Fabrication of Mesoporous PtO–ZnO Nanocomposites with Promoted Photocatalytic Performance for Degradation of Tetracycline

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ABSTRACT: Herein, we report a simple incorporation of PtO NPs at diverse percentages (0.2−0.8 wt %) onto a highly crystalline and mesoporous ZnO matrix by the wet-impregnation approach for degradation of tetracycline (TC) upon visible light exposure. These well-dispersed and small-sized PtO NPs provide the mesoporous PtO−ZnO nanocomposites with outstanding photocatalytic performance for complete TC degradation. The optimized 0.6% PtO−ZnO photocatalyst exhibits excellent TC degradation, and its degradation efficiency reached ~99% within 120 min. The photocatalytic performance of the 0.6% PtO−ZnO nanocomposite is 20 and 10 times higher than that of pristine ZnO and commercial P-25, respectively. The photodegradation rate of TC over the 0.6% PtO−ZnO nanocomposite is 34 and 12.5 times greater than that of pristine ZnO and commercial P-25, respectively. This is because of the large surface area, unique porous structure, synergistic effect, and broad visible light absorption of the PtO−ZnO nanocomposite. Moreover, mesoporous PtO−ZnO nanocomposites showed a high stability and recyclability over five iterations. This work demonstrates the remarkable role of combining PtO and ZnO photocatalysts in providing nanocomposites with significant potential for the preservation of human health through wastewater remediation.

1. INTRODUCTION

Semiconductor ZnO exhibits unique properties such as a wide band gap, large surface area, cost effectiveness, high chemical stability, and suitable positions of band edges in terms of the redox potentials for detoxification of organic compounds and hydrogen production.1−4 ZnO, as an efficient photocatalyst compared to TiO₂, has a higher harvest efficiency under UV illumination and shows little absorption of the solar spectrum.5,6 ZnO is comparatively plentiful, considering the evaluated reserves of zinc of about 230 million tonnes in mining areas of the earth.7 There has been considerable interest in the photocatalysis application of ZnO, in particular upon UV illumination; however, it cannot work well in visible light illumination; thus, scientists have been making efforts to overcome its shortcomings.8,9 To extend the photoactivity and photoresponse of ZnO in the broad visible light absorption (∼43% of the solar spectrum),10 its band structures are modified to promote H₂ generation and detoxification of organic compounds.11 This modification was carried out through several routes comprising doping noble metals, doping non-metal or metal ions, incorporating with narrow bandgap oxides such as Bi₂O₃ and Fe₃O₄, and dye sensitization.12−16

Precious metals like Pd, Pt, Au, and Ag and their oxide-based catalysts with high photocatalytic activity are considered as outstanding catalysts and are considerably employed in diverse industrial applications,17 predominately nano-sized noble metals with high utilization efficiency and excellent photocatalytic performance.18,19 Among noble metals, Pt and its oxide-based catalysts have excellent catalytic, chemical, and physical, properties, therefore possessing enormous research utilities.20−23 In the past 20 years, environmental pollution and global energy issues have encouraged significant development in photoelectric conversion and the photochemistry approach.24−28 As part of the fundamental research in electro-photochemistry, the ZnO photocatalyst has been employed and studied in photocatalytic degradation of various organic compounds and H₂ generation from water splitting.29−34 Upon light illumination, semiconductor materials are excited to create photogenerated holes with oxidizability and the
corresponding electrons with reducibility, and all of these migrate to the surface of the semiconductor materials.\textsuperscript{35} Antibiotics, in particular tetracycline, in water circumstances are commonly originated from domestic sewage, hospitals, industrial waste, and poultry farms.\textsuperscript{35} Due to the antibiotics’ stability in terms of chemical structure in aqueous solution, it is hard to eliminate them through conventional treatment and biodegradation processes.\textsuperscript{36} TC has received considerable attention as a representative antibiotic widely found in domestic wastewater. The remaining TC is eliminated by different approaches such as photocatalysis, advanced oxidation, adsorption, etc.\textsuperscript{37–39} Recently, the photocatalytic destruction of organic contaminants in aqueous solution has been considered a favorable avenue and environment-friendly green path, which directly destructs into innoxious products.\textsuperscript{38,39} With the popular use and despite the disadvantage of antibiotics, they have become critical due to their inherent resistance to bacteria, leading to intimidation to environmental pollution and global health. In the past 20 years, many research studies in photocatalytic degradation by employing different photocatalysts have attempted to synthesize appropriate, effective photocatalysts through visible light to benefit potential large-scale applications. Generally, the preparation strategies of the photocatalysts include an expensive organic stabilizer, a time-consuming process, and/or sophisticated equipment, thus emphasizing the need for further development. Consequently, it is important to fabricate an effective and simple procedure for obtaining a PtO–ZnO photocatalyst with high photocatalytic performance and well-defined structure.

