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Layer-by-Layer Self-Assembly of Metal/Metal Oxide Superstructures: Self-Etching Enables Boosted Photoredox Catalysis

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ABSTRACT: The capability of noble metal nanoparticles (NPs) as efficient charge transfer mediators to stimulate Schottkyjunction-triggered charge flow in multifarious photocatalysis has garnered enormous attention in the past decade. Nevertheless, finetuning and controllable fabrication of a directional charge transport channel in metal/semiconductor heterostructures via suitable interface engineering is poorly investigated. Here, we report the progressive fabrication of a tailor-made directional charge transfer channel in Pt nanoparticles (NPs)-inlaid WO₃ (Pt-WO₃) nanocomposites via an efficient electrostatic layer-by-layer (LbL) selfassembly integrated with a thermal reduction treatment, by which oppositely charged metal precursor ions and polyelectrolyte building blocks were intimately and alternately assembled on the WO₃ nanorods (NRs) by substantial electrostatic interaction. LbL



self-assembly buildup and in situ self-etching-induced structural variation of WO_3 NRs to a microsized superstructure occur simultaneously. We found that such exquisitely crafted Pt-WO₃ nanocomposites exhibit conspicuously enhanced and versatile photoactivities for nonselective mineralizing of organic dye pollution and reduction of heavy metal ions at ambient conditions under both visible and simulated sunlight irradiation, demonstrating a synergistic effect. This is attributed to the imperative contribution of Pt NPs as electron traps to accelerate the directional high-efficiency electron transport from WO₃ to Pt NPs, surpassing the confinement of electron transfer kinetics of WO₃ owing to low conduction level. More intriguingly, photoredox catalysis can also be triggered simultaneously in the same reaction system. The primary in situ produced active species in the photocatalytic reactions were specifically analyzed, and underlying photocatalytic mechanisms were determined. Our work would provide a universal synthesis strategy for constructing various metal-decorated semiconductor nanocomposites for widespread photocatalytic utilizations.

1. INTRODUCTION

Photocatalysis represents a promising and green technique to achieve solar energy conversion including photocatalytic H₂ and O_2 production, ¹⁻⁹ photoreduction of CO_2 to value-added fuels,¹⁰ and mineralization of organic contaminations.¹¹ With regard to the various nanostructured semiconductors utilized for photocatalysis, one-dimensional (1D) semiconductors demonstrate incomparable structural merits compared with nanoparticulate and bulk counterparts including excellent light absorption and propagation in conjunction with enhanced charge separation/transfer efficiency along the 1D framework. 12-15 Tungsten oxide (WO₃) has been deemed as an attractive light-harvesting antenna owing to a favorable band gap (2.4-2.8 eV), good physicochemical stability, and high oxidation potential.^{16–19} Nevertheless, detrimental defects on the WO₃ surface result in a high charge recombination rate and sluggish electron transfer kinetics which makes the photoreduction catalysis inaccessible considering its low reduction potential of electrons in the conduction band (CB). $^{20-25}$

Construction of metal-adorned semiconductors is regarded as an efficacious route to stimulate the directional electron transfer from semiconductor to metal nanocrystals (NCs) which is accompanied by the Schottky-junction-induced charge flow, boosting the charge transport kinetics and retarding the charge recombination.^{26–29} Inspired by this, the rational combination of metal NCs with 1D WO₃ in an appropriate fashion for fabricating metal/1D WO₃ composite photocatalytic systems would afford a feasible avenue for the fine-

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tuning of electron transport over WO₃. It has been wellestablished that interfacial charge transfer efficiency is closely associated with the integration mode between metal NCs and a semiconductor, rendering the pursuit of suitable and feasible synthesis strategies highly desirable. Conventional approaches for the construction of metal/WO₃ heterostructures are predominantly centered on hydrothermal, photodeposition, and dipping-calcination approaches.²⁶ However, most of these methods involve the preparation of nanocomposites in a slurry ensemble without exquisite interface modulation and structure engineering, which hurdles the preparation of metal/WO₃ heterostructures with a well-defined interface, failing to boost the photoactivities.

Layer-by-layer (LbL) self-assembly has been made evident as a versatile platform to design various multilayered nanostructures by rationally selecting the suitable building blocks such as polyelectrolyte (PE) and colloidal nanoparticles, rendering harmony integration of diverse assembly units in an integrated ensemble accessible.^{19,30–37} LbL self-assembly is driven by varying molecular interaction such as electrostatic force, hydrogen bonding, covalent bonding, and complementary base pairing which serves as the predominant impetus.³⁸ Among which, of particular note is the electrostatic LbL assembly which is dominated by the surface charge properties of assembly units.^{39–41} The ionic metal precursors (e.g., AuCl₄⁻¹, PtCl₄²⁻, and PdCl₄²⁻ etc.) can be harnessed as the building block for electrostatic LbL self-assembly with the oppositely charged PE on the semiconductor, by which metal precursors and PEs can be intimately and alternately deposited on the semiconductors. In this way, metal/semiconductor heterostructures are readily attained by calcination to remove the PE, and meanwhile, metal precursors are thermally reduced to metal NCs.

