energy conversion remains one of the most challenging missions⁷–⁸. Titanium dioxide (TiO₂), a key semiconductor with tunable crystal structure (rutile, anatase, brookite), and effective photocatalytic activity⁹–¹⁰. The band gaps of these three TiO₂ phases are 3.0, 3.2, and 3.25 eV, respectively. Among its useful attributes, TiO₂ is: (i) insoluble in aqueous media, (ii) chemically and biologically inert, (iii) photostable, (iv) nontoxic, (v) inexpensive, and (vi) readily available¹¹–¹⁵. Commercial TiO₂ P25 is anatase/rutile nanocomposite (phase composition in ratio of 80/20 for anatase/rutile), as a result of its superior activity in the wide variety of applications¹⁶–¹⁹. However, due to a wide band gap, TiO₂ responds primarily to UV light which only accounts for less than 5% of total solar radiation. Although the visible (Vis) light and NIR resources are abundant, under Vis light and NIR irradiation, the catalytic activity of P25 is limited by low electron transfer and high electron/hole pair recombination rates²⁰. And removal of organic pollutants from wastewater through photocatalytic degradation process also suffers drawbacks of insufficient utilization on solar energy. As far as light-harvesting is concerned, most of efforts have been focused on extending the photo-responsive region of photocatalysts to match the utmost of solar energy. The landmark cases, such as

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N-doped TiO₂ photocatalysts, plasmonic photocatalysts, morphology modification, composite photocatalysts, TiO₂ films, were developed to make the photocatalysts to be effective under Vis light. What is a pity, despite all these advances, the NIR light remains seldom be utilized. To the best of our knowledge, only several kinds of nanomaterials, including up-conversion photocatalysts, Bi₂WO₆/TiO₂, Cu₂(OH)PO₄, CsₓWO₃ and MₓWO₃/ZnO have tentatively been employed as NIR-driven photocatalysts until now, and the aim to discover a full-spectrum-responsive photocatalyst is far from being realized. We take the up-conversion composited photocatalysts for example, it can convert NIR light to Vis light or UV light and then transfer energy to UV or Vis light active photocatalysts to induce a photocatalytic effect. However, the quantum efficiency of composited up-conversion photocatalysts is much low and the excitation source is limited to 980 nm. Moreover, most promising photocatalysts only possess UV, UV-Vis, Vis-NIR, or NIR photocatalytic activity, separately. They are not compatible to utilize full-spectrum of the solar light. Therefore, it is very significant to realized full-spectrum-responsive photocatalytic activities.

For realizing the aimed full-spectrum-responsive photocatalytic properties, a broadband absorptive ability is a prerequisite for the photocatalysts. Previous research confirmed that the hexagonal tungsten bronze type compound MₓWO₃, which is WO₃ doped with monovalent ions such as K⁺, Na⁺, NH₄⁺ and others and consisting of mixed chemical valence tungsten ions (W⁶⁺ and W⁵⁺) exhibited excellent NIR absorption properties when dispersed as nanosized particles or in one-dimensional form. As a novel near-infrared (NIR) shielding material, the tungsten bronze (MₓWO₃) have been widespread applied in smart windows, gas sensors, electrochromic materials, photocatalysts, military weapon, cancer therapy and air pollution decontamination. Early on, we have exploited the synthesis of homogeneous tungsten bronze type nanocrystals of (NH₄)ₓWO₃, which consists of mixed chemical valence tungsten ions of W⁶⁺ and W⁵⁺. More importantly, the tungsten bronze type nanocrystals of (NH₄)ₓWO₃ exhibit strong optical absorption in a wide range of 200~2500 nm, covering the waveband of UV, Vis light and the whole NIR region, the low-valance W⁵⁺ sites are the origin of NIR absorption. However, only have been studied on optical properties of the thin film consisted of (NH₄)ₓWO₃ nanoparticles, and the photocatalytic properties of (NH₄)ₓWO₃ have not been studied. As expected, in this work, we combined with efficient light absorption of ammonium tungsten bronze and P25 high catalytic activity for their nanocomposites material to achieve this goal, and we present the feasibility of realizing the advanced full-spectrum-responsive photocatalytic activity by P25/(NH₄)ₓWO₃ nanocomposites, which has never been studied as photocatalysts before this work.