Herein, we report a simple method of incorporation of PtO NPs onto a highly crystalline and mesoporous ZnO matrix by the wet-impregnation method for photocatalytic degradation of TC upon visible light exposure. The optimized 0.6\% PtO–ZnO photocatalyst exhibits an excellent degradation efficiency of TC, reaching \( \sim 99\% \). The photocatalytic performance of the 0.6\% PtO–ZnO nanocomposite is 20 and 10 times higher than that of pristine ZnO and commercial P-25, respectively. The photodegradation rate of TC over the 0.6\% PtO–ZnO nanocomposites was determined for 2 h of illumination. The photodegradation efficiency was estimated by TC analysis over outgassing at 110 °C for 12 h and followed by calcination at 400 °C for 3 h to collect mesostructured 0.2, 0.4, 0.6, and 0.8 wt \% PtO–ZnO nanocomposites.

2. EXPERIMENTAL SECTION

2.1. Materials. Pt(\( \text{NH}_3 \))\(_4\)(NO\(_3\))\(_2\), CH\(_3\)COOH, Zn(NO\(_3\))\(_2\), 6H\(_2\)O, C\(_6\)H\(_5\)OH, HCl, and nonionic surfactant Pluronic F-108 with \( M_w \sim 14 600 \) were acquired from Sigma-Aldrich.

2.2. Construction of Mesoporous PtO–ZnO Nanocomposites. A typical synthesis of mesoporous ZnO matrix was as follows: 0.2 g of F-108 surfactant was dissolved in 30 mL of C\(_2\)H\(_5\)OH with magnetic stirring for 60 min to get a clear solution. Then, 0.74 mL of HCl and 2.3 mL of CH\(_3\)COOH were added to the F-108 solution with stirring for 60 min. Finally, 20.3 g of Zn(NO\(_3\))\(_2\)·6H\(_2\)O was added to the mesophase including F-108. The sol was kept at 40 °C with the humidity at 40% to polymerize the mesophase to get the gel construction and thus dried at 65 °C for 12 h prior to calcination at 450 °C for 4 h. Mesoporous PtO–ZnO nanocomposites were fabricated as follows: 1 g of mesoporous ZnO matrix with a high surface area was suspended in 100 mL of C\(_2\)H\(_5\)OH. The desired concentration of Pt(\( \text{NH}_3 \))\(_4\)(NO\(_3\))\(_2\) was gradually obtained using the mesoporous ZnO NP matrix by agitation for 60 min. Subsequently, the aqueous solution was evaporated at 110 °C for 12 h and followed by calcination at 400 °C for 3 h to collect mesostructured 0.2, 0.4, 0.6, and 0.8 wt \% PtO–ZnO nanocomposites.

