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Preparation of a $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ nanocomposite interfacial photocatalyst and its photocatalytic degradation of phenol pollutants in wastewater†

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A $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ nanocomposite interfacial photocatalyst was designed and prepared for the photocatalytic degradation of phenol pollutants in wastewater. The detailed properties of the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ nanocomposite interface (NCI) were analyzed by XRD, SEM, EDX, DRS, UPS and XPS technologies, showing that anatase TiO_2 nanospheres (NSs) were uniformly dispersed on the surface of rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ nanoparticles (NPs) and formed the nanocomposite interface. The DRS and UPS results of 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI indicated a greatly broadened light response range with a wavelength shorter than 527 nm and a shorter band gap energy of 2.37 eV. The conduction band of TiO_2 NSs, $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs and 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI were measured based on the results of the valence band and band gap energy obtained via XPS and DRS, and then the energy level diagram of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was proposed. The photocatalytic degradation of phenol at $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI with different loading ratios of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs was investigated under optimum conditions (*i.e.*, pH of 4.5, catalyst dosage of 0.45 g L^{-1} and phenol initial concentration of 95 ppm) under the illumination of ultraviolet visible light. Also, 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI exhibited the highest photocatalytic activity, with the initial rate constant (k) calculated as 0.09111 min^{-1} . After recycling six times, $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI showed good stability and recyclability. The involvement of superoxide radicals in the initial reaction at $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was evidenced by the use of a terephthalic acid (TA) fluorescent probe. Besides, UV-Vis spectroscopy, UHPLC-MS and GC-MS technologies were used to analyze the main intermediates in the photocatalytic degradation of phenol. The probable photocatalytic degradation mechanism of phenol at $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was also proposed.

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1. Introduction

Environment pollution has become a worldwide problem. Organic wastewater is one of the most typical pollution issues posing a serious threat to the health of humans and has consequently received extensive attention recently.^{1–3} Over the last several years, the utilization of direct solar light has become a much greener approach for energy generation as well as for environmental clean-up. Therefore, the development and design of a UV-Vis active photocatalyst for direct sunlight harvesting has drawn broad interdisciplinary attention and much research fascination. The photocatalytic decomposition of organic contaminants is one of the most promising techniques for wastewater treatment and purification.

Among oxide semiconductor photocatalysts, TiO_2 nanomaterials have been studied and applied widely in photocatalysis for their high photocatalytic activity, stability, nontoxicity and low cost. A variety of functional TiO_2 nanomaterials have been synthesized, such as nanoparticles (NPs),^{4–9} nanotubes (NTs),^{10,11} nanowires (NWs),^{12–15} nanocrystal films^{16–20} and nanotube arrays,^{21–25} which have been widely used in solar

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energy storage and utilization, photodegradation of pollutants and noble metal recycling.

However, the total quantum efficiency of TiO_2 is very low,^{26–28} which has limited the potential value of actual production and application of TiO_2 nanomaterials. A lot of studies have been done to address the drawbacks mentioned above, with noble metal deposition considered as one of the most effective and promising solutions. Pt is one such representative noble metal, which has been widely used to improve the performance of TiO_2 nanomaterials in wastewater treatment and air purification with a superior performance. Wang²⁹ successfully synthesised a Pt/ TiO_2 NW photocatalyst. The recombination rate of electrons and holes was reduced greatly for Pt NPs, resulting in good conductivity. Pt NPs are superior electron acceptors on the photocatalyst surface and enable the timely transfer of electrons. Emilio *et al.*³⁰ observed an increase in the lifetime of electrons by Pt modification on the TiO_2 surface due to the better separation of charge carriers caused by the Schottky barrier between Pt and TiO_2 . As expected, this helped to enhance the photocatalytic efficiency of TiO_2 .^{5–9,11,14,15,19,20,22,25,31–33} However, noble metals are scarce and particularly expensive, which may limit their large-scale application. Thus, novel relatively economical photocatalysts are highly desirable.

In the present paper, a $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was synthesized *via* a sol–gel and combustion technique, and was shown to possess several positive aspects, such as good stability, good visible light response range and effectively decreased recombination of charge carriers by a fast photogenerated electron transfer. The photocatalytic activity of the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was investigated for the degradation of phenol under simulated solar light illumination, and it showed higher photocatalytic activity. Furthermore, the main intermediates and mechanism for the photocatalytic degradation of phenol at the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI were also analyzed and discussed. This type of a photocatalyst may find application in low concentration organic wastewater clean-up.

2 Experiment section

2.1 Materials and reagents

Titanium tetrachloride (99.9%), titanium trichloride (99.9%), WCl_6 (99.9%), hexachloroplatinic acid (99.9%), carbolic acid (99.9%), HPLC-grade methanol, HPLC-grade acetonitrile and other reagents were all purchased from Shanghai Chemical Reagent Factory. Pure TiO_2 samples were commercial Degussa P-25 ($55 \text{ m}^2 \text{ g}^{-1}$). Doubly distilled water was used throughout this study. All the chemicals were of analytical grade and were used without further purification.

2.2 Synthesis of the TiO_2 NSs

The pure anatase TiO_2 NSs was prepared *via* a hydrothermal method.³⁴ First, 6 mM NaOH particles were added to 40 mL absolute ethyl alcohol and stirred for 10 min. Then, 2 mL titanium trichloride solution was added to the above NaOH solution drop-wise under vigorous stirring. After 10 min, the mixed

solution was transferred to a 50 mL Teflon-lined autoclave and heated at 150°C for 18 h. After cooling, the precipitate collected through centrifugation was rinsed with distilled water and pure ethanol several times until there were no residual ions left. Then, the products were calcined at 400°C for 2 h after being dried at 80°C .

2.3 Synthesis of the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs

The $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs were prepared by a modified sol–gel technique. First, 4 mM of WCl_6 powder was added to 10 mL of absolute ethyl alcohol with stirring for 10 min. Then, 1 mL of titanium tetrachloride solution was added to 5 mL of distilled water drop-wise under vigorous stirring. The above solutions were mixed together under air-free conditions. Then, the above mixed solution was stirred by mechanical stirring under 40°C constant temperature water for about 24 h to get a baby blue gel. The product was poured into a drying oven at 100°C for 12 h. The dry power was added to a 50 mL Teflon-lined autoclave with a moderate amount of alcohol and heated at 180°C for 8.5 h, and then the precipitate was dried and ground. Finally, the obtained powder was reduced at 1300°C in a H_2 atmosphere for 4 h to obtain a light tan powder. At this point, the W^{6+} was fully reduced to W^{4+} .^{35,36}

2.4 Synthesis of the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI

The $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was prepared *via* a simple method. First, 6 mM NaOH were added to 40 mL absolute ethyl alcohol and stirred for 10 min. Then, 2 mL titanium trichloride solution was added to the above NaOH solution drop-wise under vigorous stirring accompanied with a certain quality of pure rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs.³⁴ After 30 min, the mixed solution was transferred to a 50 mL Teflon-lined autoclave and heated at 180°C for 8.5 h, and then the precipitate obtained was dried and ground. Then, the obtained powders were calcined at 400°C in a N_2 atmosphere for 2 h. All referenced $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI samples were also prepared by the method described above and used for the photoactivity tests.

2.5 Synthesis of the Pt/ TiO_2 nanocomposites

The synthesis of the Pt/ TiO_2 nanocomposites and the characterization results are described in the ESI (Section 1, Fig. S1–S4†).

Meanwhile, the detailed information on the characterization, photocatalytic test and analysis of the intermediates in the photocatalytic degradation of phenol are shown in ESI (Section 2†).