Results and Discussion

As shown in Fig. 1, XRD analysis has been employed for analyzing the crystalline phase of samples. The reflection in Fig. 1a matches best with the single anatase TiO₂ (JCPDS 21-1272) and rutile TiO₂ (JCPDS No. 21-1276) phases. As to HT-P25, its phase structure did not change after hydrothermal method (Fig. 1b). While the main peaks at 2θ values of 13.83°, 23.701° and 27.897° can be indexed respectively to (100), (002) and (200) crystal planes, which are readily indexed to the pure ammonium tungsten bronze ((NH₄)ₓWO₃; JCPDS No. 42-0452), as displayed in Fig. 1c. Furthermore, with the increasing content of (NH₄)ₓWO₃, the intensities of the (NH₄)ₓWO₃ peaks are increased obviously (Fig. 1d–f), revealing that P/NWO nanocomposites are obtained successfully during the hydrothermal process. Meanwhile, peaks related to other phases are not observed in the synthesized samples, indicating that the P25 have not reacted with the (NH₄)ₓWO₃.

In addition, the intensity of these XRD peaks was relative weak and half-peak breadth was wide, being consistent with the general features of the nanoparticles. Enlighten by this, the average crystallite size (D) of P25 and (NH₄)ₓWO₃ of the sample was calculated to be about 30 nm and 130 nm, using the well-known Scherrer equation:

\[ D = \frac{K\lambda}{\beta \cos(\theta)} \]
where $\lambda$ is the wavelength of the X-ray radiation ($\lambda = 0.15418$ nm), $K$ is the Scherrer constant ($K = 0.89$), $\theta$ is the Bragg angle of the X-ray diffraction peak, and $\beta$ is the line broadening at half the maximum intensity (FWHM, in radians) of the (101) plane of P25 and the (200) plane of (NH$_4$)$_x$WO$_3$ of sample.

The chemical composition and valence state of the P/NWO nanocomposites were examined by X-ray photoelectron spectroscopy (XPS). The fully scanned spectra clearly reveal that elements of Ti, N, W, O and C existed in the sample (Fig. 2a). The presence of carbon element in the final product could be related to the residual chemically or physically adsorbed organics originating from the solvent molecules. For tungsten, a complex energy distribution of W4f photoelectrons was obtained as shown in Fig. 2b. The obtained XPS curve could be fitted into two spin-orbit doublets, corresponding to two different oxidation states of W atoms. The main peaks, having a W 4f$_{5/2}$ at 37.5 eV and a W 4f$_{7/2}$ at 35.4 eV, could be attributed to the W atoms being in a $+6$ oxidation state. The second doublet, with a lower binding energy at 34.4 eV and 36.5 eV, could be ascribed to the emission of W 4f$_{5/2}$ and W 4f$_{7/2}$ core levels from the W atoms in an oxidation state of $+5$. These results on the core level of tungsten ions in tungsten bronze are in good agreement with reported values.

The morphology of the as-prepared samples was characterized by SEM, which is shown in Fig. 3. As shown in Fig. 3a, the (NH$_4$)$_x$WO$_3$ exhibit smooth surface, numerous nanorods with the diameter of the nanorods ranged from 100 to 200 nm. Figure 3b shows the SEM image of the P/4NWO nanocomposites, and it could be clearly seen that TiO$_2$ particles are attached to the surface of (NH$_4$)$_x$WO$_3$ nanorods, indicating the intimate contact between P25 and (NH$_4$)$_x$WO$_3$.

To further obtain the microscopic morphology and structure information, the TEM and HRTEM analysis of as-synthesized P/4NWO nanocomposites have been performed. As shown in Fig. 4, the TEM images of P/4NWO
nanocomposites (Fig. 4a) show the specific rod-like morphology with some nanoparticles attached, which is in accordance with SEM results (Fig. 3b). In addition, the elemental composition of P/4NWO has been investigated by EDX spectrum (insert Fig. 4f) and elemental mapping analysis (Fig. 4d–e). Clearly, the homogeneous distribution of Ti, O, and W elements suggests the co-existence of (NH₄)ₓWO₃ and TiO₂. Moreover, to further confirm the co-presence of the TiO₂ and (NH₄)ₓWO₃ in P/NWO nanocomposites, the HRTEM image of the magnified view is given in Fig. 4f. The distance of 0.639 nm and 0.352 nm between the adjacent lattice fringes can be assigned to the (100) plane of hexagonal (NH₄)ₓWO₃ and the (101) plane of anatase TiO₂ nanocrystals, respectively. FFT patterns of the interface between TiO₂ and (NH₄)ₓWO₃ were also appended in Fig. 4e and f, revealing that TiO₂ and (NH₄)ₓWO₃ are of tetragonal and hexagonal crystal structures, respectively. Obviously, the P/4NWO nanocomposites are formed with favourable nanosized interfacial contact so as to exhibit excellent photogenerated carriers transfer and separation properties of photocatalytic degradation.