2.3. Characterization. XRD patterns were determined using the Bruker AXS D4 Endeavour X diffractometer. TEM images were examined by a JEOI JEM-2100F electron microscope. N\(_2\) adsorption–desorption isotherms were measured using the Quantachrome Autosorb equipment at 77 K after outgassing at 200 °C for 12 h. A spectrophotofluorophotometer (RF-5301 PC, 400 W, 50/60 Hz) was used to measure the photoluminescence (PL) by employing a xenon lamp (150 W) as the excitation source at \( \lambda \sim 365 \) nm. Spectra obtained by X-ray photoelectron spectroscopy (XPS) were analyzed using a Thermo Scientific K-Alpha spectrometer. The Zahner Zennium electrochemical workstation was employed to determine the transient photocurrent measurements. The system comprised a standard three-electrode Pt wire as the counter electrode and a calomel electrode as the reference electrode; the synthesized samples were used as working electrodes immersed in 0.1 M Na\(_2\)SO\(_4\) as the electrolyte. A 500 W xenon lamp was applied as the UV–vis light source. Spectra were recorded using a Perkin Elmer Fourier transform infrared spectrometer (FT-IR) at 400–4000 cm\(^{-1}\). Diffuse reflectance spectra were determined at \( \lambda \sim 200–800 \) nm by applying a Varian Cary 100 Scan UV–vis system.

2.4. Photocatalytic Test. The photodegradation of TC (20 mg L\(^{-1}\)) over mesoporous PtO–ZnO nanocomposites at different percentages of PtO NPs was carried out upon visible light exposure. A 300 W xenon lamp with a wavelength of <420 nm was fixed above the photoreactor (250 mL) at 10 cm distance. The mesoporous PtO–ZnO nanocomposites were sonicated in 200 mL of aqueous TC solution (20 mg L\(^{-1}\)) with air pumping, used as an O\(_2\) source. In the dark, the suspension was stirred for 30 min to obtain the adsorption equilibrium of TC. The photocatalytic efficiency of the mesoporous PtO–ZnO nanocomposites was determined for 2 h of illumination. The photodegradation efficiency was estimated by TC analysis by employing a spectrophotometer with an absorbance peak at 361 nm after separating the liquid by a 0.22 \( \mu \)m nylon filter at the regular time. % Photodegradation efficiency = \((C_0 - C_t)/C_0 \times 100\%\), where \( C_t \) and \( C_0 \) are the TC concentrations at a specific time \( t \) and zero time, respectively. Also, the mesoporous PtO–ZnO nanocomposite was reused for five further experiments to verify the recyclability and stability of the synthesized photocatalytic material.

3. RESULTS AND DISCUSSION

The XRD patterns of pristine ZnO NPs and mesoporous PtO–ZnO nanocomposites at diverse PtO percentages as depicted in Figure 1 correspond to the hexagonal wurtzite ZnO structure (JCPDS no. 36-1451).\textsuperscript{40} The pristine ZnO NPs are highly crystalline with sharp peaks. The well-defined diffraction peaks of hexagonal wurtzite ZnO at the crystal planes of (100), (002), (101), (102), (110), (103), (200), (112), and (201) correspond to \( 2\theta = 31.7, 34.2, 36.2, 47.6, 56.6, 62.8, 66.5, 67.9, \) and 69.3\(^{\circ}\), respectively. Besides, narrow XRD peaks with strong diffraction are observed, as shown in Figure 1, indicating the high crystallinity of the mesoporous PtO–ZnO nanocomposites. Furthermore, no distinct peaks were detected from the impurities, precursors, or other ZnO phases, demonstrating the high ZnO purity when synthesized.
using the present procedure. The XRD patterns of the mesoporous PtO−ZnO nanocomposites show similar diffraction peaks to those of the pristine ZnO NPs (Figure 1), indicating that the hexagonal wurtzite ZnO is the main structure for all synthesized samples. Besides, there are no overserved diffraction peaks due to the presence of PtO NPs or Pt, which is owing to their high dispersion on the mesoporous ZnO matrix, small size, and low concentration (0.2−0.8 wt %).

However, it is observed that the peak intensities of the mesoporous PtO−ZnO nanocomposites are significantly smaller than those of the pristine ZnO NPs.

