Inverse opal structured Pt/TiO$_2$–MnO$_y$ photothermocatalysts for enhanced toluene degradation activity†

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Photothermocatalysis is gaining increasing scientific attention for its potential in alleviating the ever-worsening volatile organic compound (VOC) pollution. Herein, we fabricated inverse opal (IO) structured TiO$_2$–MnO$_y$ photothermocatalysts whose photothermocatalytic toluene degradation performance varied significantly at different Ti-to-(Ti + Mn) ratios. The rate constant for photothermocatalytic toluene degradation for the best TiO$_2$–MnO$_y$ sample was 11.3 times and 12.1 times higher than that of the TiO$_2$ and MnO$_y$ sample, respectively, reaching 0.03812 min$^{-1}$. This high activity arose from the IO structure which contained abundant macropores and contributed to enhancement of catalytic activity by enhancing light absorption and toluene adsorption capability. Deposition of Pt nanoparticles which were dual-functional photo-thermal (co)catalysts led to further enhancement of toluene degradation activity by promoting the toluene adsorption on the MnO$_y$ surface and activating O$_2$ to form reactive oxygen species. Moreover, the formation of a Schottky junction between Pt and TiO$_2$ also enhanced the charge separation and utilization efficiency, allowing for more efficient generation of active species for toluene activation and catalyst re-oxidation for achieving high toluene degradation activity.

1. Introduction

Industrial activity of human beings has been accompanied by the continuous emission of volatile organic compound (VOC).¹ Most VOC, such as benzene, toluene, vinyl chloride, and polychlorinated biphenyls, pose a huge threat to human health due to their poisonous and carcinogenic characteristics.²,³ In addition, since VOC are the key precursors for ozone and secondary organic aerosols, they could also lead to serious particulate matter and ozone pollution.²,³ Therefore, developing effective pollution control techniques for addressing the VOC pollution issue has become one of the most urgent challenges faced by researchers.⁴ Photothermocatalysis (PTC) which integrates the advantages of photocatalysis (PC) and thermocatalysis (TC) has attracted widespread research attention for its potential in alleviating the VOC pollution.⁵ In recent studies, various types of hybrid materials have been explored as photothermocatalysts for VOC remediation. For instance, Yang et al. successfully synthesized a Co$_3$O$_4$/TiO$_2$ photothermocatalyst and found that the toluene degradation rate under the PTC conditions was much higher than that under the PC or TC conditions.⁶ The p–n heterojunction constructed between TiO$_2$ and Co$_3$O$_4$ provided more active radicals and holes to enhance the PTC performance. Jiang et al. prepared a Cu/MnO$_x$ composite photothermocatalyst containing abundant oxygen vacancies.⁷ The presence of oxygen vacancies could accelerate the separation of photogenerated electron hole pairs and generate more reactive.
oxygen species for improving the PTC activity. The reported toluene degradation activity was nearly 6.6 and 12.7 times higher than that of the TC and PC processes.

It is well-established that the key for PTC materials to exhibit high VOC degradation activity is for them to possess strong light absorption capability and high specific surface area.9,10 In this regard, inverse opal (IO) materials are ideal candidates because of their 3-dimensional (3D) ordered porous structures which give rise to unique optical properties such as photonic band gaps, slow photon effects, and photonic localization effects.10-12 Additionally, the 3D ordered microporous and mesoporous structures can enhance the adsorption of VOC molecules on the catalyst surface, provide more efficient catalytic sites, and facilitate mass transfer during catalytic processes.13-16 At present, although IO-structured photocatalysts, such as WO3, TiO2, TiO2-SiO2, and g-C3N4,17-20 have been extensively used for photocatalytic decomposition of organic pollutants, photocatalytic water disinfection, and methane photothermal catalytic dry reforming,21-23 there is no report on using them for PTC degradation of VOC pollutants.