3 Results and discussion

3.1 Characterization

PXRD analysis was carried out to investigate the impact of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ modification on the phase structure and on the chemical composition of the TiO_2 NSs, as these have a great influence on the photocatalytic activity. The PXRD patterns of the prepared samples are depicted in Fig. 1(A). According to previous studies, the photocatalytic property of anatase TiO_2 is



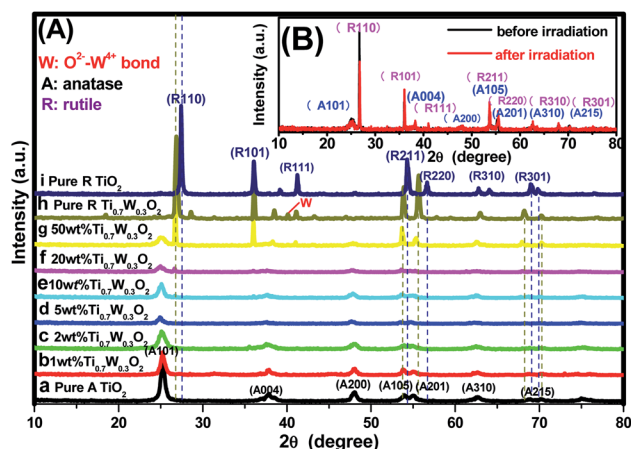


Fig. 1 PXRD patterns of the tested samples: (A) (a) pure anatase TiO_2 , $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI of (b) 1 wt%, (c) 2 wt%, (d) 5 wt%, (e) 10 wt%, (f) 20 wt%, (g) 50 wt%, (h) pure rutile $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$, (i) pure rutile TiO_2 ; (B) 50 wt% $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI before and after six cycles of irradiation, respectively.

generally considered to be superior, attributed to a higher density of localized states, consequent surface-adsorbed hydroxyl radicals and slower charge-carrier recombination.^{37–39} All diffraction peaks of the samples (a and i) could be indexed to the International Centre for Diffraction data of pure anatase TiO_2 (JCPDS no. 21-1272) and rutile TiO_2 (JCPDS no. 21-1276), respectively. The crystallite sizes were calculated by Scherrer's formula given in eqn (1).

$$D = K\lambda/\beta \cos \theta \quad (1)$$

where λ is the wavelength of the Cu-K α used, β is the full width at half-maximum of the diffraction peak, K is a shape factor (0.94) and θ is the angle of diffraction. The average crystalline size calculated from the major diffraction peak (101) of anatase TiO_2 NSs was about 149.1 nm.³⁴ The average crystalline size calculated from the major diffraction peak (110) of rutile $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs was about 1077 nm.³⁶

The average particle size and distribution of the anatase TiO_2 NSs and $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs were obtained using a laser particle size analyzer and are shown in ESI (Section 3, Fig. S6†). The average particle size and distribution of anatase TiO_2 NSs were determined to be about 287 nm, which was larger than the average crystalline size calculated from the major diffraction peak (101) in the XRD analysis. The average particle size and distribution of $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs were determined to be about 1189 nm, which was consistent with the result calculated from the major diffraction peak (110) in the XRD analysis of the rutile $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs. The possible reasons for the deviation were as follows. On the one hand, some TiO_2 NSs reunite after high temperature calcination. On the other hand, the principles of the two kinds of detection methods were different, whereby the results of the XRD analysis were estimated using an empirical formula, whereas the laser particle size analyzer detection needed the samples to be dispersed in water, and the dispersion

of the TiO_2 NSs was not very good and they were prone to reunion. This might lead to an increase in the error of the result.

Obviously, some diffraction peaks of $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs (h) were slightly shifted due to doping with W^{4+} compared with pure rutile TiO_2 (i). This phenomenon indicated an expansion of the a -axis and a contraction of the c -axis due to W–W pairing in the doped compound, which has also been observed in WO_2/TiO_2 nanocomposites.^{40–45} Meanwhile, the diffraction peaks for $\text{O}^{2-}-\text{W}^{4+}$ were very weak, demonstrating the low levels of W^{4+} .

The PXRD patterns of $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI loaded with 1 wt%, 2 wt%, 5 wt%, 10 wt%, 20 wt% and 50 wt% $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs are shown in Fig. 1(A)(b–g). All the samples were identical with the pure anatase and rutile phase after calcination at 400 °C, respectively. None of the diffraction peaks were changed significantly after deposition, which indicated that the $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs did not affect the phase structure and chemical composition of the TiO_2 NSs. However, further observation showed that the diffraction peaks corresponding to TiO_2 NSs exhibited relatively weaker peak intensities and broader diffraction peak widths. It could be inferred from this that the average crystallite size was slightly decreased by $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs modification, indicating that the $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs have a negative effect on the grain growth of TiO_2 NSs. This is because the $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs restrained the crystal growth in the solids by providing dissimilar boundaries and hindered the mass transportation, thus resulting in smaller crystallite sizes.⁴⁶ Meanwhile, no diffraction peaks of $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs were observed up to 10 wt% (e), indicating that the TiO_2 NSs were uniformly dispersed on the surface of the $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs.

The superimposed PXRD patterns for the $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI before and after six cycles of irradiation are shown in Fig. 1(B). It is obvious that the two PXRD patterns almost overlap, which indicates that the stability of the $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was encouraging, with less decomposition, thus accounting for the higher photocatalytic activity. A feeble and relatively weaker peak intensity was also revealed for the loss of a certain amount of photocatalyst during the experiment.

The detailed morphological features of the $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI were characterized by SEM technology and are shown in Fig. 2(A–D). The pure anatase TiO_2 was present as nanospheres, with a uniform size distribution as shown in Fig. 2(A). Fig. 2(B) shows the morphology of the pure rutile $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs, which were irregular and schistose particles with a smooth surface and highly dense quality. Fig. 2(C) and (D) show that the TiO_2 NSs were uniformly dispersed on the surface of the $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs and formed the $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI.

The elemental composition of the synthesis of the samples was confirmed by EDX spectra. In Fig. 2(a and b), the anatase TiO_2 revealed major peaks of Ti and O, and the rutile $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs revealed major peaks of Ti, W and O. Fig. 2(c and d) evidence the presence of Ti, W and O elements for the $\text{TiO}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI, indicating the high purity, and we can easily distinguish between the two components in the composite photocatalyst.^{47–49}

Furthermore, the atomic% of Ti/the atomic% of O of anatase TiO_2 was measured as 0.48, which was close to the mol ratio of Ti/O (0.50) in TiO_2 . The atomic% of Ti/the atomic% of W of