The N2 adsorption−desorption isotherms of pristine ZnO and the mesoporous 0.6% PtO−ZnO nanocomposite are evaluated as displayed in Figure 2A to estimate the pore size distribution and surface area. At a high relative pressure (P/P0), the isotherm for N2 adsorption of pristine ZnO is higher than that of the 0.6% PtO−ZnO nanocomposite. It is observed that both isotherms with H2 hysteresis loops can be categorized as the IV type, which is distinctive of mesostructured materials.41 The surface area of the mesoporous 0.8% PtO−ZnO nanocomposite (125 m2 g−1) is smaller than that of pristine ZnO NPs (140 m2 g−1), which also explains the fractional incorporation of the PtO NPs onto the mesoporous ZnO matrix during calcination (Table 1). The pore size of the pristine ZnO was determined to be 4.82 nm, which was slightly reduced (4.6 nm) for the 0.8% PtO NPs as a result of PtO incorporation. The pore sizes and surface area of all synthesized photocatalysts are tabulated in Table 1. The increased surface areas of the mesoporous PtO−ZnO nanocomposites in the present work are considered the best values compared to those previously reported; they could adsorb TC molecules more readily, supply more reactive sites onto the synthesized samples, and thus promote the photocatalytic efficiency. The FT-IR spectra of the PtO−ZnO nanocomposites at different PtO percentages are depicted in Figure 2B. The broad peaks for the pristine ZnO and PtO−ZnO nanocomposites were located at 3220−3550 cm−1, matching the O−H stretching vibration, and the peak located at 1634.90 cm−1 is attributed to the bending modes of the hydrated oxide surface and adsorbed H2O.42,43 The Zn−O vibration peak was observed at 784 cm−1. After incorporating PtO onto mesoporous ZnO, the characteristic Zn−O vibration peak

![Figure 1. X-ray diffraction for mesoporous ZnO nanoparticles (a). PtO−ZnO nanocomposites at varying PtO contents: 0.2 wt % (b), 0.4 wt % (c), 0.6 wt % (d), and 0.8 wt % (e). Shifted for sake of clarity.](image1)

![Figure 2. (a) N2 sorption isotherms of the mesoporous ZnO nanoparticles and 0.6 wt % PtO−ZnO nanocomposite; (b) FTIR spectra of the mesoporous ZnO nanoparticles (a) and mesoporous PtO−ZnO nanocomposites at varying PtO contents: 0.2 wt % (b), 0.4 wt % (c), 0.6 wt % (d), and 0.8 wt % (e). Shifted for sake of clarity.](image2)

| Photocatalysts | S_{BET} (m^2 g^{-1}) | Band gap (eV) | Pore size (nm) | Rate constant k (min^{-1}) | r (μmol g^{-1} min^{-1}) |
|---------------|----------------------|--------------|---------------|---------------------------|--------------------------|
| meso-ZnO      | 140                  | 3.18         | 4.82          | 0.0010                    | 0.035                    |
| 0.2% PtO−ZnO  | 138                  | 2.99         | 4.74          | 0.0077                    | 0.360                    |
| 0.4% PtO−ZnO  | 133                  | 2.70         | 4.68          | 0.0195                    | 0.865                    |
| 0.6% PtO−ZnO  | 129                  | 2.36         | 4.6           | 0.0482                    | 1.216                    |
| 0.8% PtO−ZnO  | 125                  | 2.35         | 4.6           | 0.0515                    | 1.420                    |
| P-25          | 50                   | 3.20         |               | 0.0026                    | 0.097                    |

The S_{BET} surface area, and r photodegradation rate of tetracycline.
was gradually shifted to ~743 cm\(^{-1}\) with the increment of PtO NPs from 0.2 to 0.8%, which confirms the coexistence of ZnO and PtO NPs and confirms the construction of PtO–ZnO nanocomposites. The intensity of the Zn–O peak was reduced for the synthesized PtO–ZnO nanocomposites compared with pristine ZnO NPs, indicating the replacement of Pt(II) on the mesoporous ZnO matrix.44

TEM images for the pristine ZnO NPs and mesoporous 0.6 and 0.8% PtO–ZnO nanocomposites were examined as displayed in Figure 3. Figure 3a shows that the ZnO NPs were highly dispersed, with an entirely uniform shape and size and average particle sizes of ~5–10 nm. Figure 3b,c reveals the TEM of 0.6 and 0.8% PtO–ZnO nanocomposites. The images show that PtO–ZnO particles with average particle sizes of ~5–10 nm were not agglomerated after incorporating PtO NPs of completely uniform shape and size. The HR-TEM image of the mesoporous 0.6% PtO–ZnO nanocomposite shows that the distances between two close planes were 0.25 and 0.217 nm, indicating the presence of (101) and (110) planes for ZnO and PtO with high crystallinity, which is satisfactory for the immigration of charge carriers45 (Figure 3d). The particle size of the PtO NPs is around ~3 nm (Figure 3d). Selected area electron diffraction showed polycrystalline ZnO hexagonal construction as displayed in Figure 3d, inset.

