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Visible light activity of Bi₂WO₆@TCNQ with core-shell structure in phenol degradation†

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Bi₂WO₆@TCNQ visible light photocatalyst with a core-shell structure was synthesized by adsorption methods. The core-shell structure results in the fast transfer of photogenerated carriers, reduced carrier recombination and photogenerated holes on the HOMO level of TCNQ can be injected into the VB of Bi₂WO₆ under visible light irradiation, resulting in the direct oxidation of organic pollutants. The photocatalytic activity of Bi₂WO₆@TCNQ was gradually enhanced with an increasing proportion of TCNQ. When the mass fraction of TCNQ reaches 0.5%, it exhibits the highest visible light activity. The apparent rate constant *k* of Bi₂WO₆@TCNQ-0.5% is almost 2.2 times as high as that of pure Bi₂WO₆.

1. Introduction

Semiconductor-based photocatalysis is considered to be an effective strategy for alleviating energy shortages and environmental pollution, since it is a facile and environmentally friendly way to take advantage of solar energy.^{1–6}

In recent years, Bi₂WO₆ with the corner-sharing structure of a WO₆ octahedron sandwiched between (Bi₂O₂)₂ layers has attracted considerable attention owing to its high visible-light photocatalytic activity.^{7–10} It has also been shown to possess superior photocatalytic activity for wastewater treatments under visible light irradiation.^{11,12} However, similar to other narrow-bandgap semiconductor photocatalysts, poor quantum yields caused by the rapid recombination of photogenerated electron-hole pairs is still a challenge in enhancing the photocatalytic efficiency of Bi₂WO₆ to meet the requirements for practical application.^{13,14} Therefore, the modification of Bi₂WO₆ has received considerable attention, and various routes, *e.g.* substitution,¹⁵ heterostructure assembly,^{16,17} ions doping,¹⁸ noble-metal deposition¹⁹ and carrier coupling,²⁰ have been developed to improve the photocatalytic performance of pure Bi₂WO₆.

7,7,8,8-Tetracyanoquinodimethane (TCNQ) is a neutral organic molecule, whose atoms are all in the same plane, and all the P electrons of the C and N participate in the formation of P-conjugation.²¹ TCNQ can combine with other semiconductors to form charge transfer compounds.^{22–25} These charge transfer compounds can absorb sunlight in almost the whole spectral

range, which is quite promising for expanding the absorption edge of semiconductors.

Bi₂WO₆@TCNQ as a higher efficient visible light photocatalyst with core-shell structure was synthesized *via* a facile method of adsorption and solution assembly.^{26–30} This simple method could be used as a universal pathway to improve photocatalyst activity and applied in environmental remediation.

2. Experimental section

2.1. Synthesis of photocatalysts

TCNQ was purchased from Beijing Chemical Reagent Corp, PR China. All other reagents used in this research were of analytical grade and used without further purification.

Bi₂WO₆ was prepared according to the method previously described.³¹ 0.005 mmol Bi(NO₃)₃·5H₂O and 0.0025 mmol Na₂WO₄·2H₂O were dispersed in 30 mL deionized water. After stirring for 1 h, the mixed solution was transferred into a 100 mL PTFE-lined stainless steel autoclave and then heated at 180 °C for 24 h. Finally, the products were centrifuged and dried in air for 6 h.

The preparation of Bi₂WO₆@TCNQ photocatalysts was as follows:

1.25 g TCNQ was dissolved in 250 mL tetrahydrofuran (THF) to form a 5 g L^{−1} THF solution of TCNQ. Different volumes of TCNQ solution were measured and diluted to 25 mL with ethanol. 0.3 g Bi₂WO₆ was added into the above solution after which the beaker was sealed with plastic wrap and placed in an ultrasonic bath for 1 h. The mixture was vigorously stirred in the fume hood until the THF completely evaporated and an opaque powder was obtained. Different mass ratios of Bi₂WO₆@TCNQ photocatalysts were prepared in the oven by power evaporation at 100 °C for 12 h. Bi₂WO₆ and Bi₂WO₆@TCNQ electrodes were prepared by the dip coating method: 3 mg of photocatalyst was

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suspended in 1 mL ethanol to make a slurry, the slurry was then dip-coated onto a 2 cm × 4 cm indium–tin oxide glass electrode. The electrodes were then exposed to UV light for 12 h to eliminate ethanol and calcined at 100 °C for 1 h.