Herein, potassium tetrachloroplatinate (PtCl₄²⁻) ions and poly(diallyldimethylammonium chloride) (PDDA) with oppositely charged properties were selected as the building blocks for constructing Pt-WO₃ nanocomposites by an electrostatic LbL self-assembly. Alternate attachment of $PtCl_4^{2-}$ ions and an ultrathin PDDA layer on the WO3 nanorods (NRs) via electrostatic interaction followed by postannealing treatment affords monodisperse deposition of Pt nanoparticles (NPs) on the WO₃ substrate. Simultaneously, in situ structural variation of WO₃ NRs to a spherical microsized nanostructure as a result of in situ self-etching occurs during the progressive LbL assembly, resulting in the hierarchical Pt-WO₃ nanocomposites. The results suggest that LbL-assembled Pt-WO₃ nanocomposites demonstrate considerably boosted photoactivities toward oxidation of organic dye pollution and reduction of heavy metal ions under the irradiation of visible and simulated sunlight, superior to pristine WO₃ NRs. The Pt NPs in Pt-WO₃ nanocomposites serve as highly efficient electron traps to accelerate the directional electron flow from WO₃ to Pt NPs and promote the charge separation over WO₃ NRs. Alternatively, primary active species in the photoreactions were specifically analyzed, and the photoredox catalysis mechanism along with the in situ etching mechanism were elucidated. It is hoped that our work would offer an effective and general approach to fabricate diverse metal/metal oxide heterostructures at ambient conditions for solar energy conversion.

2. EXPERIMENTAL SECTION

2.1. Preparation. 2.1.1. Preparation of WO_3 NRs. WO_3 NRs were prepared by a hydrothermal method.⁴² Detailed information is provided in the Supporting Information.

2.1.2. LbL Assembly of Pt-WO₃ Nanocomposites. PDDA (0.5 M NaCl, pH = 5.5) and poly(styrenesulfonate) (PSS, 0.5 M NaCl, pH = 3.5) were utilized as the assembly units for LbL assembly. Specifically, 100 mg of WO3 NRs was dispersed in aqueous PDDA solution, stirred for 10 min, and washed with deionized (DI) H₂O. PDDAmodified WO₃ NRs were then distributed into aqueous PSS solution, stirred, and washed with DI H2O, which leads to WO3 NRs@ PDDA@PSS. Another PDDA layer was deposited on the WO3 NRs@ PDDA@PSS by the same method, which produces the WO₃ NRs@ PDDA@PSS@PDDA. Subsequently, 10 mg of WO3 NRs@PDDA@ PSS@PDDA was redispersed into aqueous K_2PtCl_4 (1 mg/mL) solution, stirred for 2 h, and washed with DI H₂O. The above process was defined as one assembly bilayer, i.e., WO₃ NRs@PDDA@ $PSS@(PDDA-PtCl_4^{2-})_1$. The following procedures were repeated by alternate deposition of PDDA and $PtCl_4^{2-}$ ions on the WO₃ NRs@ PDDA@PSS, engendering the WO3 NRs@PDDA@PSS@(PDDA- $PtCl_4^{2-})_n$ which were finally annealed at 450 °C in air for 1 h to obtain Pt-WO3 nanocomposites.

2.2. Characterization. Zeta potentials (ξ) were detected by dynamic light scattering analysis (ZetasizerNano ZS-90). Morphologies were probed by field-emission scanning electron microscopy (FESEM, Carl Zeiss). Transmission electron microscopy (TEM) images were collected on a JEOL-2010 instrument. The crystal structure was determined by X-ray diffraction (XRD). Fourier transform infrared (FTIR) spectra were collected on an infrared spectrometer (Tianjin, China). UV-vis diffuse reflectance spectra (DRS) (Varian) were obtained using BaSO₄ as the reflectance background. Specific surface areas were probed on an automated gas sorption analyzer. Raman spectra were detected on a Raman spectroscopy (Dxr-2xi) instrument. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a photoelectron spectrometer (ESCALAB 245). Photoluminescence (PL) spectra were tested on a Varian spectrometer. Transient PL decay curves were obtained by time-correlated single photocounting technique (Edinburgh Analytical Instruments F900). Photoelectrochemical (PEC) measurements were performed utilizing a conventional three-electrode configuration, and primary active species produced in the photocatalytic reactions were probed. The detailed information is provided in the Supporting Information

2.3. Photoactivity Measurements. 2.3.1. Photooxidation Performance. Catalyst (20 mg) was added into Rhodamine B (RhB) aqueous solution (40 mL, 5 ppm). Before photocatalytic reaction, the mixture was stirred in the dark for 1 h to reach the equilibrium of adsorption-desorption at ambient conditions. After that, a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfect Light Co., Ltd.) with a UV-CUT filter ($\lambda > 420$ nm) was utilized as the light source. A 2 mL portion of the solution was withdrawn from the reaction system at every 0.5 h interval. After removing the catalyst, residual solution was analyzed by a UV-vis absorption spectrophotometer (GENESYS, 10S).

2.3.2. Photoreduction Performance. Catalyst (20 mg) was dispersed in Cr(VI) aqueous solution ($K_2Cr_2O_7$, 40 mL, 5 ppm) and stirred in the dark for 0.5 h to ensure the equilibrium of adsorption–desorption between the catalysts and reactant. A 2 mL portion of the solution was withdrawn at every 0.5 h interval and analyzed by a UV–vis absorption spectrophotometer (GENESYS, 10S). Photocatalytic efficiency was evaluated by the formula below:³²

$$conversion = (C_0 - C)/C_0 \times 100\%$$
(1)

where C_0 and C are the original concentration and concentration of reactant after reaction, respectively.