X-ray photoelectron spectroscopy (XPS) of the mesoporous 0.6% PtO–ZnO nanocomposite was done to evaluate the chemical state as displayed in Figure 4a–c. XPS of the Pt 4f spectrum of PtO–ZnO as depicted in Figure 4a showed that the two characteristic peaks of Pt 4f\(_{7/2}\) and Pt 4f\(_{5/2}\) appeared at binding energies of 72.6 and 75.9 eV, respectively, indicating the existence of the chemical state of Pt(II) and further demonstrating the incorporation of PtO NPs onto the mesoporous ZnO matrix.46 Furthermore, it is shown that PtO NPs incorporated on the mesoporous PtO–ZnO nanocomposites are typically deposited on the surface of the ZnO matrix. Figure 4b exhibits two main peaks of the Zn 2p XPS spectrum; the peaks located at 1021.6 and 1044.7 eV are attributed to Zn(II) 2p\(_{3/2}\) and Zn\(^{2+}\) 2p\(_{1/2}\), respectively, which indicates the formation of the Zn\(^{2+}\) state. The variance between Zn 2p\(_{3/2}\) and Zn 2p\(_{1/2}\) in terms of binding energy is estimated at around 23.1 eV.47 The XPS of the O 1s spectrum exhibits one main peak located at 530.1 eV as depicted in Figure 4c, indicating the presence of the lattice oxygen of Zn–O and Pt–O.48 XPS of the mesoporous 0.6% PtO–ZnO nanocomposite revealed that the final product’s weight percentages are compatible with the Pt\(_2\)O/ZnO ratio and the atomic percentages of the Pt, Zn, and O are determined to be 0.55, 54.07, and 45.38%, respectively.

To evaluate the optical performances of the newly synthesized pristine ZnO NPs and mesoporous PtO–ZnO nanocomposites at different PtO percentages, diffuse reflectance UV–vis spectra (DRS) were determined (Figure 5). The absorbance edge of pristine ZnO NPs showed a broad peak in the UV region at 300–400 nm (Figure 5a). However, mesoporous PtO–ZnO nanocomposites exhibited the absorption edge from 400 to 600 nm within the visible absorbance range, as depicted in Figure 5a. Defect sites could explain this enhanced visible light harvest in the wide region as due to the presence of O\(^{2-}\) vacancies in the lattices. Therefore, the increment of PtO percentages leads to a decrease in the bandgap energies. In addition, for calculation of the direct bandgap energy (\(E_g\)) of the synthesized samples, the relation between photon energy and \((\alpha h\nu)^2\) was analyzed by applying the equation \((\alpha h\nu)^2 = A(h\nu - E_g)\), where \(A\) is the absorbance.

Figure 3. TEM images of mesoporous ZnO nanoparticles (a); 0.6 wt % PtO–ZnO (b) and 0.8 wt % PtO–ZnO nanocomposites (c); HRTEM image of 0.6 wt % PtO–ZnO nanocomposite (d).
constant, $E_g$ is the bandgap energy, and $h\nu$ is the incident photon energy. The $E_g$ value was derived from the Tauc plot in Figure 5b by the linear tangential versus $h\nu$ axis. The bandgap values for pristine ZnO, and 0.2, 0.4, 0.6, and 0.8% PtO–ZnO nanocomposites are estimated to be around 3.18, 2.99, 2.70, 2.36, and 2.35 eV, respectively (Table 1). The reduction of the band gap and red shift in the absorption upon PtO incorporation onto the mesoporous ZnO matrix are owing to the electronic transformations from the ZnO band edge to Pt(II) NPs.