2.2. Characterization

The crystallinity of the composites was determined on a Bruker D8 ADVANCE diffractometer under Cu K α radiation. The structure and morphologies were examined by field-emission scanning electron microscopy (SEM, LEO-1530).

High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEM 2010F field-emission gun transmission electron microscope at an accelerating voltage of 200 kV. Fourier transform infrared (FTIR) spectra were obtained using a Bruker V70FTIR spectrometer. UV-vis diffuse reflectance spectroscopy (UV-DRS) was performed on a Hitachi U-3010 UV-vis spectrophotometer with BaSO₄ as the reference. Raman spectra were obtained using a Horiba JY HR800 confocal microscope Raman spectrometer under an Ar-ion laser (514 nm). The photocurrent was measured on an electrochemical system (CHI-660B).

2.3. Photocatalytic evaluation

The photocatalytic degradation of phenol was conducted under visible light (>420 nm). The light source was a 500 W Xe lamp with a 420 nm cutoff filter, produced by Institute for Electric Light Sources, whose average light intensity was 35 mW cm⁻². In the photocatalytic experiments, 25 mg of the composite photocatalyst powder was dispersed in an aqueous solution of phenol (50 mL, 5 ppm). Before light irradiation, the suspensions were stirred in the dark for 1 h to ensure absorption-desorption equilibrium. At intervals of 1 h, aliquots of 2 mL were withdrawn and centrifuged. The concentration of phenol was analyzed by high-performance liquid chromatography (Shimadzu LC-20AT) with UV detection (270 nm). A Venusil XBP-C18 (Agela Technologies Inc.) column was used, and the mobile phase consisted of methanol and pure water (55 : 45 for phenol, v/v) at a flow rate of 1 mL min⁻¹.

2.4. Electrochemical measurement

To investigate the photoelectrochemical performance of the composites, a standard three-electrode cell was employed, with the composite as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode. Na₂SO₄ was used as the electrolyte solution. The working electrodes were prepared as follows: The composite (3 mg) was suspended in 1 mL of pure/deionized water under grinding and ultrasound. A slurry was obtained and dip-coated onto an indium tin oxide (ITO) glass electrode.

3. Results and discussion

3.1. Photocatalytic activity

Fig. 1a and c present the photocatalytic activity of the photocatalysts on the degradation of phenol under visible light (>420 nm). Dramatically, the apparent rate constant of degradation

for 5 ppm phenol initially increased and then decreased with increasing TCNQ content. However, pure TCNQ exhibited no visible light activity. When the mass ratio of TCNQ reached 0.5%, the apparent rate constant of degradation reached a maximum of 0.0286 h⁻¹, nearly 2.2 times that of Bi₂WO₆ (0.0136 h⁻¹).

At the same time, HPLC was utilized to investigate the changes of phenol and its degradation intermediates along with irradiation time. Fig. 1b shows the changes of phenol and its degradation intermediates with visible light irradiation. The peak at 1.1 min was TCNQ, the peaks at 2.0 and 2.2 min were lower fatty acid, the peak at 3.1 min was phenol. As the reaction proceeded, the intensity of phenol decreased with the irradiation time whereas the lower fatty acid peaks increased gradually indicating that phenol degraded into small organic molecules.

The stability of Bi₂WO₆@TCNQ was tested by repeated cycling experiments. As shown in Fig. 1d, the photocatalyst exhibited excellent stability. The cyclic photodegradation of 5 ppm phenol was carried out 4 times, for a duration of 6 hours each time. After each cycle, we centrifuged the solution to separate out the photocatalyst; however, because of its nano-scale size and excellent dispersibility in water, there was always a large amount of photocatalyst that did not completely settle, resulting in a loss. However, the subsequent four cycles exhibited similar reaction rates, thus confirming the cycling performance and stability of the photocatalyst for application in photodegradation.