Introduction of noble metals also proves to be effective since they are excellent (co)catalysts for TC and PC reactions.24,25 For example, Liu et al. reported that introduction of Pt nanoparticles in the CoAl-layered-double-hyroxide/CeO2 (LDH/CeO2) catalyst promoted charge transfer kinetics, allowing for efficient utilization of charge carriers to generate more active species for VOC degradation. More importantly, it also brought in a unique optical effect called localized surface plasmon resonance (LSPR), which contributed to enhancement of VOC degradation activity by increasing the light absorption efficiency. As a result, the conversion rate of toluene increased from 20% for LDH/CeO2 to 85% for Pt-LDH/CeO2.26 Wang et al. reported that significantly enhanced toluene degradation activity can be achieved by embedding Pt single-atoms into MnO2 since this could activate surface oxygen species to generate more hydroxyl radicals for replenishing lattice oxygen.27 Li et al. found that the loading of Pt onto Mn-TiO2 can enhance the toluene degradation efficiency by promoting absorption of visible light and activation of lattice oxygen.28

In this study, a set of IO-structured TiO2-MnO2 photothecatalysts [termed TM-x, where x represents the ratio of Ti to (Ti + Mn)] were fabricated by the colloidal crystal templating (CCT) method. Pt nanoparticles were further loaded on their surface using a chemical reduction method. The PTC activity of samples with varying Ti-to-(Ti + Mn) ratios and Pt loading percentages was evaluated by using toluene as a typical VOC pollutant under Xe lamp irradiation. Degradation of toluene reached 97.1% at 60 min for the best TM-0.4 sample, and the time required for achieving the same level of degradation was reduced by half for the 0.5% Pt/TM-0.4 sample, far exceeding a variety of state-of-the-art catalysts reported in the literature. Control experiments which compared the activity of TM-0.4 prepared with and without the PS template showed that the IO structure was the key to achieving high activity. The active species for toluene degradation over PTC were probed by electron spin resonance (ESR) analyses and free radical trapping experiments. The results showed that the active species produced in the PC process (e-, h+, O2- and OH-) were beneficial to toluene oxidation. Moreover, the redox properties of the different samples were assessed through the H2-TPR test and showed that the 0.5% Pt/TM-0.4 also exhibited the best redox properties. This was consistent with the results observed for toluene degradation.19 O2 isotope labelling experiments indicated that the degradation of toluene on TM-0.4 and Pt/TM-0.4 followed the Mars–van Krevelen (MvK) mechanism. On the basis of the above experiment results, it was revealed that the degradation of toluene was a synergy of the PC and TC processes, in which the photocatalysis-induced active species (other than activated toluene) but also accelerated the cyclic conversion of lattice oxygen and oxygen vacancies in MnO2. Pt loading improved the catalytic activity by promoting the adsorption of toluene and O2, as well as activating O2 to form reactive oxygen species.

2. Experimental section

2.1 Synthetic methods

2.1.1 Synthesis of polystyrene (PS) nanoparticles. 0.6000 g of potassium persulfate and 0.4500 g of sodium dodecyl sulfate were dissolved in a mixture of 160 mL ethanol and 260 mL water in a round bottom flask. Under a N2 atmosphere, 36 mL of styrene was added into the above flask and the temperature of the reaction solution was kept at 71 °C for 19 h. After the completion of the polymerization reaction, the obtained PS nanoparticles were collected by centrifugation at 4000 rpm for 8 h and dried at 70 °C overnight.

2.1.2 Synthesis of IO structured TiO2-MnO2. 2.1014 g of citric acid was dissolved in 10 mL of ethanol, followed by addition of different proportions of TiCl4 and Mn(NO3)2·4H2O (with a total molar amount of 0.01 mol). 0.1000 g of PS nanoparticles was soaked in the above solution for 0.5 h and then filtered and dried at 71 °C for 0.5 h. The above processes were repeated four times. Finally, the dried samples were calcined at 500 °C for 2 h to remove the PS nanoparticles. The resulting photothermocatalyst was denoted as TM-x, where x represents the ratio of Ti to (Ti + Mn).