2.3.3. Simultaneous Photoredox Catalytic Performances. Simultaneous photocatalytic reduction of Cr (VI) (5 ppm) and mineralization of RhB (5 ppm) were carried out under visible light



Scheme 1. Schematic Flowchart for LbL Self-Assembly of Pt-WO₃ Nanocomposites

Figure 1. (a) XRD results, (b) FTIR spectra, and (c) DRS results with (d) band gap determination for the WO_3 NRs and $(Pt)_2$ - WO_3 nanocomposite.

 $(\lambda > 420 \text{ nm})$ irradiation. The detailed analysis process is analogous to the aforementioned elucidation.

3. RESULTS AND DISCUSSION

Scheme 1 demonstrates the fabrication of Pt-WO₃ nanocomposites via an electrostatic LbL assembly. First of all, an ultrathin PDDA layer was deposited on the surface of WO₃ NRs (WO₃ NRs@PDDA) to provide a positively charged surface considering that WO₃ NRs are negatively charged. Subsequently, an ultrathin PSS layer with a negatively charged surface was deposited on the positively charged WO₃ NRs@ PDDA, after which another PDDA layer was electrostatically deposited to produce WO₃ NRs@PDDA@PSS@PDDA. The favorable surface charges of PEs and WO₃ NRs are beneficial for electrostatic LbL self-assembly. The variation of the WO₃ NRs' surface charge after PE modification can be monitored by ζ potential results. As displayed in Figure S1, ζ potentials of WO3 NRs are negative, indicating that WO3 NRs are intrinsically negatively charged in the aqueous phase. The changes of WO3 NRs surface charge after PDDA and PSS modifications are unveiled in Figure S2 which shows that PDDA is responsible for the generation of a positively charged surface, and PSS favors the formation of a negatively charged surface (Table S1). Hence, PtCl₄²⁻ ions as the precursor of Pt NCs can be deposited on the WO3 NRs@PDDA@PSS@ PDDA via electrostatic interaction, and its amount is mediated by the assembly number, which produces the multilayered WO₃ NRs@PDDA@PSS@(PDDA/PtCl₄²⁻)_n nanocomposites. Eventually, Pt-WO₃ nanocomposites were obtained by calcining WO₃ NRs@PDDA@PSS@(PDDA/PtCl₄²⁻)_n to enable the reduction of PtCl₄²⁻ precursor to Pt NPs, and meanwhile, PEs (PDDA and PSS) were removed to afford a more intimate interface. Intriguingly, a spherical hierarchical WO₃ superstructure was produced owing to the acidic etching in the LbL self-assembly.

As displayed in Figure 1a, the $(Pt)_2$ -WO₃ nanocomposite exhibits a similar XRD result to blank WO3 NRs with all the characteristic peaks corresponding to hexagonal WO₃ (JCPDS 75-2187), respectively. No diffraction peak of Pt NPs is discerned, which is due to the relatively low deposition percentage of Pt NPs. As shown in Figure S3a, two obvious peaks at 758 and 810 cm⁻¹ in the Raman spectrum of blank WO₃ NRs are attributable to the vibration mode of W—O bonds [i.e., v(O-W-O)];^{43,44} the peak at 927 cm⁻¹ corresponds to the W=O bonds, 57 and the peak at 326 cm^{-1} arises from the bending mode of O—W—O bonds [i.e., $\delta(O-W-O)$].^{25,55,57} A red-shift of the peak position was visualized in the Raman spectrum of the (Pt)₂-WO₃ nanocomposite compared with WO₃ NRs, implying that electron transport occurs between WO3 and Pt NPs due to electronic interaction (Figure S3b). Figure 1b shows an apparent peak at 825.2 cm⁻¹ in the FTIR spectrum of the $(Pt)_2$ -WO₃ nanocomposite, and it is assigned to the stretching vibration mode of W-O-W bonds. Besides, another two peaks at 2922.7 and 2854 cm⁻¹ (Figure 1b, inset) were also visualized, and they stem from the stretching vibration mode of the -- CH_2 group (Table S2) from the minute remaining PDDA on the WO₃ surface.

As displayed in Figure 1*c*, both WO₃ NRs and the (Pt)₂-WO₃ nanocomposite demonstrate almost the same absorption band edge at ca. 455 nm, and it arises from the photoexcitation of the WO₃ substrate. Note that light absorption of the (Pt)₂-WO₃ nanocomposite was enhanced compared with WO₃ NRs, suggesting that Pt NPs deposition reinforces the light absorption of the (Pt)₂-WO₃ nanocomposite, consistent with the sample color (Figure 1*c*, inset). Band gaps (E_g) of WO₃ NRs and the (Pt)₂-WO₃ nanocomposite are identified by the formula below:⁴⁴

$$\alpha h \gamma = A (h \gamma - E_{\rm g})^{n/2} \tag{2}$$

where α , $h\gamma$, and A are the absorption coefficient, light energy, and constant, respectively. According to this formula, $E_{\rm g}$ values of WO₃ NRs and the (Pt)₂-WO₃ nanocomposite are estimated as ca. 2.73 and 2.69 eV (Figure 1d), respectively. The result suggests that in situ etching and Pt NP deposition fail to change the $E_{\rm g}$ of WO₃.