The interfacial charge separation efficiency of photo-generated electrons and holes is a crucial factor for photocatalytic activity. Photocurrents of Bi₂WO₆@TCNQ electrodes were measured to investigate the interfacial charge separation efficiency of photogenerated electrons and holes. It can be seen from Fig. 2a, photocurrents of Bi₂WO₆@TCNQ increased remarkably and then decreased with increasing proportion of TCNQ. Bi₂WO₆@TCNQ-0.5% exhibited the highest photocurrent response. The increase of photocurrent indicates that the separation efficiency of the photoinduced electrons and holes was enhanced greatly, which is the reason for the enhanced photocatalytic activity. It also implies that there may be some interaction between Bi₂WO₆ and TCNQ. The photocurrent responses decreased gradually when the proportion of TCNQ was over 0.5%, which may be associated with the formation of bulk crystals of TCNQ. The higher the content of TCNQ, the smaller the Bi₂WO₆ and TCNQ interaction, resulting in lower catalyst activity (Fig. 1a). Electrochemical impedance spectroscopy (EIS) was performed and the results are shown in Fig. 2b. A smaller arc radius on the EIS Nyquist plot of Bi₂WO₆@TCNQ-0.5% under visible light irradiation can be observed, suggesting a more effective separation efficiency of the photoinduced electron-hole pairs and a faster charge transfer. The fluorescence emission of Bi₂WO₆@TCNQ-0.5% showed a significant reduction (Fig. 3b). This phenomenon reflected the low recombination probability of photogenerated electrons and holes in Bi₂WO₆@TCNQ-0.5%.

The UV-vis DRS spectra of Bi₂WO₆ and different mass ratios of the Bi₂WO₆@TCNQ photocatalyst are shown in Fig. 2d. As expected, a sharp fundamental absorption edge rises at 477 nm