2.1.3 Synthesis of Pt/TM-0.4. 0.1000 g of IO structured TM-0.4 and a certain amount of chloroplatinic acid (H2PtCl6) aqueous solution (2 g L-1) were added in a 50 mL flask and sonicated for 10 min. After that, 20 mL ethylene glycol (EG) solution of polyvinylpyrrolidone (PVP) with a Pt-to-PVP molar ratio of 1 : 20 was added into the above solution. After the mixture was stirred for 20 min, it was refluxed for 4 h at 130 °C in an oil bath under magnetic stirring. Then, the product was centrifuged and washed with deionized water and anhydrous ethanol several times before being dried at 70 °C for 12 h. Finally, the residual PVP and ethylene glycol were removed by calcination at 550 °C in air for 1 h. By adjusting the amounts of H2PtCl6 and PVP added, Pt/TM-0.4 catalysts with different Pt loadings were obtained.

2.2 Characterization

The morphologies of the prepared samples were imaged by several microscopic techniques using a TESCAN VEGA 3 SBH.
scanning electron microscope (SEM), a JEM2000EX transmission electron microscope (TEM), and a JEOL JEM2100 high resolution transmission electron microscope (HR-TEM). The crystalline structures of the samples were analyzed using a Rigaku D/max 2550 VB/PC X-ray diffractometer with Cu Kα radiation (\(\lambda = 0.15406 \text{ nm}\)). The surface element composition and chemical states of TM-0.4 and 0.5% Pt/TM-0.4 were investigated using a Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectrometer (XPS) with Al Kα radiation, operated at 250 W. The binding energies of different elements were calibrated by assuming the C 1s peak at 284.6 eV. The average pore diameters and specific surface areas of the samples were determined on a Quantachrome Autosorb IQ instrument and calculated by Barrett–Joyner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) methods. The UV-vis-infrared diffuse reflectance spectra (DRS) of the samples were recorded on a Lambda 950 spectrophotometer assembled with an integrating sphere assembly, using BaSO₄ as the reference material. The gases in the catalytic reactor were analyzed using a gas chromatograph equipped with a nickel-based methanator and flame ionization detector (INESA GC126N), a gas chromatograph-mass spectrometer (GC: Clarus 680, MS: Clarus SQ 8 T, TurboMatrix 650 ATD), and a Fourier transform infrared spectrometer (Nicolet Nexus 670). The active species generated in the catalytic reactions were detected using an electron spin resonance (ESR) spectrometer (Bruker EMX-8/2.7) in the 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) solution (aqueous solution for DMPO-•OH and methanol solution for DMPO-•O₂⁻). The transient photocurrent, electrochemical impedance spectra (EIS) and Mott–Schottky plot were obtained on a Zahner electrochemical workstation using a standard three-electrode system consisting of a working electrode (FTO glass with 0.2 mg as-prepared sample with an active area of 1 cm²), a Pt wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The following formula (\(E_{\text{SHE}} = E_{\text{Ag/AgCl}} + 0.197\)) was used to convert the Ag/AgCl electrode to the normal hydrogen electrode (NHE). Photoluminescence (PL) spectra were obtained using a SHIMADZU RF5301PC spectrophotometer at an excitation wavelength of 320 nm in the range of 400–550 nm. Hydrogen temperature-programmed reduction (H₂-TPR) measurements were conducted on a Xianquan TP5076 Chemisorption Analyzer. The samples were pretreated by heating at 300 °C for 1 h under an N₂ gas flow. The data of H₂-TPR were collected in the range of room temperature to 800 °C, with a heating rate of 10 °C min⁻¹. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis was conducted on a TENSOR II FT-IR spectrometer (Bruker).