As shown in Figure 2a-c and Figure S4a, WO₃ NRs demonstrate a 1D nanostructure with an average size of ca. 100 nm and length of ca. 5 μ m. Figure 2d reveals that the morphology of the $(Pt)_2$ -WO₃ nanocomposite is different from WO₃ NRs with a nanoarchitecture varying from NR to microsized nanostructure comprising various small NPs (Figure 2e) along with sporadic Pt NPs deposited on the WO₃ surface. A series of control experiments were performed to unlock the reason for the structure change of WO₃ NRs. First, the morphology of WO3 NR annealed at the same temperature was explored, and the result is exhibited in Figure S4b, wherein WO₃ NRs still exhibit a rodlike structure, verifying that the structure change of the $(Pt)_2$ -WO₃ nanocomposite did not originate from calcination. As unveiled in Figure S4c,d, FESEM images of the (Pt)₂-WO₃ nanocomposite before calcination are different from WO3 NRs without the appearance of NRs, corroborating that the structure of the $(Pt)_2$ -WO₃ nanocomposite has been altered before calcination. Alternatively, the morphology of HCl-



Figure 2. FESEM images of (a-c) blank WO₃ NRs and (d-f) the $(Pt)_2$ -WO₃ nanocomposite with corresponding (g-i) elemental mapping results. (j) HRTEM images of WO₃ NRs. (k) TEM and (l) HRTEM images of the $(Pt)_2$ -WO₃ nanocomposite.

treated WO₃ NRs was also probed, wherein a HCl solution possessing the same pH as the K₂PtCl₄ precursor was utilized to treat WO₃ NRs under the same conditions. It is obvious that morphologies of HCl-etched WO₃ NRs without (Figure S4e) and with (Figure S4f) calcination are similar to the $(Pt)_2$ -WO₃ nanocomposite, substantiating that WO3 NRs are etched by the acidic precursor solution in the LbL self-assembly process. Consistently, as shown in Figure 2f-i, EDX and elemental mapping results of the (Pt)₂-WO₃ nanocomposite uncover a homogeneous distribution of W, O, and Pt elements, indicative of the attachment of Pt NPs on the WO₃ NRs. TEM images of WO₃ NRs in Figure S5a,b exhibit the 1D structure with smooth surface, and the HRTEM image (Figure 2j) uncovers the lattice fringe of ca. 0.159 nm corresponding to the (311) crystal plane of WO3 NRs. TEM images of the (Pt)2-WO3 nanocomposite in Figure 2k and Figure S5c make evident that Pt NPs are deposited on the WO₃ NRs. Figure 2l and Figure S5d show the HRTEM images of the $(Pt)_2$ -WO₃ nanocomposite, wherein a lattice fringe of 0.139 nm is attributable to the (220) crystal plane of Pt NPs.

Survey spectra of pristine WO₃ NRs and the $(Pt)_2$ -WO₃ nanocomposite (Figure 3a) reveal the presence of W and O elements from the WO₃ substrate, but no Pt signal was visualized owing to its low loading amount. As mirrored in Figure 3b, the high-resolution Pt 4f spectrum of the $(Pt)_2$ -WO₃ nanocomposite demonstrates two peaks at 71.04 (Pt 4f_{7/2}) and 73.15 (Pt 4f_{5/2}) eV which point to the metallic Pt species (i.e., Pt⁰), verifying that the PtCl₄²⁻ precursor has been reduced to Pt NPs after annealing.⁴⁵ The high-resolution W 4f spectrum of the (Pt)₂-WO₃ nanocomposite (Figure 3cI) exhibits two peaks at 35.93 (W 4f_{7/2}) and 38.08 (W 4f_{5/2}) eV which correspond to W⁶⁺, coincidental with the high-resolution W 4f spectrum of WO₃ NRs (Figure 3cII).⁴⁶ Analogously, the high-resolution O 1s spectrum (Figure 3dI) of the (Pt)₂-WO₃



Figure 3. (a) Survey spectra and high-resolution (b) Pt 4f, (c) W 4f, and (d) O 1s spectra of (I) the $(Pt)_2$ -WO₃ nanocomposite and (II) blank WO₃ NRs.

nanocomposite demonstrates two peaks at 530.48 and 532.38 eV which are attributable to lattice oxygen (W–O) and the hydroxyl (–OH) group,⁴⁷ which is in line with the high-resolution O 1s spectrum of WO₃ NRs (Figure 3dII). Alternatively, high-resolution N 1s (Figure S6a) and Cl 2p spectra (Figure S6b) of the (Pt)₂-WO₃ nanocomposite make evident that most of the PEs were removed after annealing. For reference, chemical bond species vs binding energy are summarized in Table S3.