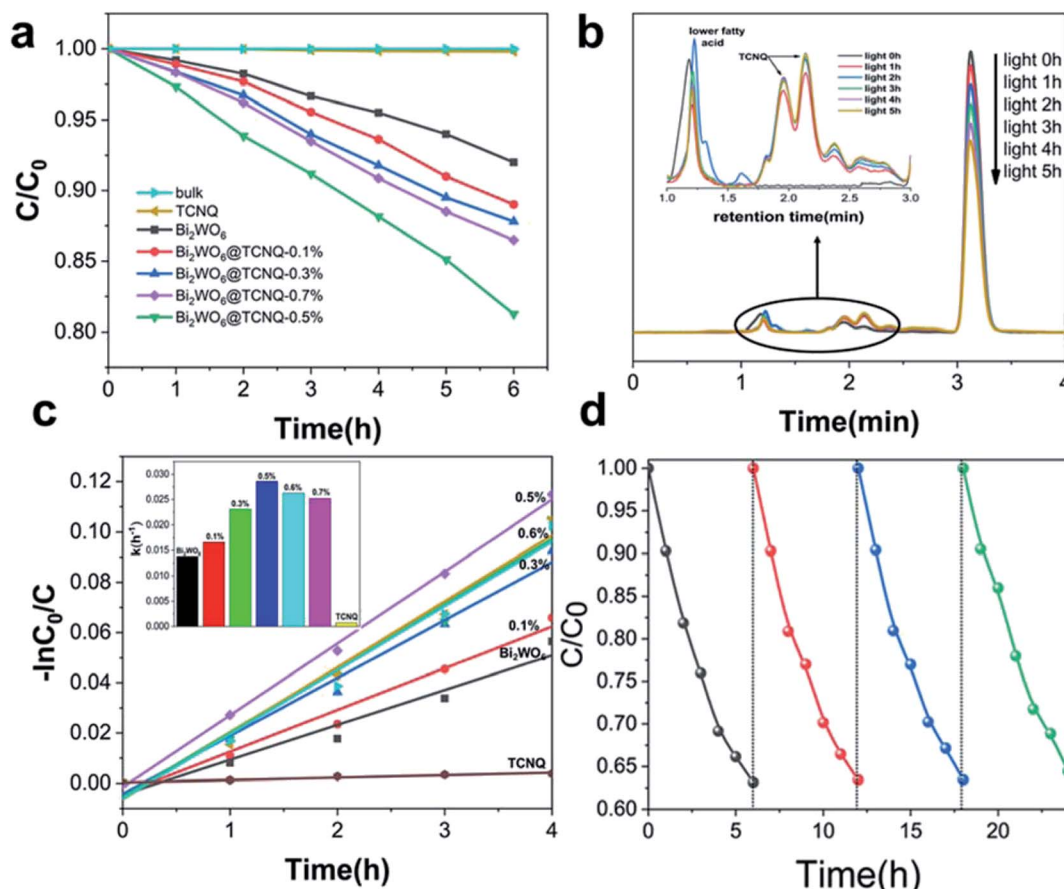


Fig. 1 Comparison of different photocatalysts for photodegradation of phenol (a), HPLC map of initial 5 ppm phenol to the map of phenol after 5 h of photocatalytic degradation (b). Apparent rate constants k of Bi_2WO_6 @TCNQ composite photocatalysts for the degradation of 5 ppm phenol with different TCNQ mass ratios under visible light ($\lambda > 420$ nm) (c) and cyclic experiments using Bi_2WO_6 @TCNQ-0.5% for phenol (5 ppm) degradation (d).

for Bi_2WO_6 , while the absorption edge of Bi_2WO_6 @TCNQ exhibits an apparent gradual redshift with increasing TCNQ loading. The absorption edge of Bi_2WO_6 @TCNQ-0.5% was at about 521 nm, indicating that absorption edge expanded. The band-edge shift is significant because, in this case, electrons can be stimulated under lower-energy irradiation, allowing for fuller use of the spectrum in comparison to UV photocatalysts. And an apparent red shift for Bi_2WO_6 @TCNQ composites appears as compared to Bi_2WO_6 , which may be related to the charge-transfer transition between the CB or VB of Bi_2WO_6 and TCNQ.³² Meanwhile, less photo-corrosion occurs with decreasing excitation energy.

In other words, the faster the charge transfer, the higher the separation efficiency of photoinduced electron-hole pairs and the lower the recombination probability of photo induced carriers in Bi_2WO_6 @TCNQ-0.5%. This is also the main reason for the high catalytic activity of Bi_2WO_6 @TCNQ-0.5%.

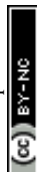
3.2. Core-shell structure of Bi_2WO_6 @TCNQ

The properties of a material are determined by its structure. Transmission electron microscopy (TEM) analysis shows that the nanosized Bi_2WO_6 crystals display mainly a thin sheet

shaped morphology and the border lengths of the thin sheets are less than 100 nanometers (Fig. 3a). It can be seen from Fig. 3b, the morphology of Bi_2WO_6 @TCNQ does not change significantly; with no aggregation phenomenon than that of Bi_2WO_6 , and TCNQ is exfoliated into sheet structures with rolled edges, the resulting morphology of Bi_2WO_6 @TCNQ is likely to be of a core-shell structure.

XRD was employed to characterize the crystal phases of Bi_2WO_6 and Bi_2WO_6 @TCNQ composites. As shown in Fig. 3c, all the samples present the typical XRD diffraction character of the orthorhombic Bi_2WO_6 phase (JCPDS 39-0256). However, no distinct diffraction peaks attributed to TCNQ can be detected in Bi_2WO_6 @TCNQ composites, which may be due to the low diffraction intensity, its relatively low dosage amount and good exfoliation of TCNQ in the composite. The results suggest that the incorporation of TCNQ in Bi_2WO_6 @TCNQ composites does not lead to the development of a new crystal phase or changes in preferential orientations of Bi_2WO_6 .