### 3.1. Photocatalytic Degradation of TC

The photocatalytic performances of mesoporous PtO–ZnO nanocomposites at various PtO percentages were assessed by TC degradation under ambient conditions during visible light exposure illumination to commercial P-25 and pristine ZnO NPs. The photolysis of TC without a photocatalyst was carried out for 120 min of illumination as a blank control. The results exhibited nearly no TC degradation without photocatalysts upon illumination, and the photolysis of TC was determined to be less than 2% for within 120 min. However, the maximum adsorption capacity of TC over mesoporous PtO–ZnO nanocomposites was determined to be around 5–10% for 120 min. Figure 6a indicates that the incorporation of PtO NPs onto the mesoporous PtO–ZnO nanocomposites increases the photocatalytic efficiency for degradation of TC through visible light exposure for 120 min. It is revealed that the photocatalytic efficiency enhancement of mesoporous PtO–ZnO nanocomposites is mainly produced from the incorporation of
PtO NPs onto PtO–ZnO nanocomposites compared to pristine ZnO or commercial P-25. The photocatalytic efficiency over mesoporous PtO–ZnO nanocomposites was significantly improved, and their efficiency reached 40, 80, 99, and 100% for 0.2, 0.4, 0.6, and 0.8% PtO–ZnO nanocomposites compared to undoped ZnO (5%) and commercial P-25 (10%) through visible light exposure. It was revealed that the photocatalytic performance of the 0.6% PtO–ZnO nanocomposite is 20 and 10 times greater than that of the pristine ZnO NPs and commercial P-25, respectively. The photodegradation rate of TC over 0.2, 0.4, 0.6, and 0.8% PtO–ZnO nanocomposites was calculated to be 0.360, 0.865, 1.216, and 1.420 μmol g$^{-1}$ min$^{-1}$ compared to pristine ZnO NPs (0.035 μmol g$^{-1}$ min$^{-1}$) and commercial P-25 (0.097 μmol g$^{-1}$ min$^{-1}$). The photodegradation rate of TC over the 0.6% PtO–ZnO nanocomposite is 34 and 12.5 times greater than that of pristine ZnO and commercial P-25, respectively. In Figure 6b, to evaluate the TC degradation rate constant $k$ upon visible light illumination, $\ln(C_t/C_0)$ was plotted versus illumination time $t$, where $C_t$ and $C_0$ are the TC concentration after a certain time $t$ and zero time, respectively, and $k$ is the apparent rate constant. According to the equation $\ln(C_t/C_0) = -kt$, a fitting model of pseudo-first order was applied to determine the $k$ values. As displayed in Figure 6b, all synthesized mesoporous PtO–ZnO nanocomposites are figured out to have a quite longitudinal interdependence of time and $\ln(C_t/C_0)$ (Figure 6b). The $k$ values for mesoporous 0.2, 0.4, 0.6, and 0.8% PtO–ZnO nanocomposites were determined to be $\sim$0.0077, 0.0195, 0.0482, and 0.0515 min$^{-1}$, respectively. However, the $k$ values for pristine ZnO NPs and commercial P-25 were 0.001 and 0.0026 min$^{-1}$, respectively. The $k$ value of the 0.6% PtO–ZnO nanocomposite was 18 and 48 times higher than that for commercial P-25 and pristine ZnO NPs, respectively. Meanwhile, this calculated $k$ value could help to determine the degradation rate of TC in the aqueous solution; plausibly the $k$ values of 0.6 and 0.8% PtO–ZnO nanocomposites were high in terms of photocatalytic efficiency. The 0.6 and 0.8% PtO–ZnO nanocomposites revealed much higher photocatalytic efficiency than either pristine ZnO NPs or commercial P-25. As exhibited, the 0.6 and 0.8% PtO–ZnO nanocomposites show outstanding photocatalytic performance by achieving nearly full TC degradation within 120 min. Ultimately, the photocatalytic efficiency noted follows the trend 0.8% PtO–ZnO $\geq$ 0.6% PtO–ZnO $>$ 0.4% PtO–ZnO $>$ 0.2% PtO–ZnO $>$ TiO$_2$–P25 $>$ ZnO NPs. Such high photocatalytic performance of the mesoporous PtO–ZnO nanocomposites in comparison with pristine ZnO NPs and commercial P-25 could be explained by diverse factors, such as an accumulated $^*$OH concentration, a broad visible light absorption, a narrow band gap, a lower light scattering, or a rapid transfer and facile diffusion of the TC molecule through the porous structure, which for the commercial P-25 is suppressed by the bulk sample. In addition, the mesoporous PtO–ZnO nanocomposites could reduce the recombination of carriers and hence enhance the TC photodegradation efficiency compared to the pristine ZnO NPs and commercial P-25. Also, the narrow band gap of the mesoporous PtO–ZnO nanocomposites could create a wide effective visible region and thus build up their photocatalytic efficiency. The second main reason is thought to be the mesostructure of the PtO–ZnO matrix with a high surface area. This is explained by the increase in TC adsorption, TC diffusion, and the number of active sites on the PtO–ZnO surface. It could be inferred that the PtO NPs incorporated on the ZnO surface acted as an effective cocatalyst and better electron sink, which could facilitate the separation of the photoinduced carrier. The ZnO and PtO NPs preserved the particles sizes of around 5–10 and 3 nm, respectively. The ZnO Fermi level was lower than that of PtO; the electric field was generated from the potential interaction barriers of the PtO–ZnO. These potential barriers support the transformation of photoelectrons from the conduction band of ZnO to PtO, inhibiting the recombination of carriers. PtO NPs (3 nm) can not only decrease the consumption of Pt but also help in effective electron trapping, thus enhancing the charge carrier separation. Besides, the strong interaction between PtO and ZnO could also have contributed to the charge separation through TC degradation.