2.3 Catalytic activity measurements

2.3.1 Toluene degradation under the PTC conditions.

Toluene was selected as a representative VOC to assess the PTC activity of the obtained samples. As shown in Fig. S1,† the degradation reactions were conducted in a cylindrical stainless-steel reactor (volume: 2 L, diameter: 18.2 cm, high: 7.8 cm) equipped with a quartz window and a cooling water jacket, using a 300 W Xe lamp (CHF-XM300) as the light and heat source. First, 50 mg of catalyst was uniformly coated on a ceramic sheet (4 cm × 4 cm) and fixed in the reactor. After that, the reactor was evacuated before injecting 0.01 mL of toluene solution and 2 L of fresh air to reach a final concentration of 1150 ppm. The fan in the reactor was then turned on for toluene molecules to reach the adsorption–desorption equilibrium on the catalyst surface. Finally, the Xe lamp was turned on to initiate the PTC reaction. At the given time interval, 1 mL gas was extracted and analyzed with a gas chromatograph for determining its composition.

2.3.2 Toluene degradation under the PC conditions.

Degradation of toluene under the PC conditions was conducted under identical conditions to those in the PTC process except that the reaction temperature was maintained at room temperature with the aid of cooling water.

2.3.3 Toluene degradation under the TC conditions.

Degradation of toluene under the TC conditions was conducted without light irradiation. The reaction temperature under the TC conditions was kept the same as the surface temperature of the catalyst after 5 min of light irradiation using an electrical heating system. All the other conditions were kept the same as those in the PTC process.

2.3.4 Isotope labeling experiments.

Isotope labeling experiments were carried out by replacing the fresh air with a mixed gas of 21% ¹⁸O₂ and 79% N₂ (v/v). All the other experimental conditions were kept the same.

3. Results and discussion

3.1 Synthesis of Pt/TM-x

The synthetic route and formation mechanism of IO structured TM-x and Pt/TM-x are illustrated in Fig. S2.† We started by fabricating a well-arranged 3D PS opal as colloidal crystal templates (Fig. S3†) using a low-speed centrifugation method. This was followed by impregnating the PS template with a solution mixture of the Ti⁴⁺ and Mn²⁺ precursors. We performed four rounds of dipping and drying process to ensure that the interfaces of the PS template were filled with the Ti⁴⁺ and Mn²⁺ precursor. After that, the PS template impregnated with the Ti⁴⁺ and Mn²⁺ precursors was subjected to calcination treatment for the formation of IO structured TM-x. The key to obtain the IO structure was to transform the Ti⁴⁺ and Mn²⁺ precursors into their corresponding oxides before the PS nanoparticles were removed. This makes it important to add citric acid into the solution mixture of the Ti⁴⁺ and Mn²⁺ precursors to form their corresponding citrate complexes since the temperature required for transforming titanium citrate into TiO₂ (300 °C) was lower than the combustion temperature of the PS template (380 °C). As a result, when the PS template was removed, the framework of the IO structure can still be maintained for further transformation of magnesium citrate into MnO₂ which occurred at 500 °C. The last step in the synthesis was the loading of Pt nanoparticles, in which EG functioned as the solvent and reducing agent, and PVP as the stabilizer to prevent the aggregation of Pt nanoparticles. After the reaction was completed, excess amounts of PVP and EG were removed by calcination.
3.2 Characterization of morphology

Fig. 1A–F show the SEM images of the TM-x photothermal-catalysts with various Ti-to-(Ti + Mn) molar ratios. As is shown, the 3D ordered macroporous IO structure was observed for the TiO$_2$, TM-0.8, TM-0.6, TM-0.4, and TM-0.2 samples, while the MnO$_y$ sample took the form of aggregated nanoparticles since the PS template was removed before magnesium citrate was transformed into MnO$_y$. As expected, the MnO$_y$ sample had the lowest specific area among all (as shown in Table S1†), while the surface area of TM-x decreased with increasing Mn content, which is probably due to the partial collapse of the IO structure during the calcination process. From the N$_2$ adsorption–desorption isotherms and pore-size distribution curves (Fig. S4 and S5†), it can be seen that all samples except MnO$_y$ gave typical IV type adsorption–desorption isotherms with an H3 hysteresis loop, indicating the existence of a mesoporous structure in the IO framework of these samples.\(^{34}\) Closer inspection of the TM-0.4 sample (which exhibited highest toluene degradation activity) under TEM characterization shows that its macropore size was ≈200 nm and its wall thickness ranged from ≈10 to 15 nm (Fig. 1G). In the HR-TEM image (Fig. 1H), the lattice spacing of 0.32 nm matched with the [110] planes of rutile TiO$_2$, while the lattice spacing of 0.28 nm corresponded to the [103] planes of Mn$_3$O$_4$, which is consistent with the XRD pattern results.\(^{35,36}\) Meanwhile, the EDX element mapping images in Fig. S6† confirmed the uniform distribution of Ti, Mn, and O elements in the TM-0.4 structure.