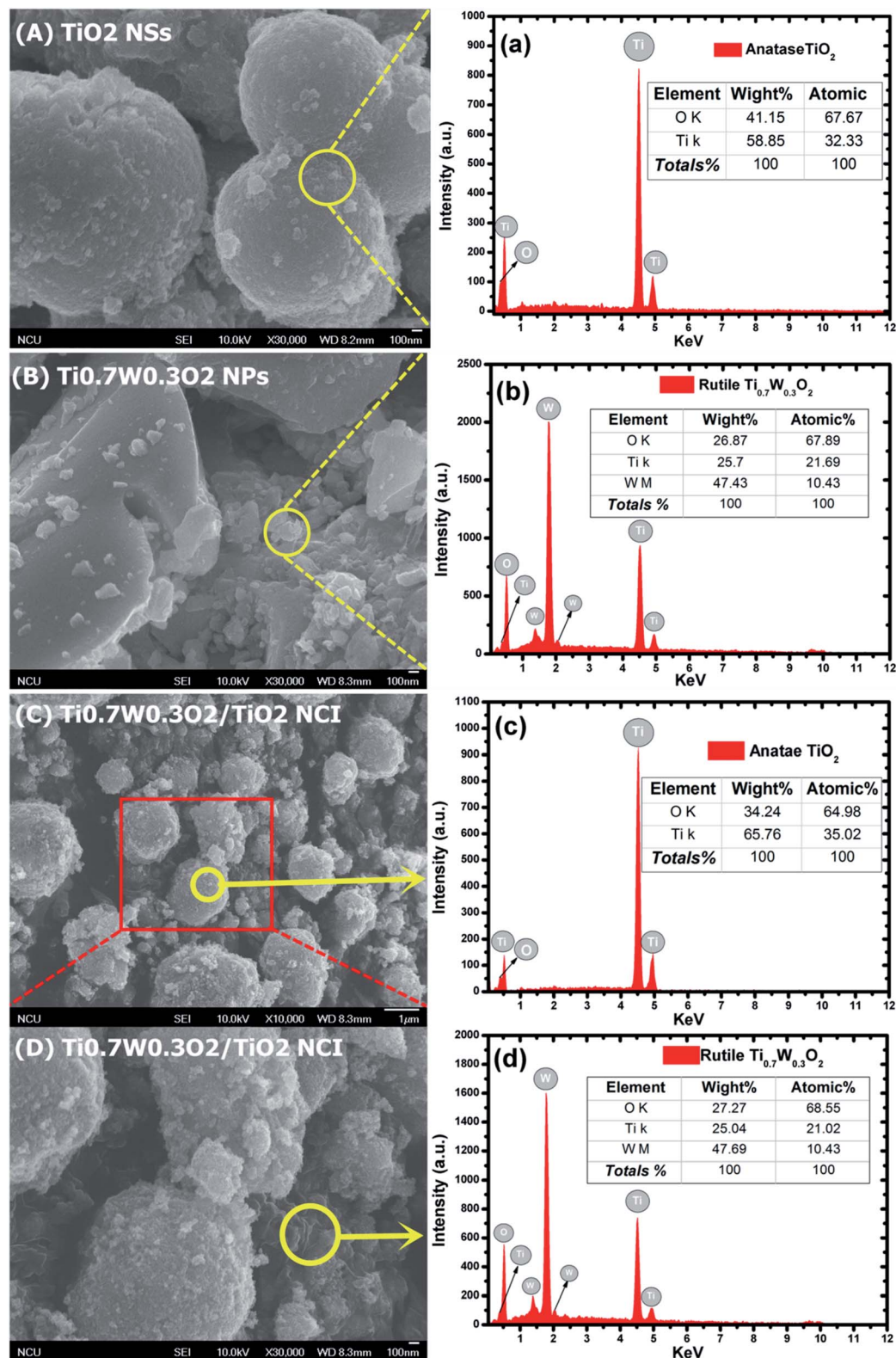


Fig. 2 SEM images of: (A) anatase TiO₂, (B) Ti_{0.7}W_{0.3}O₂ and (C)/(D) 5 wt% Ti_{0.7}W_{0.3}O₂/TiO₂ NCI. The corresponding EDX test results of: (a) anatase TiO₂, (b) Ti_{0.7}W_{0.3}O₂ and (c) and (d) 5 wt% Ti_{0.7}W_{0.3}O₂/TiO₂ NCI, respectively.

rutile Ti_{0.7}W_{0.3}O₂ NPs was measured as 2.08, which was close to the mol ratio of Ti/W (2.33) in Ti_{0.7}W_{0.3}O₂. The EDX results for each synthesized sample were a little different with the

theoretical mol ratio of elements as EDX merely involved a local analysis of the entire surface of samples, and so these represented acceptable errors.^{50–52}



However, the atomic% of Ti/the atomic% of O of anatase TiO_2 and the atomic% of Ti/the atomic% of W of rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs in $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI were measured to be 0.54 and 2.02, respectively. The error of the results had thus increased, which might be due to the interaction between the two nanomaterials.

A UV-Vis spectrometer was used to record diffuse reflectance spectra in the range 200–800 nm. Fig. 3 (A) shows the DRS of pure TiO_2 NPs, pure rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ and 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI. The band gap values of the synthesized photocatalysts were calculated by plotting $(F(R_\infty)h\nu)^{1/2}$ versus the photo energy and the plot is shown in Fig. 3 (B). The pure TiO_2 NPs and the pure rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ demonstrated a photoabsorption modification ability for the UV light region with wavelength shorter than 396 and 598 nm, corresponding to band gap energies of 3.21 and 2.05 eV, respectively. The pure rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ had a shorter band gap energy due to W^{4+} doped into the lattice of TiO_2 . When the pure rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ was irradiated, conduction band electrons (e_{cb}^-) were generated and quickly spread to the valence band due to the shorter band gap energy, which might make the semiconductor have higher conductivity.⁵³ The volume resistivity and conductivity of pure anatase TiO_2 , 0.3 wt% Pt/TiO_2 and 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ are shown in

Fig. 3(F). The volume resistivity of pure anatase TiO_2 was over 10 times that of 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$. The volume resistivity of 0.3 wt% Pt/TiO_2 was over 2 times that of 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$. It was thus indicated that the conductivity of pure anatase TiO_2 could be improved greatly by modifying the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs, and that the performance of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs was superior to that of Pt NPs, which could fully prove the above conjecture.

Meanwhile, the 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was extended to the visible absorbance region with a wavelength shorter than 527 nm and had a shorter band gap energy of 2.37 eV. The above results were fully proved by ultraviolet photoemission spectroscopy (UPS) and the results are shown in ESI (Section 4, Fig. S7†). The band gap energies of the pure TiO_2 NPs and 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI were 3.38 and 2.43 eV, respectively, which were slightly larger than that from the DRS. The reasons for the deviation may be due, on the one hand, to the detection depth of UPS technology, which was 10 atoms, while on the other hand, the carbon pollution signal would be higher for the solid powder sample.

In short, $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs with higher conductivity can cause fast electron transfer and effectively restrain the recombination of $e_{cb}^- - h_{vb}^+$ pairs in $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI, which can diffuse to the surface and react with pollutants and produce more