Photocatalytic performances of WO₃ NRs and the Pt-WO₃ nanocomposite were assessed by mineralization of Rhodamine B (RhB) under the irradiation of visible ($\lambda > 420$ nm) and simulated sunlight.⁴⁸ Blank experiments (without light or catalyst) demonstrate no photoactivity (Figure S7), confirming that the reaction is indeed a photocatalytic process. Figure 4a exhibits the visible-light-driven photocatalytic activities of WO₃ NRs and (Pt)_n-WO₃ (n = 1, 2, 3, 4) nanocomposites, and the result suggests that (Pt)_n-WO₃ (n = 1, 2, 3, 4) nanocomposites exhibit substantially improved photoactivities with respect to blank WO₃ NRs with the involvement of Pt NPs, implying that Pt NP can serve as electron traps for efficiently capturing electrons photoexcited from WO₃ NRs. Photoactivities of the



Figure 4. (a) Photoactivities of blank WO₃ NRs and (Pt)_{*n*}-WO₃ (n = 1, 2, 3, 4) nanocomposites toward RhB mineralization under the irradiation of visible light ($\lambda > 420$ nm). (c) Photoactivities of blank WO₃ NRs and the (Pt)₂-WO₃ nanocomposite under the irradiation of simulated sunlight with kinetic curves in parts b and d, respectively. Cyclic photoreactions of the (Pt)₂-WO₃ nanocomposite under (e) visible ($\lambda > 420$ nm) and (f) simulated sunlight irradiation. Photocatalytic reduction of Cr₂O₇²⁻ ions over blank WO₃ NRs and the (Pt)₂-WO₃ nanocomposite under (g) visible ($\lambda > 420$ nm) and (h) simulated solar light irradiation with kinetic curves in parts i and j, respectively.

samples follow the order of $(Pt)_2$ -WO₃ > $(Pt)_3$ -WO₃ > $(Pt)_1$ - $WO_3 > (Pt)_4$ - $WO_3 > WO_3$ NRs, by which the optimal assembly bilayer number is determined to be 2. As displayed in Figure 4b, according to the first-order-kinetic model,⁴² kinetic rate constants of the samples were determined as 0.0074, 0.020 25, 0.033, 0.0309, and 0.0173 min⁻¹ (Figure S8) corresponding to WO₃ NRs, (Pt)₁-WO₃, (Pt)₂-WO₃, (Pt)₃-WO₃, and $(Pt)_{4}$ -WO₃, respectively. $(Pt)_{n}$ -WO₃ demonstrates a markedly enhanced reaction kinetic rate constant relative to blank WO3 NRs, verifying that the Pt NP loading amount is closely associated with the photoactivities of the $(Pt)_n$ -WO₃ nanocomposite, among which the (Pt)₂-WO₃ nanocomposite exhibits the optimal photoactivity. Besides, as mirrored in Figure $4c_1$ the $(Pt)_2$ -WO₃ nanocomposite still exhibits a considerably improved photoactivity and larger kinetic constant (Figure 4d) in comparison with blank WO₃ NRs under the irradiation of simulated sunlight. The general contributing role of Pt NPs as an electron trap was thus ascertained regardless of utilizing visible or simulated sunlight as the light source. Subsequently, photostability of the catalysts was probed. Cyclic photoreactions indicate that the $(Pt)_2$ -WO₃ nanocomposite demonstrates good photostability with no obvious photoactivity decay under visible ($\lambda > 420$ nm) (Figure 4e) and simulated sunlight (Figure 4f) irradiation. Consistently, as reflected by the XPS results (Figure S9) of the (Pt)₂-WO₃ nanocomposite after cyclic reaction, chemical valence states of W, O, and Pt elements were not altered. Alternatively, XRD patterns (Figure S10a) of the (Pt)₂-WO₃ nanocomposite before and after cyclic reaction also exhibit the same crystalline structure. In addition, FTIR spectra of (Pt)₂-WO₃ (Figure S10b) were not changed after cyclic reaction, once again corroborating the good photostability of the (Pt)₂-WO₃ nanocomposite.

Photoreduction of heavy metal ions (e.g., $Cr_2O_7^{2-}$) over WO_3 NRs and the $(Pt)_2$ -WO₃ nanocomposite was also performed. Blank experiments (Figure S11) suggest that it is a light-driven photocatalytic process. As displayed in Figure $4g_{1}h_{1}$, the $(Pt)_{2}$ -WO₃ nanocomposite exhibits significantly improved photoreduction performances compared with blank WO_3 NRs toward $Cr_2O_7^{2-}$ reduction under visible ($\lambda > 420$ nm) (Figure 4g) and simulated sunlight (Figure 4h) irradiation. The results suggest that more electrons are involved in the reaction as a result of more enhanced electron-hole separation over the (Pt)₂-WO₃ nanocomposite. This deduction can be verified by the kinetic rate constants of WO_3 NRs and the $(Pt)_2$ - WO_3 nanocomposite (Figure 4i,j). With a view to highlighting the crucial role of electrons in the photoreduction of $Cr_2O_7^{2-}$ over the $(Pt)_2$ -WO₃ nanocomposite, a control experiment with adding $K_2S_2O_8$ as the electron scavenger was performed. Figure S12 implies that the photoreduction performances of the (Pt)₂-WO₃ nanocomposite were substantially reduced under light (visible and simulated sunlight) irradiation upon adding K₂S₂O₈, verifying that the electrons are the active species in the reaction.

Simultaneous photocatalytic removal of RhB and Cr(VI) over the $(Pt)_2$ -WO₃ nanocomposite under the irradiation of visible light ($\lambda > 420$ nm) was performed.⁴⁹ As reflected by Figure 5a,b, the $(Pt)_2$ -WO₃ nanocomposite shows enhanced photoactivity with a higher removal efficiency of 99.1% for RhB and reduction efficiency of 54.5% for Cr(VI) than those of WO₃ NRs, i.e., 94% for RhB and 38.4% for Cr (VI). As displayed in Figure 5c,d, consistently, the $(Pt)_2$ -WO₃ nanocomposite exhibits a larger kinetic rate constant relative to



Figure 5. Photocatalytic performances of blank WO₃ NRs and the $(Pt)_2$ -WO₃ nanocomposite for simultaneous removal of (a) RhB and (b) Cr (VI) ions under the irradiation of visible light ($\lambda > 420$ nm) with kinetic rate constants in parts c and d, respectively.

blank WO_3 NRs in simultaneous photocatalytic RhB mineralization and Cr(VI) photoreduction under visible light irradiation, highlighting the essential role of Pt NPs in boosting the photoredox catalysis in an integrated reaction system.