Figure 4. (a) TEM images of the obtained P/4NWO. (b) The STEM image of the element distribution map. (c–e) The representative element mapping images of nanocomposite P/4NWO with the same scale bar of 200 nm. (f) The HRTEM images of as-synthesized P/4NWO nanocomposite (the inset shows EDX spectrum of P/4NWO nanocomposite) and (f,g) corresponding FFT patterns.
The higher BET specific surface area is beneficial to enhancing the photocatalytic activity of the composites study, which were measured and are listed in Table 1. BET specific surface area of HT-P25 (50.7 m²/g) did not reduce via the hydrothermal treatment. The (NH₄)ₓWO₃ nanorods exhibited a relatively lower BET specific surface area (11.4 m²/g) than P25 (51.2 m²/g). The surface area of the P/NWO nanocomposites increased to three times more than (NH₄)ₓWO₃ nanorods when (NH₄)ₓWO₃ nanorods was combined with P25. The higher adsorption capacity could lead to the easier and faster photocatalytic degradation process because the photocatalytic reaction is a surface-based process.

The optical property is another critical factor on determining whether certain material is a potential candidate as photocatalyst. The UV-Vis-NIR absorption spectra of P25 and as-obtained powder were measured and shown in Fig. 5. It clearly reveals that TiO₂ shows a strong absorption in the UV region, and the Eg of TiO₂ is approximately 3.05 eV, which corresponds to the absorption of wavelength <400 nm. As for (NH₄)ₓWO₃ and P/NWO particles, the spectrum shows a broad and strong light absorption in the whole solar region of 200–2500 nm, especially for the NIR light of 800–2500 nm. This phenomenon suggests that the P/NWO nanocomposites have a potential photocatalytic activity under irradiation of UV, Vis and NIR light, which also is highly necessary for investigating the aimed full-spectrum-response photocatalytic activity.

To prove the photocatalytic activity of the P/NWO nanocomposites, the decomposition of RhB in water under UV, visible light, near-infrared light and simulated solar light irradiation as a function of irradiation time were investigated (Fig. 6a–d). For comparison, decomposition abilities of P25, the processed P25 (HT-P25), (NH₄)ₓWO₃ nanorods and RhB with absence of photocatalysts were measured under the same experimental conditions.

As shown in Fig. 6, (NH₄)ₓWO₃ nanorods have very limited UV photocatalytic activities (Fig. 6a). When combined P25 with (NH₄)ₓWO₃ nanorods, the UV photocatalytic performance of the P25/NWO nanocomposites is dramatically improved, especially when the value of y is 40%. The corresponding decomposition rate increases to nearly 100% after 20 min UV irradiation (Fig. 6a), which is much higher than that of P25 (83%), HT-P25 (47%), and (NH₄)ₓWO₃ nanorods (8%). Similar to the results in the previous works, P25 exhibits poor visible photocatalytic activities, and P/NWO nanocomposites possess good visible photocatalytic degradation property. The corresponding RhB degradation degree under 140 min visible light irradiation for P25, HT-P25 and (NH₄)ₓWO₃ nanorods is 17.5%, 13.3% and 37.8% respectively (Fig. 6b). Surprisingly, the decomposition rate of the P25/4NWO nanocomposites increases to 81% after visible light irradiation for 140 min.

Here, (NH₄)ₓWO₃ nanorods exhibited good near-infrared catalytic activity. The RhB degradation degree for (NH₄)ₓWO₃ nanorods under 12 h near-infrared light irradiation is 68%. It is significant that P/NWO nanocomposites possess enhanced near-infrared photocatalytic activities compared with P25 and HT-P25, and the RhB degradation degree for P25 and HT-P25 under 12 h near-infrared light irradiation is 60% (P/5NWO) (Fig. 6c). In contrast, P25 and HT-P25 nearly have no near-infrared degradation ability to RhB. The corresponding RhB degradation rate for P25 and the processed P25 is only 2.1% and 1.8% in the same conditions. We also checked

| Sample      | S_BET (m²/g) |
|-------------|--------------|
| P25         | 51.2         |
| HT-P25      | 50.7         |
| (NH₄)ₓWO₃  | 11.4         |
| P/3NWO      | 47.6         |
| P/4NWO      | 44.1         |
| P/5NWO      | 40.9         |