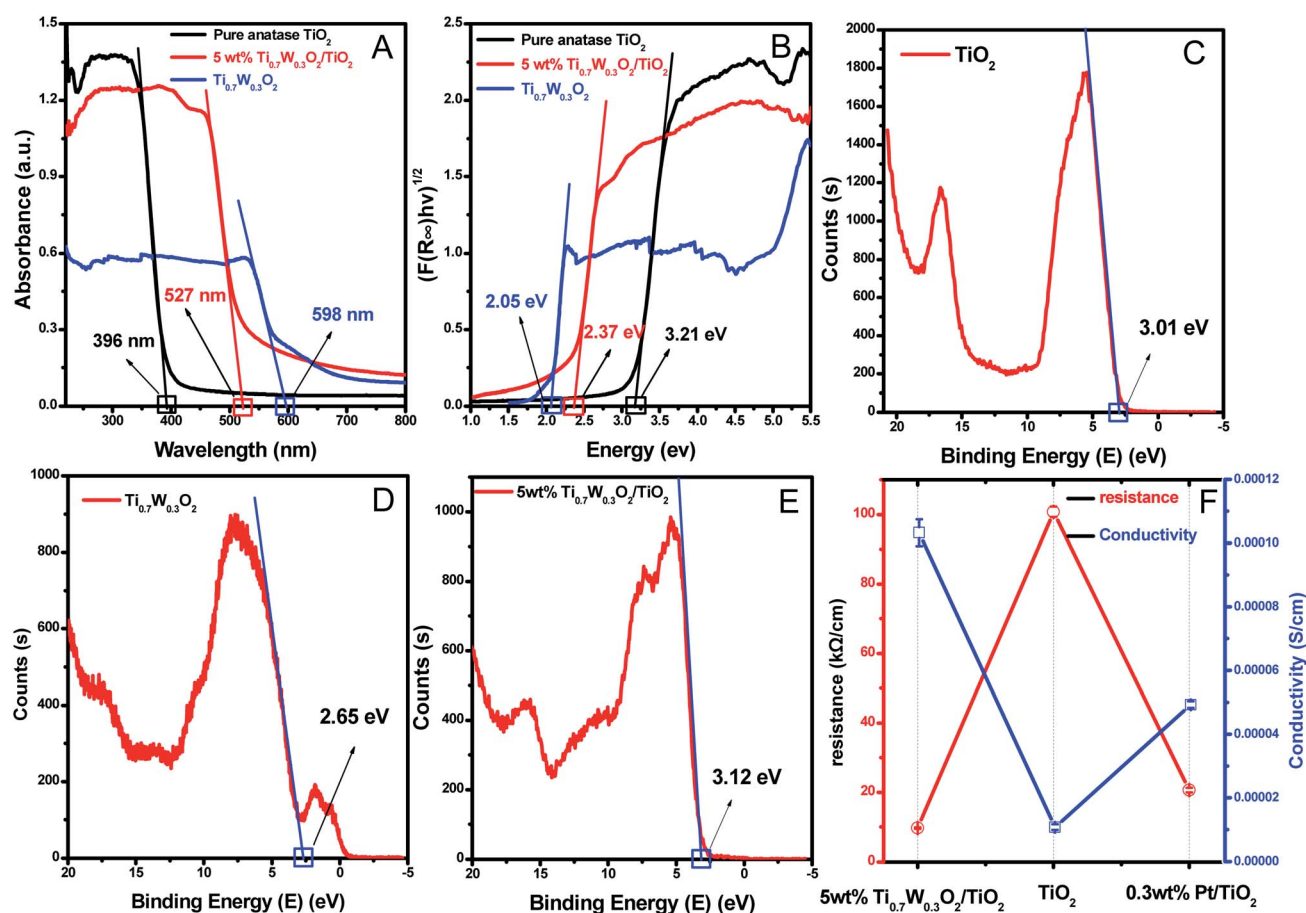


Fig. 3 (A) DRS and (B) plots of the transformed Kubelka–Munk function versus the energy of absorbed light for the pure anatase TiO_2 , $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ and 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI. The XPS valence band scan spectra of: (C) pure anatase TiO_2 NPs, (D) rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ and (E) 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI. (F) The volume resistivity and conductivity of pure anatase TiO_2 , 0.3 wt% Pt/TiO_2 and 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI.

superoxide radical anions ($\cdot\text{O}_2^-$)/ $\cdot\text{OH}^-$. Furthermore, the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI could also improve the utilization of visible light, which might account for the higher photocatalytic activity.

The XPS valence band scan spectra of pure anatase TiO_2 NSs, rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ and 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI are shown in Fig. 3(C–E). The valence bands of TiO_2 NSs, rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ and 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI were 3.01, 2.65 and 2.83 eV, respectively. According to the band gap energy result from DRS, the conduction bands were measured as -0.20 , 0.60 and 0.46 eV, and the energy level diagram of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI could be proposed and is shown in ESI (Section 4, Fig. S8†).

The rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ was further characterized by XPS, as seen in Fig. 4(A–D), to illustrate the structural features and composition. The XPS survey scan spectrum of rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ is shown in Fig. 4(A). The relative concentrations of Ti and W of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ were determined by the respective XPS peak areas and atomic sensitivity factors and $n_{\text{Ti}}/n_{\text{W}}$ was measured as 2.13, which is close to the mol ratio of Ti/W (2.33) in $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ ⁵⁴ and consistent with the EDX result.

The XPS narrow scan spectra of Ti 2p, W 4f and O 1s of the rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ are shown in Fig. 4(B–D). The Ti 2p_{1/2} and Ti 2p_{3/2} peaks of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ were located at 464.6 and 458.8 eV and assigned to TiO_2 , respectively. The W 4f_{5/2} and W 4f_{7/2} peaks were located at 34.2 and 33.1 eV, and assigned to WO_2 , proving that the W^{6+} was fully reduced to W^{4+} in $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$.

3.2 Photocatalysis

3.2.1 Optimal photocatalytic conditions (pH, initial phenol concentration, photocatalyst dosage). In order to find the optimal initial pH value of the solution, the photocatalytic degradation of phenol was carried out at a pH of 3.5–10.0, catalyst dosage of 0.45 g L^{-1} , irradiation time of 360 min and phenol concentration of 95 ppm and the results are shown in Fig. 5(A). Obviously, the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI showed the highest photocatalytic activity under pH 4.5, indicating that phenol photodegradation in the acidic solution was higher than that in natural solution, neutral solution and alkaline solution, which was consistent with the research conclusions of Kha-tae⁵⁵ and Kim.⁵⁶ They believed that the oxidation ability of the hydroxyl radical ($\cdot\text{OH}^-$) under acidic conditions was higher than in alkaline solution. The formation of HCO_3^- and CO_3^{2-} in alkaline solution would interfere in the reaction between pollutants and $\cdot\text{OH}^-$, resulting in reducing its oxidation potential and leading to a lower photocatalytic activity. Meanwhile, with the appearance of HCO_3^- and CO_3^{2-} , the low adsorption of negatively charged system components resulted in a lower production of superoxide radical anions ($\cdot\text{O}_2^-$) and hence a lower oxidation ability. However, the phenol photodegradation at pH 3.5 was also lower than that at pH 4.5. This may be due to the change in the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI structure