Predominant active species generated in the photocatalytic reactions were probed to reveal the underlying reaction mechanism of the $(Pt)_2$ -WO₃ nanocomposite. To this end, a series of control experiments with adding potassium persulfate $(K_2S_2O_8)$, benzoquinone (BQ), ammonium oxalate (AO), and tert-butyl alcohol (TBA) for trapping electrons (e⁻), superoxide $(^{\bullet}O_2^{-})$ radicals, holes (h^+) , and hydroxyl $(^{\bullet}OH)$ radicals were carried out.²³ As mirrored by Figure 6a, when AO and BQ were added into the reaction system, visible-light-driven photoactivity of the (Pt)₂-WO₃ nanocomposite was remarkably reduced, implying that holes and ${}^{\circ}O_2^{-}$ radicals are the main active species. However, when TBA and K₂S₂O₈ were added, photoactivity of the $(Pt)_2$ -WO₃ nanocomposite was not markedly influenced. Based on this, the contributing role of the active species is ${}^{\bullet}O_2^- > h^+ > e^- > {}^{\bullet}OH$. Besides, photoactivities of the (Pt)₂-WO₃ nanocomposite in the presence of N₂ and O₂ purge were also probed. Figure 6b shows that photoactivity of the $(Pt)_2$ -WO₃ nanocomposite was decreased in the N2-saturated reaction system but increased in the O_2 -saturated reaction environment, verifying that O_2 is in favor of boosting the photoactivity of the $(Pt)_2$ -WO₃ nanocomposite. This is reasonable since dissolved O_2 is closely related to the ${}^{\bullet}O_2^{-}$ and ${}^{\bullet}OH$ radical generation. As reflected by Figure 6c,d, when these control experiments were carried out under simulated solar light irradiation, analogous results were observed. 'OH radical production in the reaction system can also be probed by liquid-phase PL spectra.48 As shown in Figure 6e,f, the peak intensity at 426 nm increases gradually with prolonging the irradiation time, confirming the progressive generation of [•]OH radicals.⁴² Additionally, as revealed in Figure 6g, the amount of OH[•] radicals produced over the (Pt)₂-WO₃ nanocomposite under simulated solar light irradiation is higher than that produced under visible light irradiation because of larger light intensity. On the other hand, H_2O_2 can be probed by a DPD-POD method.⁵⁰ As shown in



Figure 6. Photoactivities of the $(Pt)_2$ -WO₃ nanocomposite with adding different scavengers under the irradiation of (a) visible ($\lambda > 420$ nm) and (c) simulated sunlight. Photoactivities of the $(Pt)_2$ -WO₃ nanocomposite with O₂ and N₂ purge under (b) visible ($\lambda > 420$ nm) and (d) simulated solar light irradiation. Liquid-phase PL spectra of the $(Pt)_2$ -WO₃ nanocomposite under (e) visible ($\lambda > 420$ nm) and (f) simulated solar light irradiation using TA as a probe molecule. (g) PL peak intensity vs irradiation time for the $(Pt)_2$ -WO₃ nanocomposite under ($\lambda > 420$ nm) visible and simulated solar light irradiation. H₂O₂ production amount over blank WO₃ NRs and the $(Pt)_2$ -WO₃ nanocomposite under (h) visible ($\lambda > 420$ nm) and (i) simulated solar light irradiation based on a DPD-POD method.

Figure S13a, the peak intensity (512 and 552 nm) gradually increases under visible light irradiation ($\lambda > 420$ nm) with elongating the irradiation time, indicating the generation of H₂O₂ in the reaction system. Similar results were observed for the (Pt)₂-WO₃ nanocomposite under simulated solar light irradiation (Figure S13b). It is noteworthy that the H₂O₂ amount produced over the (Pt)₂-WO₃ nanocomposite is higher than that produced over blank WO₃ NRs (Figure S13c,d) under visible ($\lambda > 420$ nm) (Figure 6h) and simulated sunlight irradiation (Figure 6i), confirming the important role of Pt NPs in promoting the H₂O₂ production. This is understandable considering the crucial role of Pt NPs as electron reservoirs, which is beneficial for H₂O₂ production.