Table 1. Specific surface area (S_BET) of the prepared samples and P25 sample.
the photocatalytic property of the above photocatalysts under conditions similar to natural solar light irradiation. The natural solar light was generated by a solar-simulator (300 W xenon arc lamp with AM 1.5 G filter, 100 mW cm\(^{-2}\), microsolar300), the photocatalytic degradation efficiency under solar-light follows the order P/4NWO > P/5NWO > P/3NWO > P25 > HT-P25 (Fig. 6d). Moreover, with regard to UV light photodegradation (Fig. 6a), no photolysis of RhB is observed after 30 min UV light irradiation with the absence of photocatalysts, and similar phenomena have been observed in the other light photodegradation (Fig. 6b–d). These results further confirm that the photocatalytic properties of above samples are attributed to the photocatalysis reaction, instead of the self-degradation of RhB solution. So far, the full-spectrum-responsive photocatalytic properties of P/NWO nanocomposites were demonstrated. To the best of our knowledge this phenomenon has never been reported.

Then, to investigate the stability of (NH\(_4\))\(_x\)WO\(_3\) in the solution under tested conditions the concentration of tungsten element of the filtrated photocatalytic reaction solution was measured. As shown in Fig. S1, ICP analysis revealed that in the presence of the W elements is 0.09, 1.22, 3.05 and 1.02 mg/L in after UV, visible, near-infrared and solar light photocatalytic reaction, respectively. The results indicate the loss of (NH\(_4\))\(_x\)WO\(_3\) is very few in photocatalytic reaction.

In addition, the XRD and XPS of (NH\(_4\))\(_x\)WO\(_3\) after the photocatalytic reaction were examined. As shown in Fig. 7a, it could be seen that the XRD patterns of P/4NWO samples before and after the reaction were essentially identical except for decreasing of the intensities of the diffraction peaks after the photocatalytic reactions. Fig. 7b–d shows the XPS spectra of W 4f profiles of the P/4NWO after the photocatalytic reactions. The results shown that there are still two spin-orbit doublets in this spectrum, which can be indexed to W\(^{5+}\), while the peaks at 35.4 eV and 37.5 eV are assigned to W\(^{6+}\), which still reaches a good agreement with the reported results\(^{51}\). These results further indicate the (NH\(_4\))\(_x\)WO\(_3\) act as a stable photocatalyst under UV, visible, near infrared and even solar light illumination.

Recently, photocatalytic degradation mechanism of dye under the UV or Vis light irradiation on semiconductors has been well established as an oxidative process in which three consecutive steps are involved. Firstly, light with higher energy than bandgap of semiconductor is absorbed and afterwards induces a transition of electrons from the valence band to the conduction band, leaving an equal number of holes in the valence band. Secondly, the excited electrons and holes migrate to the surface. Thirdly, the superficial photogenerated electron/hole pairs produce several reactive intermediate species for destruction of dye molecules. Generally, the photogenerated electrons are scavenged by dissolved oxygen, and then superoxide (O\(_2\)\(^{-}\)) would be obtained first, followed by

![Figure 6. Photocatalytic degradation of RhB in the presence of P25, HT-P25, (NH\(_4\))\(_x\)WO\(_3\) nanorods and P25/(NH\(_4\))\(_x\)WO\(_3\) nanocomposites and pure RhB under (a) UV (b) Vis (c) NIR (d) solar light.](image-url)
formation of other reactive oxygen species including hydroperoxyl radical (HOO•), H₂O₂, or hydroxy radical (OH•)⁵³. All these reactive oxygen species possess sufficient energy for oxidation of pollutants. Based on the above discussion, the enhanced UV and Vis photocatalytic activities of P/NWO nanocomposite are contributed to the improvement capacity of light absorption and efficient separation of photo-induced carriers. To clarify the possible mechanism of the enhancement of photocatalytic activity, the positions of conduction band (CB) and valence band (VB) of P₂₅ and (NH₄)ₓWO₃ are determined by flat-band potentials (Vfb) and UV-Vis-NIR absorption spectra, as displayed in Fig. 8. The Vfb can be quantified by the Mott–Schottky equation:

\[
\frac{1}{C^2} = 2 \left( V - V_{fb} - \frac{kT}{e} \right) \frac{\varepsilon\varepsilon_0eN}{kT}
\]