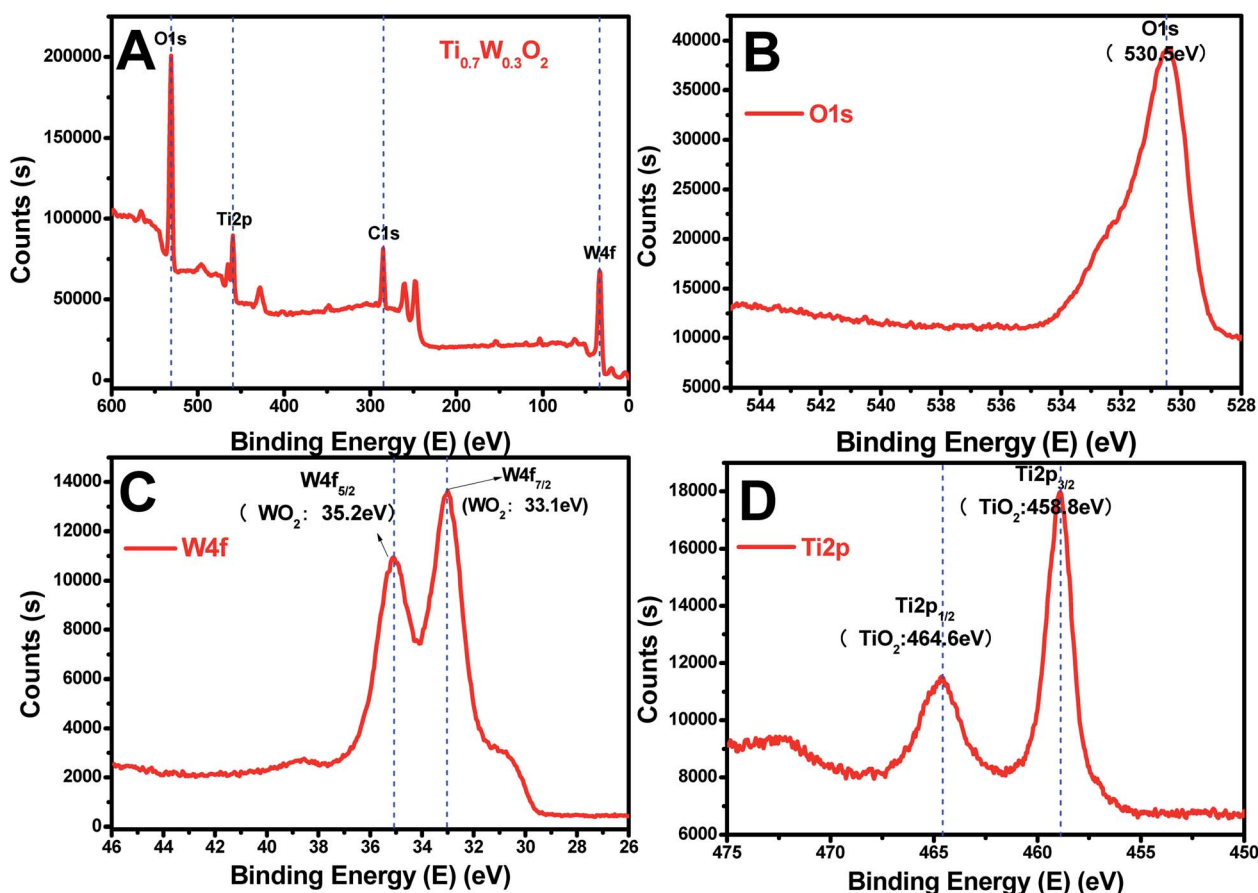


Fig. 4 XPS survey scan spectra of: (A) rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$, and XPS narrow scans of: (B) O 1s, (C) W 4f and (D) Ti 2p of the rutile $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$.



under a too acidic environment. Herein, the results revealed that the optimal initial pH value was 4.5.

The most appropriate initial phenol concentration was investigated with the initial concentration ranging from 50–125 ppm and the results are shown in Fig. 5(B). Obviously, the complete photodegradation time of phenol increased with the increase in the initial concentration from 50–95 ppm, and the photodegradation of phenol at 95 ppm could be just finished with 360 min irradiation. The photocatalytic efficiencies of 110 ppm and 125 ppm phenol were 94.3% and 86.3% after 360 min irradiation, respectively. Further increases decreased the photocatalytic efficiency, indicating that there was an optimum value. The reasonable explanations for this are as follows: first, too many phenol molecules and its intermediates would also absorb a part of the irradiation and limit the light absorption capability of the photocatalysts. Second, excessive amounts of phenol molecules and its intermediates also deactivate more active sites and reduce the light penetration to active sites situated on the surfaces of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI. The above two disadvantages also result in a lower production of superoxide radical anions ($\cdot\text{O}_2^-$)/ $\cdot\text{OH}^-$ and ultimately a lower oxidation ability.⁵⁷

The effect of the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI dosage was investigated by varying the dosage from 0.15 g L^{-1} to 0.90 g L^{-1} and the results are shown in Fig. 5(C). When raising the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI dosage from 0.15 g L^{-1} to 0.60 g L^{-1} , the phenol photocatalytic efficiency increased from 58.7% to 100% as more active sites were available, increasing the response surface area and leading to a greater production of $\cdot\text{O}_2^-$ / $\cdot\text{OH}^-$. However, further increasing the dosage to 0.90 g L^{-1} decreased the photocatalytic efficiency. According to the literature,^{58–62} the reasons for this might be due to the following aspects: on the one hand, an excessive dosage of photocatalysts would result in lower solution transparency, light scattering and interception and the prevention of the light induction of some catalysts particles. On the other hand, too many photocatalysts particles would prevent the effective collisions between phenol molecules and a variety of free radicals. Moreover, the pore volume and available surface area of the photocatalysts would also be diminished with excessive dosage, resulting in a lower photocatalytic activity.

The stability and recyclability of all heterogeneous photocatalysts are critically important for application in wastewater treatment plants. The stability and recyclability of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI were investigated in a batch reactor under pH 4.5,

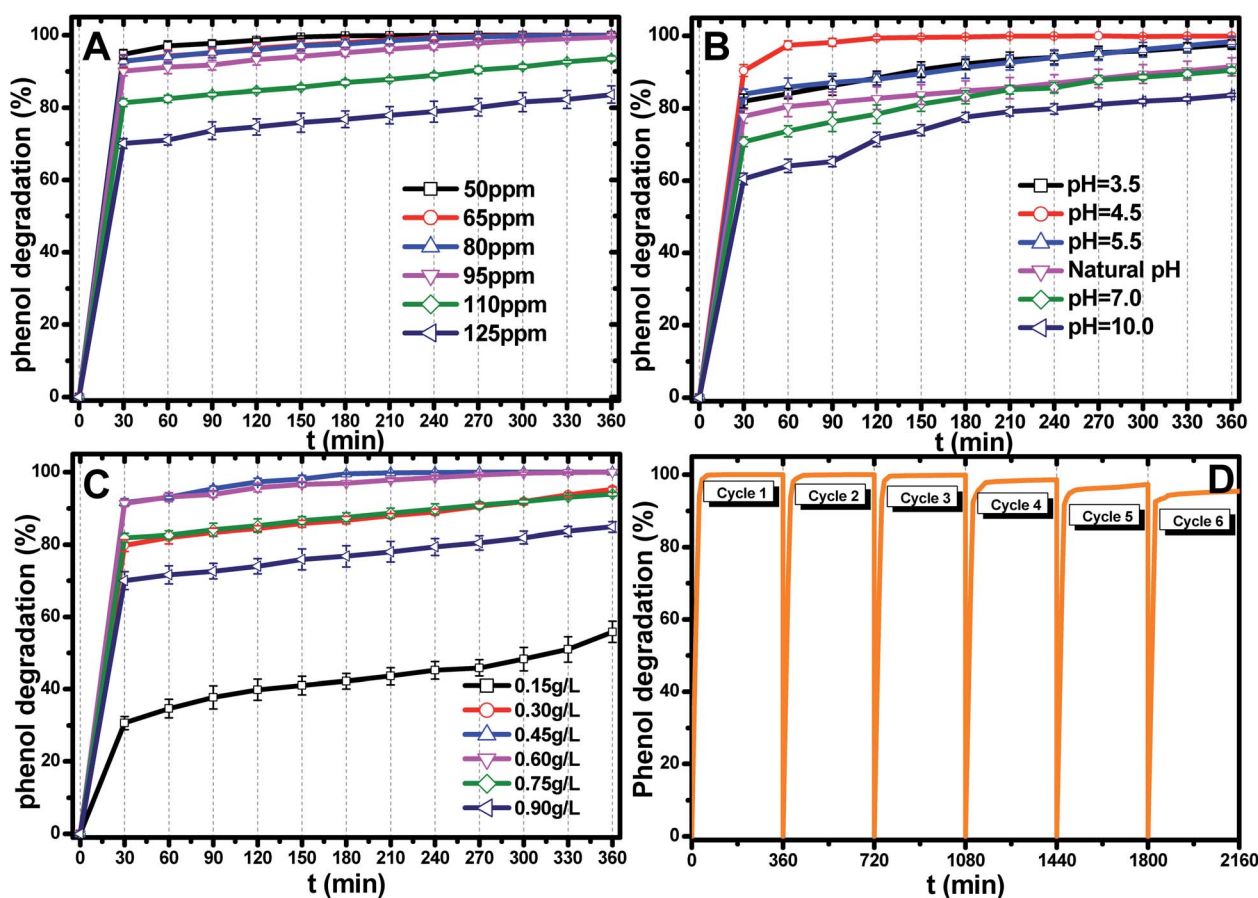


Fig. 5 (A) Effect of the initial pH value on phenol photocatalytic degradation; catalyst dosage: 0.45 g L^{-1} , phenol concentration: 95 ppm. (B) Effect of the initial catalyst dosage on phenol photocatalytic degradation; pH: 4.5, phenol concentration: 95 ppm. (C) Effect of the initial phenol concentration on phenol photocatalytic degradation; catalyst dosage: 0.45 g L^{-1} , pH: 4.5. (D) Recyclability of the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI in the phenol photodegradation process under visible light illumination through six cycles at initial concentration: 95 ppm, pH: 4.5, catalyst dosage: 0.45 g L^{-1} .



a catalyst dosage of 0.45 g L^{-1} and phenol concentration of 95 ppm. After each experiment, the used photocatalyst was collected from the suspension turbid solution and washed with 50% ethanol solution to remove residue phenol and other photodegradation products on the photocatalysts surface. Then, the wet photocatalyst was dried at 105°C for 4 h. This sequence was repeated six times and the phenol photodegradation efficiency of each cycle recorded and the results are shown in Fig. 5(D). After six recycles, the photocatalytic degradation efficiency of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was reduced from 100% to 94.5%, indicating that the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI showed high photocatalytic activity with good stability and recyclability. The reduction could be explained by a loss of photocatalyst during the washing process, which was consistent with the PXRD results.