The HRTEM image (Fig. 3d) shows clear lattice fringes. The fringes of $d = 0.325$ nm match that of the (002) crystallographic plane of Bi_2WO_6 . The lattice structure of Bi_2WO_6 was very orderly and the outer boundary of the as-prepared sample was distinctly different from the Bi_2WO_6 core. A distinct core-shell



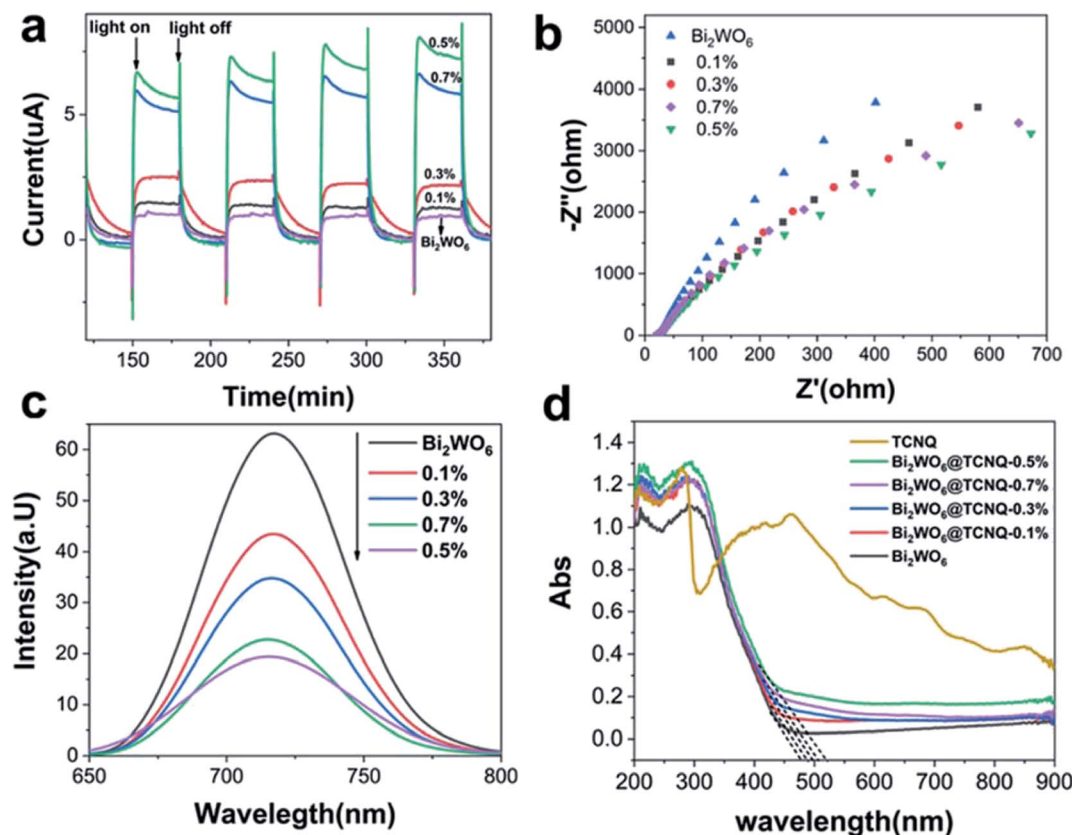


Fig. 2 (a) Photoresponses of Bi_2WO_6 and $\text{Bi}_2\text{WO}_6@\text{TCNQ}$ composites electrodes under the irradiation of visible light (>420 nm) [Na_2SO_4] = 0.1 M. (b) Electrochemical impedance spectroscopy (EIS) Nyquist plot of Bi_2WO_6 and $\text{Bi}_2\text{WO}_6@\text{TCNQ}$ composites upon irradiation ($\lambda > 420$ nm). (c) Fluorescence spectra of Bi_2WO_6 and $\text{Bi}_2\text{WO}_6@\text{TCNQ}$ composites. (d) UV-DRS spectra of pure Bi_2WO_6 , TCNQ and $\text{Bi}_2\text{WO}_6@\text{TCNQ}$.