where C is the total measured capacitance, V is the electrode applied potential, Vfb is the flat band potential, ε₀ is the vacuum permittivity, ε is the dielectric constant of the material, e is the electron charge, k is the Boltzmann constant, T is the temperature, and N is the acceptor concentration. According to the Mott–Schottky equation, a linear relationship of C⁻² vs. V can be observed (Fig. 8a and b) and the intercepts of the straight lines with the potential axis indicate the Vfb values of P₂₅ and (NH₄)ₓWO₃ are -0.24 V vs NHE and -0.55 V vs NHE⁵⁴, thus the CB of P₂₅ and (NH₄)ₓWO₃ are -0.44 V vs NHE and -0.75 V vs NHE, respectively⁵⁵. Furthermore, combining with the bandgap energy of P₂₅ (~3.05 eV) and (NH₄)ₓWO₃ (~2.67 eV) as displayed in Fig. S2a and b, the energy level diagrams of P/NWO heterojunction with the presence of TiO₂, (NH₄)ₓWO₃ are obtained and displayed in Fig. 9. As shown in Fig. 9 (case 1), under UV light irradiation, both P₂₅ and (NH₄)ₓWO₃ could be excited to generate electrons and holes. Electrons photoexcited from (NH₄)ₓWO₃ transfer to the CB of TiO₂, and holes photoexcited from P₂₅ transfer from the VB of P₂₅ to that of (NH₄)ₓWO₃. This transfer process is thermodynamically advantageous because both the CB and VB of (NH₄)ₓWO₃ are more negative than those of P₂₅. Under the circumstances, more effective transfer and separation of the photoinduced carriers between P₂₅ and (NH₄)ₓWO₃ interfaces, resulting in markedly improved UV photocatalytic activity. When the P/NWO nanocomposite is irradiated by Vis light, only (NH₄)ₓWO₃ could act as a sensitizer benefits by its narrow band gap. As displayed in Fig. 9 (case 2), under Vis light illumination, electrons in the VB of (NH₄)ₓWO₃ could be excited to a higher CB,
and then transfer to the CB of P25. Meanwhile, the photogenerated holes accumulated in the VB of (NH₄)ₓWO₃ will accelerate the decomposition of organic pollutants into non-toxic substances. In such a way, the photoinduced electrons and holes could be separated effectively, so as to settle the high recombination probability of the photo-induced carriers in (NH₄)ₓWO₃ and greatly enhance photocatalytic activity under Vis light irradiation.

As for NIR light, it could be clearly seen from Fig. 9 (case 3) that the NIR-driven photocatalytic activity of P/NWO nanocomposites and (NH₄)ₓWO₃ nanorods are only attributed to the low-valence W⁵⁺ sites of (NH₄)ₓWO₃ nanorods. When P/NWO nanocomposites were irradiated by the NIR, W⁵⁺ sites as photosensitive sites can induce one electron out from low-valence W⁵⁺ site and then this W⁵⁺ will convert to W⁶⁺ (Eq. (3)). In our previous work, we have confirmed the probability that the NIR generated electron from W⁵⁺ site can also transfer to third party in the photoreaction system. Subsequently, photogenerated electrons could be trapped by absorbed O₂ to form O₂⁻, followed by the generation of •OH, •OOH and ^O₂ (Equations (4) and (5)). On the other side, the W⁶⁺ sites can react with OH⁻ and return to W⁵⁺, realizing a full photocatalytic circle. Finally, the reactive species, including •OH, •OOH and ^O₂ all possess sufficient energy for oxidation of dyes (Equation (7)).

$$\text{W}^{5+} + h\nu (\text{NIR}) \rightarrow \text{W}^{6+} + e^- \quad (3)$$

$$e^- + O_2 \rightarrow \cdot O_2^- + H^+ \rightarrow \cdot OOH \rightarrow \cdot OH \quad (4)$$

$$\cdot O_2^- + \cdot OH \rightarrow O_2 + OH^- \quad (5)$$

$$\text{W}^{6+} + OH^- \rightarrow \text{W}^{5+} + \cdot OH \quad (6)$$

$$\cdot O_2^- + \cdot OH, ^O_2 + \text{RhB} \rightarrow \text{Degradation of RhB} \quad (7)$$