The influence of the loading amount of mesoporous 0.6% PtO–ZnO nanocomposite (0.6–3 g L$^{-1}$) was determined.
from the TC photodegradation efficiency (Figure 7a). The results revealed a linear improvement of TC degradation by increasing the loading amount of PtO–ZnO nanocomposite from 0.6 to 1.8 g L\(^{-1}\). The increase of TC degradation efficiency is associated with the comparable widening of accessible active sites for the reactant and light adsorption. By increasing the loading amount of PtO–ZnO from 0.6 to 1.8 g L\(^{-1}\), the TC degradation efficiency enhanced significantly from 50 to 99\%, respectively. However, at a high loading amount of the photocatalyst, the TC degradation efficiency was minimized to 85\% at 3 g L\(^{-1}\) due to the increment turbidity of the solution, which is considered as one of the foremost reasons for reduction of the TC degradation efficiency. Besides, the increment turbidity of the solution led to the light scattering and hence the loss of light energy. In general, the light scattering resulting from the suspended photocatalyst reduces the light transmission, resulting in an inadequate TC degradation. Besides photocatalytic performance, stability and reusability are indispensable for photocatalyst applications. As depicted in Figure 7b, repeated TC degradation over five cycles demonstrated that the 0.6% PtO–ZnO nanocomposite exhibited good stability for the TC degradation under similar conditions. A much higher (95\%) TC degradation efficiency could be achieved after recycling for five times. It is revealed that the PtO–ZnO nanocomposite is preserved through five-times-recycled photodegradation of TC. According to our current research, the mesoporous PtO–ZnO nanocomposite with structural stability and high photocatalytic performance could be anticipated as an excellent promising photocatalyst for practical applications.