The PEC investigation was performed to evaluate the charge separation efficiency.³⁶ Figure 7a,b shows the photocurrents of WO₃ NRs and the (Pt)₂-WO₃ nanocomposite under both visible ($\lambda > 420$) and simulated solar light irradiation, from which it is obvious that the (Pt)₂-WO₃ nanocomposite demonstrates a significantly enhanced photocurrent with respect to blank WO₃ NRs, implying a higher charge separation efficiency over the (Pt)₂-WO₃ nanocomposite

than WO₃ NRs. This is ascribed to the fact that electrons produced in the conduction band (CB) of WO₃ NRs can smoothly transfer to the Pt NPs on account of the occurrence of Schottky-junction-driven electron flow under light irradiation, resulting in the enhanced charge separation. In this case, Pt NPs act as efficient electron reservoirs to prolong the charge lifetime.⁵¹ As displayed in Figure 7c,d, EIS Nyquist plots of the (Pt)₂-WO₃ nanocomposite exhibit a smaller semicircle arc radius than WO₃ NRs under both visible ($\lambda > 420$ nm) and simulated sunlight irradiation, corroborating that a combination of Pt NPs with WO₃ NRs reduces the interfacial charge transfer resistance.^{52,53} As reflected by the fitted EIS results in Tables S4 and S5, the (Pt)₂-WO₃ nanocomposite exhibits a much lower charge transfer resistance (R_{ct}) under both visible $(\lambda > 420 \text{ nm})$ and simulated solar light irradiation relative to WO₃ NRs. Figure 7e shows the Mott–Schottky (M–S) plots of the $(Pt)_2$ -WO₃ nanocomposite and WO₃ NRs, by which the flat-band potentials (E_f) of blank WO₃ NRs and the $(Pt)_2$ -WO₃ nanocomposite are determined as 0.36 and 0.30 V vs NHE, respectively. Apparently, E_f potential of WO₃ was almost unchanged, and this indicates that Pt NPs deposition does not



Figure 7. (a, b) Photocurrent and (c, d) EIS Nyquist plots of blank WO₃ NRs and the (Pt)₂-WO₃ nanocomposite under (a, c) visible ($\lambda > 420$ nm) and (b, d) simulated sunlight irradiation, respectively. (e) M–S curves and (f) charge density (N_D) of blank WO₃ NRs and the (Pt)₂-WO₃ nanocomposite with a PEC cell diagram in part g. (h) Solid PL spectra ($\lambda_{ex} = 380$ nm) and (i) time-resolved PL decay curves ($\lambda_{ex} = 375$ nm) of blank WO₃ NRs and the (Pt)₂-WO₃ nanocomposite.

alter the energy level position of the WO₃ substrate; this is in faithful agreement with previous work.¹⁹ Besides, note that the M–S plot slope of the (Pt)₂-WO₃ nanocomposite is smaller than WO₃ NRs, which indicates that the (Pt)₂-WO₃ nanocomposite possesses a larger charge carrier density than WO₃ NRs. Charge density (N_D) of photoelectrodes is calculated based on the following formula:⁴²

$$N_{\rm D} = \left(\frac{2}{\epsilon_r \epsilon_0 e}\right) \left[\frac{d\left(\frac{1}{C^2}\right)}{dU_{\rm FL}}\right]^{-1}$$
(3)

where $e = 1.6 \times 10^{-19}$ C, $\varepsilon_0 = 8.86 \times 10^{-12}$ F m⁻¹, $\varepsilon = 300$ for WO₃,⁴⁸ and C is the capacitance. As displayed in Figure 7f,g, $N_{\rm D}$ values of WO₃ NRs and the (Pt)₂-WO₃ nanocomposite are 1.88 × 10¹⁸ and 3.0 × 10¹⁸ cm⁻³, for which (Pt)₂-WO₃ demonstrates a larger $N_{\rm D}$ than WO₃ NRs, consistent with the photoactivities.

PL and time-resolved PL (TRPL) spectroscopy were harnessed to probe the charge separation efficiency over the $(Pt)_2$ -WO₃ nanocomposite and to further understand the essential role of Pt NPs in facilitating electron transfer.⁵⁴ Figure 7h shows that WO₃ NRs possess a higher PL intensity

compared with the $(Pt)_2$ -WO₃ nanocomposite, which suggests that charge separation over $(Pt)_2$ -WO₃ is more efficient than that over blank WO₃ NRs, wherein electrons transfer from WO₃ to Pt NPs leading to the prolonged charge lifetime. This deduction can be confirmed by the TRPL results of WO₃ NRs and the $(Pt)_2$ -WO₃ nanocomposite.^{54,55} As unveiled by Figure 7i, the lifetime of charge carriers produced over the $(Pt)_2$ -WO₃ nanocomposite is longer than blank WO₃ NRs, consistent with the PL emission spectra (Figure 7h). The results suggest that Pt NPs decoration can effectively inhibit the charge recombination and elongate the lifetime, manifesting the imperative role of Pt NPs as an efficient charge transport medium for accelerating the unidirectional electron transfer from WO₃ NRs to Pt NPs.

Specific surface areas of WO₃ NRs and the $(Pt)_2$ -WO₃ nanocomposite were explored to evaluate whether they contribute to the enhanced photoactivities. As displayed in Figure S14, according to the IUPAC classification, WO₃ NRs and the $(Pt)_2$ -WO₃ nanocomposite exhibit the type IV isotherm which implies the formation of a mesoporous solid.¹⁹ Specific surface area and pore volume of the $(Pt)_2$ -WO₃ nanocomposite are determined as 7.2 m² g⁻¹ and 0.012 cm³ g⁻¹, which are comparable to WO₃ NRs (i.e., 9.44 m² g⁻¹

and 0.012 cm³ g⁻¹), as summarized in Table S6. The results suggest that enhanced photoactivity of the $(Pt)_2$ -WO₃ nanocomposite relative to WO₃ NRs is attributed to the improved charge separation as a result of the Pt NPs' deposition.