In conclusion, as exactly in accordance with the essence of Eq. (3), when the NIR light irradiates on (NH₄)ₓWO₃ nanorods, induces one electron to escape from its W⁵⁺ site and then oxidizes the original W⁶⁺ into
In summary, full-spectrum-responsive photocatalytic activities have been realized by a stable P/NWO hybrid photocatalysts, which were successfully synthesized via a simple one-step hydrothermal method, and P/NWO nanocomposites are an excellent optical absorber that can efficiently harvest the light in a wide range of 200–2500 nm. The high UV and visible light photodegradation activity of P/NWO nanocomposites can attribute to the synergy of P25 and (NH₄)ₓWO₃ nanorods, such as large extended absorption of solar light, high electron–hole separation efficiency and stronger adsorptivity of pollutants. The low-valance W⁵⁺ sites are the origin of NIR absorption, also upon which the free electrons could be generated under the NIR irradiation and subsequently formed reactive oxygen species for photodegradation of RhB molecules. This work realizes utmost match of solar energy for the aimed photocatalytic reaction and this result is of significance in the utilization of all solar band energy for efficiently removal of organic dyes, whether UV, visible or near infrared light.

**Methods**

**Preparation of P25/(NH₄)ₓWO₃ nanocomposites.** All reagents were of analytical grade and used without further retreatment. First of all, different amounts of the ammonium paratungstate hydrate were dissolved into 40 ml ethylene glycol (EG) at about 190 °C. After cooling down this EG solution to the room temperature, 0.4 g of P25 were added into mixed solution, stirring and ultrasonic dispersing for a certain amount of time. Next, 20 ml acetic acid was added into the solution and stirred 30 min. Then, the obtained solution was transferred into a Teflon-lined autoclave of 100 ml internal volume, followed by hydrothermal reaction in an electric oven at 200 °C for 40 h. After the reaction, the powder was centrifuged, washed 4 times with deionized water and ethanol, respectively, and finally dried at 60 °C. As-obtained powder are P25/(NH₄)ₓWO₃(y%), with y = 30, 40, 50, and it represents the weight of the (NH₄)ₓWO₃ in the nanocomposites. These samples are labelled as P(P25)/3NWO[(NH₄)ₓWO₃], P/4NWO, and P/5NWO, respectively.

As a comparison, control samples were prepared in the absence of the ammonium paratungstate (HT-P25) or P25 ((NH₄)ₓWO₃) according to the above procedure.

**Characterization.** The phase purity of samples was analyzed by X-ray powder diffraction (XRD) using a Bruker D2 PHASER X-ray diffractometer with graphite monochromator using Cu Kα radiation (λ = 1.54184 Å) at room temperature. X-ray photoelectron spectroscopy (XPS, PHI-5702, Physical Electronics) was performed using a monochromated Al Ka irradiation. The chamber pressure was ~3 × 10⁻⁸ Torr under testing conditions. The morphologies of different samples were observed by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F30, operated at 300 kV). The XPS data was obtained by employing an Al Kα source (1486.6 eV) in a physical electron spectrometer, which was equipped with a hemispherical analyzer. The chamber pressure was 2 × 10⁻⁸ Torr under testing conditions.

**Evaluation of photocatalytic activity.** The photocatalytic activity of the sample was evaluated by measuring the degradation ratio of Rhodamine B (RhB). The initial concentration of RhB solution was 20 mg/L, and the amount of photocatalysts was 0.05 g and 0.10 g per 50 mL of RhB solution, respectively. After the sample suspension was stirred for 30 min, the solution was collected and centrifuged. The absorbance of the sample solution was measured at 554 nm using a spectrophotometer (Perkin Elmer Lambda 950). The photodegradation ratio of RhB was calculated from the absorbance measured at 554 nm using a spectrophotometer compared to a blank experiment.

**Photoelectrochemical Measurements.** The flat-band potentials (Vfb) were determined from Mott–Schottky plots by an electrochemical analyzer (CS 310, Wuhan Corrtest Instrument Co. Ltd.) in a standard two-electrode system using the pure P25, and (NH₄)ₓWO₃ (effective area was 1 cm²) as working electrodes, a Pt foil and an Ag/AgCl (saturated KCl) electrode were used as the counter electrode and reference electrode, respectively. The photoanode was suspended into Na₂SO₄ (0.1 mol L⁻¹) aqueous solution. The Mott–Schottky measurements were performed at a fixed frequency of 1000 Hz with 10 mV amplitude, at various applied potentials.

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Author Contributions
L.Y. and B.L. conducted the most of investigation for the samples. L.Y. wrote the main paper. B.L. designed the concept and the experiment method of the research. B.L. and Y.W. supervised the project, had given valuable advices on the proceeding of this work and revised the manuscript. S.Y. and T.S. had provided precious suggestions on the selection of tungsten bronze as NIR shielding materials. H.L. and X.M. revised the manuscript. All authors discussed the results and commented on the manuscript at all stages.

Additional Information
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