To further prove the effective separation and migration of photo-created carriers on mesoporous PtO–ZnO photocatalysts, photoluminescence spectra and transient photocurrent measurements were taken as shown in Figure 8. As depicted in Figure 8a, the mesoporous PtO–ZnO nanocomposite at diverse PtO contents revealed a highly reduced-intensity PL compared to pristine ZnO NPs, indicating the efficacious prohibition of the recombination of photoinduced electrons and holes in these nanocomposites. Note that the PL of pristine ZnO NPs appeared at λ \sim 388 nm; however, the PL intensity of the PtO–ZnO nanocomposite at diverse PtO percentages still obviously decreased and red-shifted to 421, 497, 567, and 567 nm for mesoporous
0.2, 0.4, 0.6, and 0.8% PtO−ZnO nanocomposites, indicating that the much higher photocatalytic performance of the 0.6 and 0.8% PtO−ZnO nanocomposites is explained by the restraining of the electron and hole recombination. Also, the transient photocurrent response shown in Figure 8b indicates that the PtO−ZnO nanocomposites produced a constant transient photocurrent through five discontinuous illumination cycles. All PtO−ZnO nanocomposites and pristine ZnO NPs displayed instantaneous responses to light. The results indicated that the photocurrent responses of the 0.6 and 0.8% PtO−ZnO nanocomposites are the highest, suggesting that the recombination rate of the carriers is low. The photocurrent intensity followed the sequence 0.8% PtO−ZnO = 0.6% PtO−ZnO > 0.4% PtO−ZnO > 0.2% PtO−ZnO > ZnO. Particularly, the findings of photocurrent response and PL measurements are consistent with the photocatalytic performances; PtO−ZnO heterojunctions could thus enhance the effective transfer and separation of photoinduced electrons and holes and exhibited an outstanding photocatalytic effect. These phenomena show that the recombination rate of carriers could be prohibited by incorporation of PtO NPs on the ZnO matrix.

A photocatalytic mechanism of the mesoporous PtO−ZnO photocatalyst was suggested according to the above results for TC degradation (Scheme 1). The mesoporous PtO−ZnO network facilitates the mass transfer of TC molecules. The incorporation of PtO NPs on the mesoporous ZnO matrix could improve its photocatalytic efficiency, as shown by the obvious construction of close contacts between the PtO and ZnO NPs in the TEM images (Figure 4d) that facilitates the immigration of charge carriers. Upon illumination, ZnO can be photo-excited to create the electrons and holes on the PtO−ZnO surface. The photoinduced electrons are transferred to PtO to form a superoxide radical; Pt2+ doping reduces the band gap of ZnO to enhance light absorption.46 The photoinduced electrons might reduce O2 to yield O2− in the reaction solution and subsequently the protonation of O2− might produce HO2• radicals, leading to the H2O2 formation. The formed H2O2 molecules could react with the excess electrons to produce the highly oxidizing •OH radicals. On the other side, the photoinduced holes are easily trapped by the adsorbed H2O/OH− to yield •OH; then the TCs are degraded to the environment-friendly CO2 and H2O by the •OH, •O2• radical, and holes. Obviously, the reactive species generated through the photocatalysis reaction are concomitantly excited, including the •O2•, h+, and •OH in the reaction solution.

4. CONCLUSIONS

In summary, we report a simple method of incorporation of PtO NPs onto a highly crystalline and mesoporous ZnO matrix by the wet-impregnation approach for degradation of tetracycline (TC) upon visible light exposure. The uniform crystal structure of the mesoporous ZnO matrix with high crystallinity contributes to the construction of PtO NPs on the ZnO matrix with high dispersity and small size. The resultant mesoporous PtO−ZnO nanocomposites exhibit a significant enhancement of photocatalytic efficiency for TC degradation compared with commercial P-25 and pristine ZnO NPs. The optimized 0.6% PtO−ZnO photocatalyst exhibits an excellent degradation efficiency of TC, reaching ~99%. The photocatalytic efficiency is observed to follow the trend 0.8% PtO−ZnO ≥ 0.6% PtO−ZnO > 0.4% PtO−ZnO > 0.2% PtO−ZnO > TiO2−P2S > ZnO NPs. The rate constant value of the 0.6% PtO−ZnO nanocomposite was 48 and 18 times higher than that for pristine ZnO NPs and commercial P-25, respectively. These mesoporous PtO−ZnO nanocomposites showed excellent photocatalytic performance due to their more effective separation of photoinduced electrons and holes, small particle sizes, and larger surface area. Accordingly, mesoporous PtO−ZnO nanocomposites with structural stability and high photocatalytic performance could be anticipated as excellent promising photocatalysts for practical application.

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Notes

The authors declare no competing financial interest.

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