structure was formed and the thickness of the TCNQ layer coated on the $\text{Bi}_2\text{WO}_6@\text{TCNQ}$ -5% sample was approximately 1 nm, corresponding to two TCNQ layers.^{33,34}

In the FT-IR spectrum of TCNQ, the 2207 cm^{-1} peak was attributable to $\text{C}\equiv\text{N}$ stretching vibration modes. The characteristic vibration of TCNQ at 2207 cm^{-1} nearly disappeared when TCNQ was loaded onto Bi_2WO_6 , which indicates that the $\text{C}\equiv\text{N}$ bond strength weakened, suggesting that there was a covalent bond between TCNQ and Bi_2WO_6 . This interaction is beneficial to the charge migration and the stability of core-shell structure. The characteristic vibration of TCNQ at 2165 cm^{-1} gradually weakened with increasing TCNQ, which indicates that the bond strength of W-O weakened and Bi_2WO_6 combined with TCNQ by chemical bonding rather than mechanical mixing.

Fig. 4b shows the Raman spectra of Bi_2WO_6 and various $\text{Bi}_2\text{WO}_6@\text{TCNQ}$ photocatalysts. The Raman shifts at 333, 600 and 708 cm^{-1} arise from the lattice vibrational peaks of TCNQ crystal, corresponding to the Ag (9) mode, Ag (8) mode and Ag (7) mode of TCNQ crystal,³⁴ respectively. The peak at 143 cm^{-1} was attributable to the lattice vibrational peaks of Bi_2WO_6 crystal, which move to a lower wavenumber with increasing TCNQ. The red shift of this band indicates that the bond strengths of W-O weakened, suggesting that there is a covalent bond between the conjugated bond of TCNQ and

Bi_2WO_6 .³⁵ The interaction is concerned with the charge transfer absorption peaks and the red shift of the absorption sideband shown in Fig. 2d.

3.3. Mechanism

To reveal the photocatalytic mechanism, the main oxidative species in the photocatalytic process are detected through the trapping experiments of radicals using $t\text{BuOH}$ ³⁶ as a hydroxyl radical scavenger, and formic acid³⁷ as holes radical scavenger. As shown in Fig. 5a, the photocatalytic activity of $\text{Bi}_2\text{WO}_6@\text{TCNQ}$ under visible light irradiation significantly decreases with the addition of a holes scavenger (formic acid) and reduces slightly with the addition of a hydroxyl radical scavenger ($t\text{BuOH}$), indicating that holes radicals are the main oxidative species rather than hydroxyl radicals. On the basis of the above experimental results, a possible mechanism for the degradation of phenol under visible light irradiation is proposed, as shown in Fig. 5b. Photogenerated electrons and holes are generated on the HOMO and LUMO of TCNQ, at the same time they are generated on the VB and CB of Bi_2WO_6 when irradiated by visible light. As the HOMO orbit of TCNQ is lower than the VB of Bi_2WO_6 ,³⁸ photogenerated holes on the HOMO of TCNQ can be injected easily into the VB of Bi_2WO_6 . The holes injected into the VB of Bi_2WO_6 can directly oxidize the organic pollutant, which contributes to the drastic visible light activity of