3.2.2 Comparison of the phenol photocatalytic degradation efficiency of P-25, Pt/TiO_2 and $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI. The photocatalytic activity of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was examined by monitoring phenol photocatalytic degradation under UV-visible light illumination and then compared with P-25 and Pt/TiO_2 . All experiments were carried out under pH 4.5, a catalyst dosage of 0.45 g L^{-1} and phenol initial concentration of 95 ppm with the highest photocatalytic activity. The UV-Vis spectra of the

photocatalytic degradation of phenol by P-25, Pt/TiO_2 and $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI are shown in ESI (Section 5, Fig. S9†).

Fig. 6(A and B) present the phenol photocatalytic degradation by P-25, Pt/TiO_2 and $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI, showing the differences in the phenol degradation activity with the varying loading rates of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ and Pt/TiO_2 . The phenol degradation rate of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI increased with the loading value of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ up to 5 wt%; however, a further increase would decrease the photocatalytic activity, indicating that there was an optimum loading value. The optimum value had a close relationship with the dispersion and particle sizes of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs. Meanwhile, one could easily find that the phenol degradation rate of 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was always higher than that of 0.3 wt% Pt/TiO_2 at any synchronous irradiation time, revealing its higher photocatalytic activity.

Fig. 6(C and D) compare the phenol photocatalytic degradation rates of P-25, Pt/TiO_2 and $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI after 360 min irradiation. The phenol photocatalytic degradation rate after various intervals of time was estimated using the following eqn (2).

$$\text{Phenol photocatalytic degradation rate (\%)} = (c_{t=0} - c_t)/c_{t=0} \times 100\% \quad (2)$$

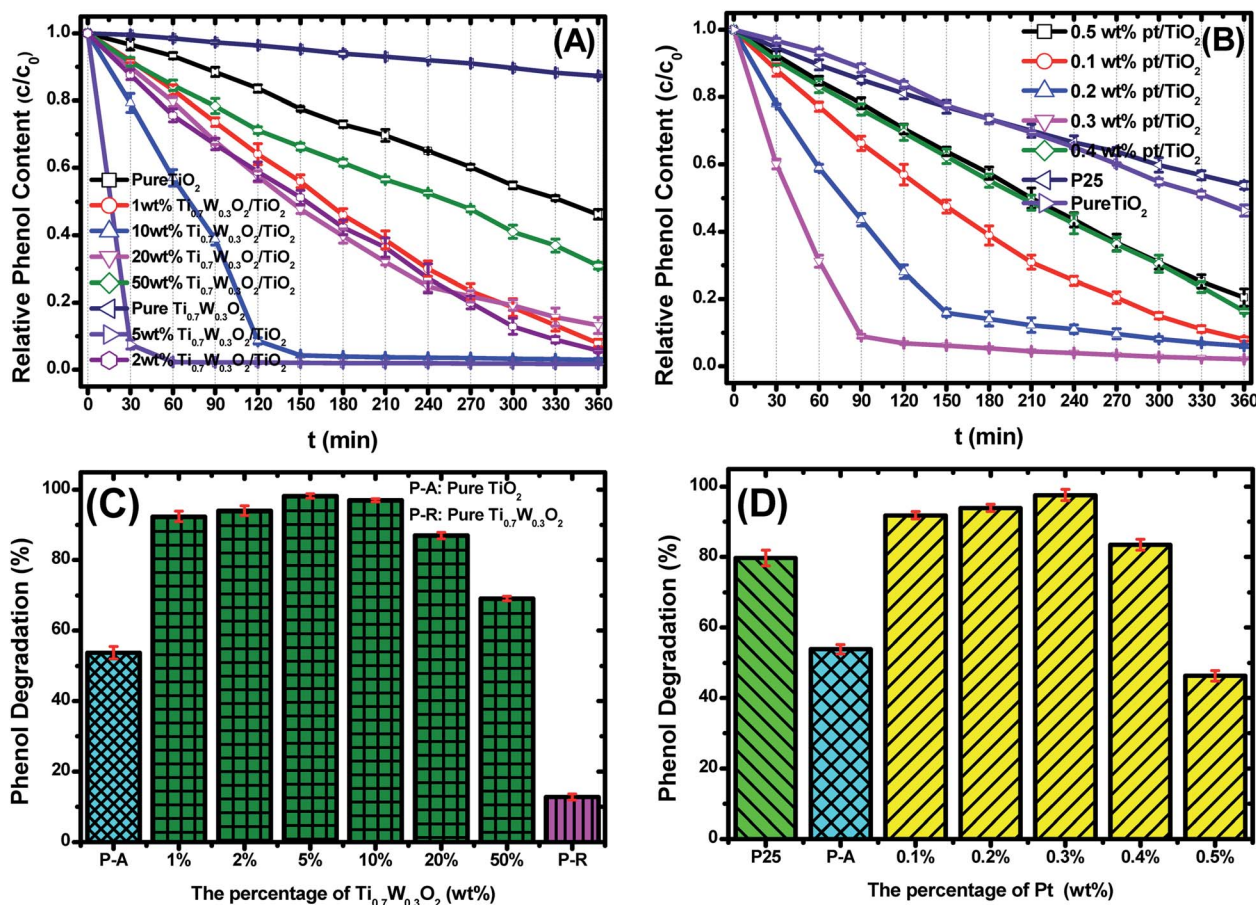


Fig. 6 Photocatalytic degradation of phenol over: (A) $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI, (B) P-25 and Pt/TiO_2 , c = concentration, c_0 = initial concentration. The phenol photocatalytic degradation rates of: (C) $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI, (D) P-25 and Pt/TiO_2 after 360 min irradiation.

where $c_{t=0}$ is the initial concentration of phenol and c_t is the concentration of phenol obtained after various intervals of time (t). From the experimental study, it was observed that 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI showed higher photocatalytic activity. The phenol photocatalytic degradation trend was: 5 wt% > 10 wt% > 2 wt% > 1 wt% > 20 wt% > 50 wt% > pure TiO_2 > pure $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$. Here, 98.7% of the phenol was photodegraded by 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI after 50 min irradiation, indicating a higher photocatalytic activity. However, only about 47.23% and 90.79% of the phenol was photodegraded for P-25 and 0.3 wt% Pt/TiO_2 after 360 min irradiation. It was indicated that the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs may be much superior to Pt NPs for modifying the photocatalytic performance of TiO_2 nanomaterial.

3.2.3 Kinetic study of the phenol photocatalytic degradation. Additionally, kinetic analysis of phenol degradation was performed for a better comparison of the photocatalytic efficiency of the different photocatalysts. The dependence of $\ln(c_0/c)$ on the irradiation time (t) in P-25, Pt/TiO_2 and $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ is shown in Fig. 7. It was indicated that the initial photodegradation of phenol followed a quasi-first-order-type kinetics, as evidenced by the linear relationship between $\ln(c_0/c)$ and the time (t). Actually, c_0 is the initial concentration of phenol, and c is the concentration of phenol after irradiation for time (t).