Figure S15 depicts the energy level configuration of the Pt-WO₃ nanocomposite to elucidate the charge transfer mechanism. CB and VB potentials of WO₃ were determined as 0.36 and 3.08 V vs NHE (Figure S15). The work function (Φ_A) of Pt is ca. 5.7 V (vs V_{ac}) according to previous work,⁵⁵ and the electron affinity (χ) of WO₃ is determined by the potential difference between E_{vac} and E_{CB} and is ca. 3.50 V (vs V_{ac}).^{42,48,56,57} Hence, when Pt NPs are decorated on the WO₃, electrons in the CB of WO₃ can flow to Pt NPs, resulting in negatively charged Pt NPs, while a positively charged space layer is generated on the WO₃, giving rise to a built-in electric field accompanied by the band bending and Schottky junction formation at the interface. Schottky barrier height $(\Phi_{\rm b})$ between WO₃ and Pt is calculated as 2.199 V (vs V_{ac}) according to the χ of WO₃ and work function of Pt. Note that the work function of WO₃ is smaller than that of Pt ($\Phi_A = 5.7$ V) (Figure S16a). Therefore, the electron can spontaneously transfer from WO₃ to Pt NPs (Figure S16b).

According to the above discussion, the photocatalytic mechanism of $Pt-WO_3$ nanocomposites was proposed (Scheme 2). When the $Pt-WO_3$ nanocomposite was irradiated

Scheme 2. Schematic Demonstration of the Photocatalytic Mechanism of the Pt-WO₃ Nanocomposite



by visible or simulated sunlight, electrons (e⁻) were photoexcited from the valence band (VB) of WO₃ to the CB with holes (h⁺) remaining in the VB. Immediately, electrons transfer from the CB of WO₃ to Pt NPs because of favorable energy level alignment between the CB of WO₃ and work function of Pt, wherein Pt NPs act as electron reservoirs to trap electrons and accelerate charge transfer, retarding the charge recombination. Subsequently, electrons captured by Pt NPs and holes in the VB of WO₃ participate in the following cascade reactions (eqs 4–8) to produce •OH radicals and H₂O₂.

$$WO_3 + h\nu \to e^- + h^+ \tag{4}$$

$$\bullet O_2^{-} + \bullet O_2^{-} + H^+ \to H_2 O_2 + O_2$$
(5)

$$H_2O_2 + \bullet O_2^- \to \bullet OH + OH^- + O_2 \tag{6}$$

$$h^{+} + -OH/H_2O \rightarrow 2 \bullet OH + 2H^{+}$$
⁽⁷⁾

$$Cr(VI) + e^- \rightarrow Cr(III)$$
 (8)

Notably, ${}^{\bullet}O_2^{-}$ radicals are generated by reducing O_2 with electrons; ${}^{\bullet}OH$ radicals result from direct oxidation of H_2O with holes, and the H_2O_2 intermediate stems from reduction of O_2 with two electrons. Ultimately, these in situ formed active species produced over Pt-WO₃ nanocomposites synergistically promote the mineralization of organic dye pollutant. With regard to the photoreduction reaction, electrons trapped by Pt NPs are able to reduce $Cr_2O_7^{2-}$ under light irradiation.

4. CONCLUSIONS

In summary, a directional electron transfer pathway was constructed in the Pt-WO₃ nanocomposite by an efficient electrostatic LbL self-assembly approach, wherein negatively charged noble metal precursor $(PtCl_4^{2-})$ and positively charged PDDA assembly units were alternately deposited on the WO₃ NRs surface. Etching of WO₃ NRs occurs owing to the use of the acidic metal ion precursor and then thermal reduction of the PtCl₄²⁻ precursor to Pt NPs by annealing, giving rise to the hierarchical Pt-WO3 superstructure with Pt NPs evenly deposited on the surface. Significantly, $(Pt)_n$ -WO₃ exhibit considerably enhanced photoredox performances toward mineralization of organic dye pollutants and photoreduction of $Cr_2O_7^{2-}$ with respect to WO_3 NRs under both visible and simulated solar light irradiation. This is attributed to the imperative role of Pt NPs as electron traps to efficiently capture the electrons for accelerating the electrons' transport from WO₃ to Pt NPs, boosting the charge separation and endowing the Pt-WO3 nanocomposite with considerably improved photoactivities. In situ etching of WO3 NRs to a hierarchical nanostructure afforded by LbL self-assembly benefits light harvesting, which also favors the improved photoactivities of the $(Pt)_n$ -WO₃ nanocomposites. The main active species in the photoredox catalysis were probed, and the photocatalytic mechanism was clearly determined. Our work would afford an efficacious and universal synthesis strategy for the construction of diverse metal/semiconductor heterostructures for photocatalytic applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00229.

Additional experimental details; ζ potentials; Raman spectra; FESEM images; TEM and HRTEM images; high-resolution N 1s and Cl 2p spectra; blank experiments; kinetic rate constants; survey and high-resolution spectra; XRD patterns and FTIR spectra; control experiments; UV–vis absorption spectra; N₂ adsorption–desorption isotherms; schematic illustration; M–S result; DRS result; chemical structure and surface charge properties; peak position with corresponding functional groups; chemical bond species vs B.E. for different samples; fitted EIS results; and a summary of specific surface area, pore volume, and pore size (PDF)

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Notes

The authors declare no competing financial interest.

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