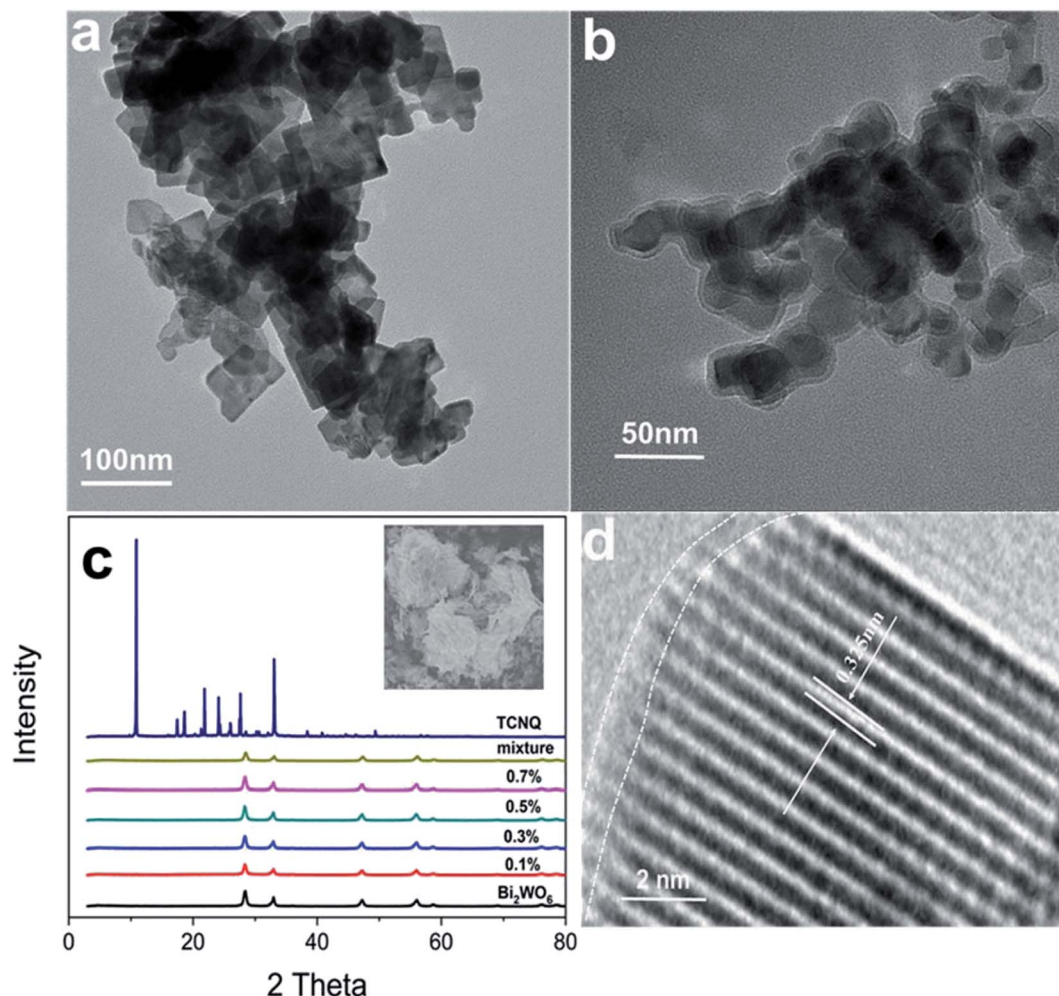


Fig. 3 TEM images of (a) Bi_2WO_6 and (b) $\text{Bi}_2\text{WO}_6@\text{TCNQ}-0.5\%$; (c) XRD patterns of Bi_2WO_6 and $\text{Bi}_2\text{WO}_6@\text{TCNQ}$; (d) HRTEM images of $\text{Bi}_2\text{WO}_6@\text{TCNQ}-0.5\%$.

$\text{Bi}_2\text{WO}_6@\text{TCNQ}$ photocatalyst in phenol degradation. As the CB position of Bi_2WO_6 is higher than the lowest unoccupied molecular orbital (LUMO) of TCNQ,³⁸ photogenerated electrons on the CB of Bi_2WO_6 can be easily injected to the LUMO orbit of

TCNQ. However, the LUMO orbit of TCNQ is too low for electrons to easily combine with O_2 , which prevents the formation of hydroxyl radicals.