The initial rate constant (k) for phenol photocatalytic degradation in P-25 was calculated as 0.00346 min^{-1} , while the initial rate constant (k) for phenol photocatalytic degradation in 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ and 0.3 wt% Pt/TiO_2 was about 26 and 6.8 times that of P-25, respectively. This indicated that the photocatalytic activity of TiO_2 was enormously improved with the proper amount of loading $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ and Pt NPs. Furthermore, the initial rate constant (k) for 5 wt% $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ was over 3.9 times that in 0.3 wt% Pt/TiO_2 , illustrating that the as-prepared $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ NPs may be much superior to Pt NPs in embellishing the photocatalytic properties of TiO_2 nanomaterials and could even replace them.

Herein, to better assess the photocatalytic activity of the synthesized $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI, we compared our results with

the photodegradation of phenol reported in previous studies, as shown in Table 1. The $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI showed several advantages in the photocatalytic performance, photocatalytically degrading the most amount of phenol with the least irradiation time and catalyst dosage. The initial rate constant (k) of the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was over 2.6 times that of $\text{SnS}_2/\text{TiO}_2$ nanocomposite catalyst, which showed a higher photocatalytic activity than the other catalysts. Therefore, it was concluded that the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was one of the most efficient catalysts for the photocatalytic degradation of phenol under the selected experimental parameters.

3.2.4 Analysis of the intermediates in the photocatalytic degradation of phenol. It is well known that phenol decomposition could follow different complicated multistage pathways, following various by-products. It has also been demonstrated that two types of oxidizing species, namely hydroxyl radicals and positive holes, are involved in oxygenated aqueous TiO_2 suspensions.^{79–84} Ilisz *et al.*⁸⁵ found that phenol was degraded into various by-products (such as hydroquinone, catechol and other ring-opened compounds) with different oxidizing agents under UV-Vis irradiation in the presence of different electron scavengers. Catechol, hydroquinone and 2,4-hexadiendioic acid were found during phenol degradation at mesoporous $\text{TiO}_{2-x}\text{B}_x$ by Xiong *et al.*⁷³

The UV-Vis absorption spectra from the photodegradation of phenol over P-25, Pt/TiO_2 and $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ are compared in ESI (Section 6, Fig. S10†). At P-25, besides the characteristic absorption bands at 270 nm of phenol, a new absorption band at 289 nm appeared, which might be attributed to the ring-retaining compounds.^{29,59,86,87} However, besides the two absorption bands at 270 and 289 nm, there were two new absorption bands at 247 and 257 nm for Pt/TiO_2 , and another two new absorption bands at 333 and 363 nm for $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$, which might be attributed to ring-opened products.^{87,88} It can be concluded that the phenol photodegradation pathway over $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI was partially different from that over P-25 and Pt/TiO_2 .

The aqueous solutions of phenol degradation over P25, Pt/TiO_2 and $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ were detected by UV-Vis spectrometry, UHPLC-MS and GC-MS. Then, the main intermediates were analyzed and inferred by the molecular ions and mass fragment peaks present and from library data. The LC chromatograms, UV-Vis spectrograms and mass spectra from HPLC-MS are shown in ESI (Section 7, Fig. S11a–k†). The GC chromatograms and mass spectra from GC-MS of the intermediates are shown in ESI (Section 8, Fig. S12 and S13†). The analytical results and possible structures of each intermediate are shown in ESI (Section 9, Table S1 and Fig. S14†).

In short, five and six kinds of intermediates were identified in the aqueous suspension of P-25 and Pt/TiO_2 , respectively. Six kinds of intermediates were found in the aqueous suspension of $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$. The further degradation of all the intermediates might include oxidative hydroxylation and oxidative decarboxylation products, *etc.* from several reaction pathways operating simultaneously.

3.2.5 Determination of the superoxide radicals using a terphthalic acid (TA) fluorescent probe. Superoxide radicals can

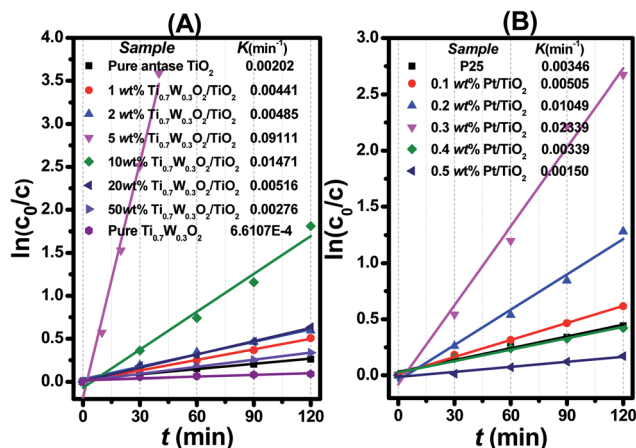


Fig. 7 Dependence of $\ln(c_0/c)$ on the irradiation time (t) for: (A) $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI, (B) P25 and Pt/TiO_2 .



Catalyst	Concentration (mg L ⁻¹)/volume (mL) of phenol	Catalyst amount (g L ⁻¹)	Degradation (%)	Irradiation time (min)	Initial rate constant (<i>k</i>) (min ⁻¹)	Reference
Pt–ZnO	15	—	>95	540	—	63
ZnO	50/200	1.0	69.75	480	0.0150	64
GO/TiO ₂	14/100	1.48	100	180	—	65
RGO/TiO ₂	50/1700	—	96	180	0.0154	66
MWCNT/TiO ₂	50/800	1.0	96	300	0.0074	67
Fe/S/TiO ₂	20/60	1.0	99.4	600	—	68
CNT/Ce–TiO ₂	50/500	0.4	95	180	0.0012	69
BiPO ₄	50/100	0.5	100	240	0.0370	70
Co/Pd/BiVO ₄	18.4/100	0.8	90	180	0.0130	71
ZnO/TiO ₂	60/250	0.6	100	160	0.0124	72
TiO _{2–x} B _x	94/50	6	97	240	0.0084	73
BiMnO ₄	20/100	1.0	90	480	0.0049	74
Fe(III)–TiO ₂	100/1500	0.5	93.8	210	0.0190	75
TiO ₂ /Ag/C	20/100	1.0	95	60	—	76
N–TiO ₂ @CS	9.4/40	2.5	90	180	—	77
V ₂ O ₅ /N,S–TiO ₂	100/20	1.0	88	240	—	78
Pt/TiO ₂	—	—	87.7	180	—	79
TiO ₂ –Fe ₂ O ₃ –graphene	5/100	1.5	—	150	0.01415	80
SnS ₂ /TiO ₂	10/100	0.5	—	150	0.03595	81
<i>Ti</i> _{0.7} <i>W</i> _{0.3} <i>O</i> ₂ / <i>TiO</i> ₂ <i>NCI</i>	95/1000	0.45	98.7	50	0.09111	<i>This study</i>

The phenol photocatalytic degradation mechanism involves initial reactions at the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{TiO}_2$ NCI, as shown in