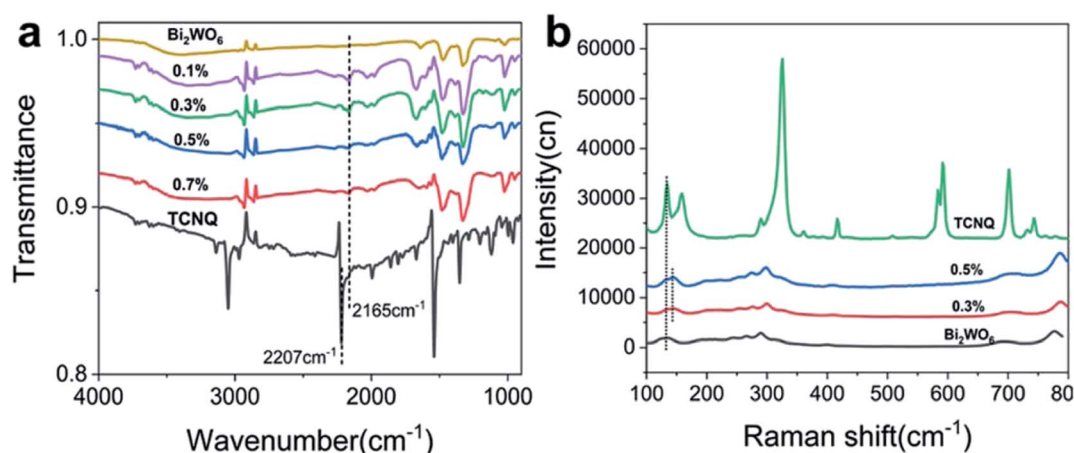


Fig. 4 (a) FTIR and (b) Raman spectra of Bi_2WO_6 and $\text{Bi}_2\text{WO}_6@\text{TCNQ}$ photocatalysts.



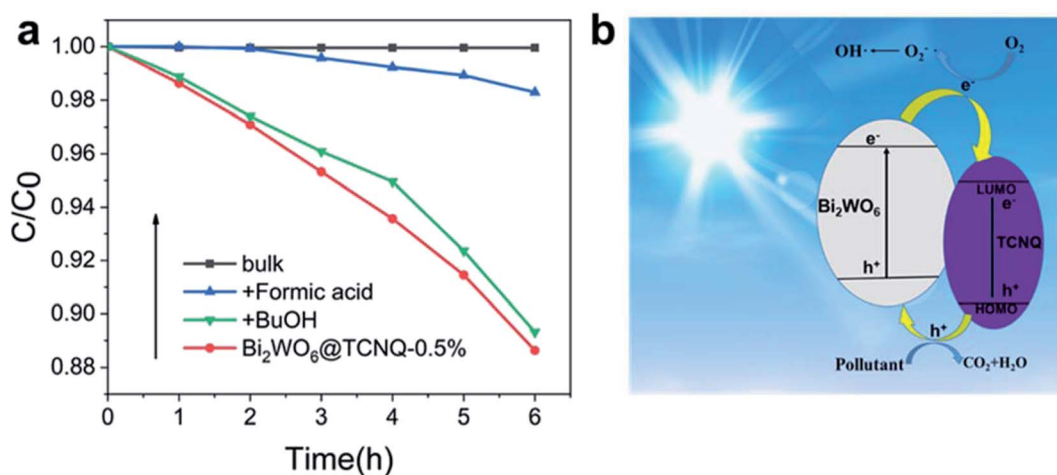


Fig. 5 The plots of photogenerated carriers trapping in the system of photodegradation of phenol by (a) Bi₂WO₆@TCNQ-0.5% under visible light (b) mechanism plots under visible light.

4. Conclusion

Bi₂WO₆@TCNQ photocatalyst with a core-shell structure was synthesized. This structure enhances the photocatalytic properties of the materials. When the mass ratio of TCNQ reached 0.5%, the apparent rate constant of degradation was nearly 2.2 times that of Bi₂WO₆. Its visible light activity comes from the injection of photogenerated holes on the HOMO of TCNQ into the VB of Bi₂WO₆ under visible light irradiation. The holes injected into the VB of Bi₂WO₆ could directly oxidize the organic pollutant.

Conflicts of interest

There are no conflicts to declare.

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