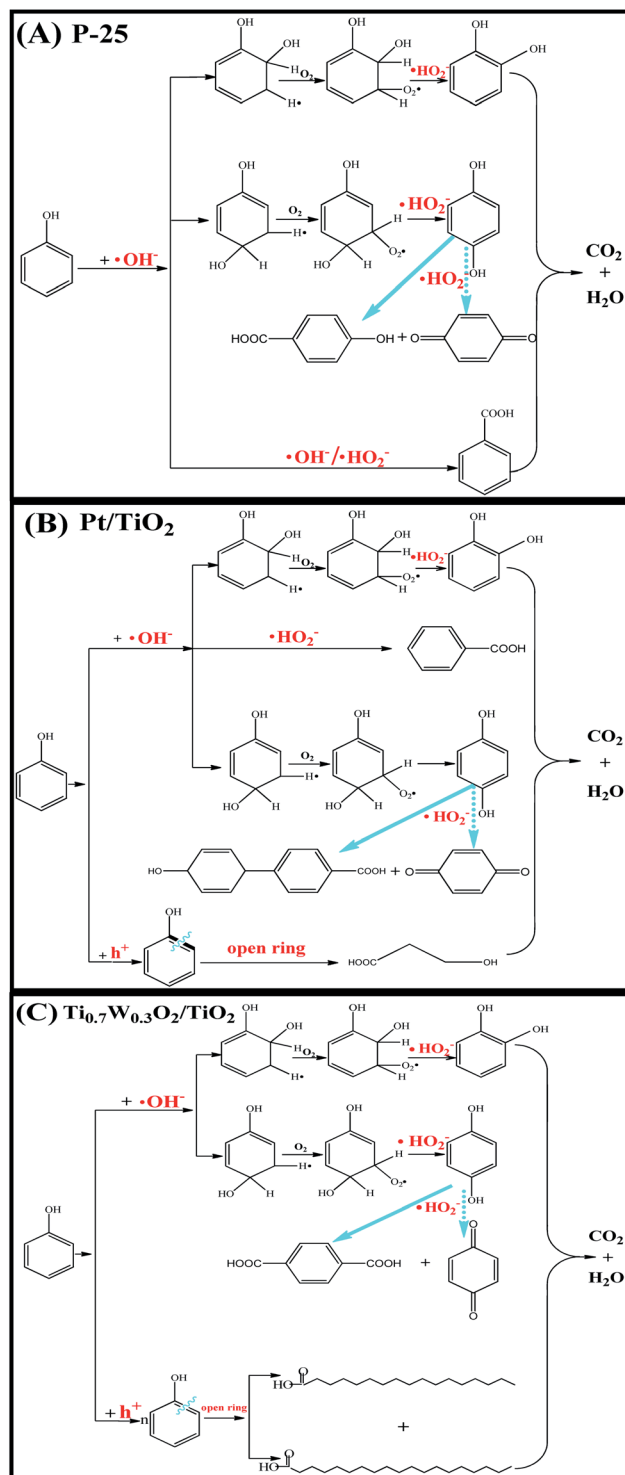
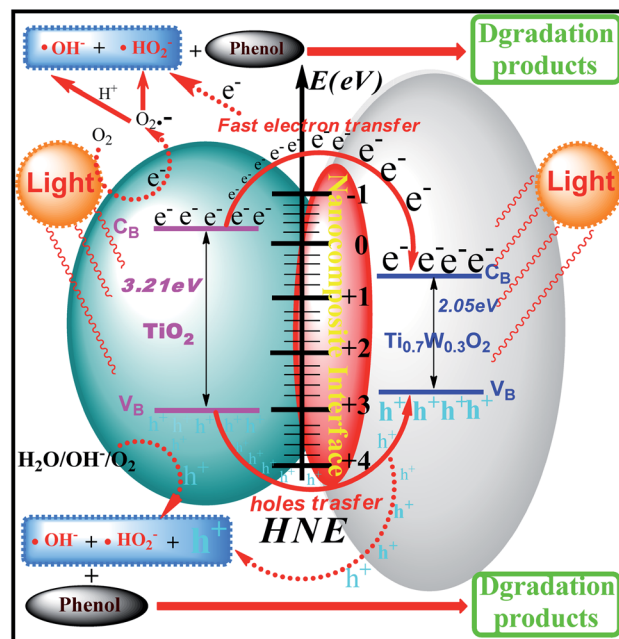


Fig. 9 Proposed photocatalytic degradation process of phenol over: (A) P-25, (B) Pt/TiO₂ and (C) Ti_{0.7}W_{0.3}O₂/TiO₂ NCI.

Scheme 1. It was well established that conduction band electrons (e_{cb}^-) and valence band holes (h_{vb}^+) were generated when the suspension was irradiated. A Schottky barrier might be formed at the NCI between TiO₂ NSs and Ti_{0.7}W_{0.3}O₂ NPs, leading to a greater formation of h_{vb}^+ and e_{cb}^- and an enhanced photocatalytic activity.⁵⁹ Ti_{0.7}W_{0.3}O₂ NPs with high conductivity



Scheme 1 Proposed phenol photocatalytic degradation mechanism at the Ti_{0.7}W_{0.3}O₂/TiO₂ NCI.

might cause fast electron transfer and effectively restrain the recombination of $e_{cb}^- - h_{vb}^+$ pairs in the bulk catalyst, which can then diffuse to the surface and react with pollutants.⁵⁴ Hydroxyl radical ($\cdot OH$) formation occurred at the Ti_{0.7}W_{0.3}O₂/TiO₂ NCI by h_{vb}^+ trapping adsorbed hydroxyl and hydration molecules (OH^-/H_2O). Meanwhile, e_{cb}^- could react with molecular oxygen (O_2) adsorbed at the NCI and produce superoxide radical anion ($\cdot O_2^-$). Acidic conditions could generate a higher affinity towards unpaired e_{cb}^- of NCI, leading to the formation of more hydroxyl radicals ($\cdot HO_2^-$).^{98,99} The h_{vb}^+ could also oxidize pollutants directly. These might account for the extraordinary photocatalytic activity of Ti_{0.7}W_{0.3}O₂/TiO₂ NCI.

4. Conclusions

In summary, Ti_{0.7}W_{0.3}O₂/TiO₂ nanocomposite interfacial photocatalysts with loading of different weight ratios of Ti_{0.7}W_{0.3}O₂ NPs were designed and synthesized for the photocatalytic degradation of phenol in wastewater under the illumination of ultraviolet visible light. The optimum photocatalytic degradation of phenol conditions were pH 4.5, a catalyst dosage of 0.45 g L⁻¹ and phenol initial concentration of 95 ppm. The 5 wt% Ti_{0.7}W_{0.3}O₂ NPs was the best loading level, and the initial rate constant (k) for 5 wt% Ti_{0.7}W_{0.3}O₂/TiO₂ NCI was over 3.9 times that in 0.3 wt% Pt/TiO₂. The valence bands of TiO₂ NSs, Ti_{0.7}W_{0.3}O₂ NPs and 5 wt% Ti_{0.7}W_{0.3}O₂/TiO₂ NCI were 3.01, 2.65 and 2.83 eV, the band gap energies were 3.21, 2.05 and 2.37 eV, respectively. Then the conduction bands of the above three materials were measured to be -0.20, 0.60 and 0.46 eV. Ti_{0.7}W_{0.3}O₂/TiO₂ NCI showed a greatly broadened light response range, shorter band gap energy and good stability and recyclability. A Schottky barrier was formed at the NCI between TiO₂ NSs and Ti_{0.7}W_{0.3}O₂ NPs, leading to

a higher formation of h_{vb}^+ and e_{cb}^- , and the $Ti_{0.7}W_{0.3}O_2$ NPs could quickly transfer e_{cb}^- and effectively restrain the recombination of e_{cb}^- - h_{vb}^+ pairs for high conductivity. A large number of superoxide radicals were generated in the suspension in the photocatalytic degradation of phenol by the $Ti_{0.7}W_{0.3}O_2/TiO_2$ NCI, which enhanced the photocatalytic activity. Besides, five and six kinds of intermediates were identified in the suspension of P-25 and Pt/TiO_2 , respectively, and six kinds of intermediates were found in the suspension of $Ti_{0.7}W_{0.3}O_2/TiO_2$. The photocatalytic degradation of phenol over P-25 followed a radical reaction mechanism. The photocatalytic degradation of phenol over Pt/TiO_2 and $Ti_{0.7}W_{0.3}O_2/TiO_2$ followed both a radical reaction mechanism and hole reaction mechanism, which proceeded in parallel.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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