Fig. 1I–K show the SEM images of different Pt/TM-0.4. It can be seen that the Pt loading did not destroy the IO morphology of TM-0.4. Successful loading of Pt nanoparticles can be confirmed by the observation of the lattice spacing of 0.22 nm which corresponded to the (111) planes of Pt nanoparticles.\(^{37}\) As shown in Fig. 1L and S7† the size of Pt nanoparticles in Pt/TM-0.4 was ≈3 nm. The EDX element mapping images in Fig. S8† confirmed the uniform distribution of Pt nanoparticles on the surface of TM-0.4.

3.3 Characterization of the crystalline structure and surface composition

Fig. 2A shows the X-ray diffraction (XRD) spectra of the TiO$_2$, MnO$_y$ and TM-x samples with different Ti-to-(Ti + Mn) ratios. It can be seen that the contents of anatase and rutile TiO$_2$ and
manganese oxides had a strong dependence on the Ti-to-(Ti + Mn) ratio. For example, the TiO₂ sample showed almost exclusively the characteristic diffraction peaks for anatase TiO₂ (JCPDS No. 01-0562). Interestingly, the characteristic diffraction peaks for rutile TiO₂ (JCPDS No. 21-1276) started to appear when the Ti-to-(Ti + Mn) ratio was 0.8. This is because the size of the Mn²⁺ ion (0.80 Å) is larger than that of the Ti⁴⁺ ion (0.68 Å), so that doping of Mn²⁺ would cause defects in the anatase to stabilize while those that correspond to the rutile TiO₂ weakened while those that correspond to the rutile TiO₂ were strengthened when the Ti precursor was not added, and all the peaks can be attributed to Mn₃O₄. As shown in Fig. 2B, the diffraction peaks of the Pt-loaded samples (0.5% Pt/TM-0.4) were similar to those of the TM-0.4 sample. No Pt diffraction peak can be found due to the relatively low loading and small particle size of Pt nanoparticles.

The surface element composition and chemical states of TM-0.4 and 0.5% Pt/TM-0.4 were studied using X-ray photoelectron spectroscopy (XPS). As shown in Fig. 3A, for the TM-0.4 sample, the two discernible peaks at 458.6 eV and 464.3 eV were ascribed to Ti 2p½ and Ti 2p½, respectively. As shown in Fig. 3B, the Mn 2p spectra were resolved into three sets of double peaks. The two peaks at 641.9 eV and 653.6 eV can be ascribed to Mn²⁺, while the other two at 643.5 eV and 655.1 eV can be ascribed to Mn³⁺. Two satellite peaks were also observed at 646.3 eV and 658.0 eV, which were attributed to shake-up excitation of the Mn²⁺ ion (0.80 Å) is larger than that of the Ti⁴⁺ ion (0.68 Å), and O 1s spectra of 0.5% Pt/TM-0.4 exhibited patterns similar to those of TM-0.4. The slight shift of Ti 2p (+0.1 eV), Mn 2p (+0.2 eV) and O 1s (+0.1 eV) peaks to higher binding energies upon Pt introduction suggested a strong electronic interaction between Pt and TM-0.4. Moreover, the ratio of O₂ to O₂ increased from 12.3% (TM-0.4) to 21.8% (0.5% Pt/TM-0.4), indicating that the loading of Pt nanoparticles promoted the generation of surface oxygen vacancies, as confirmed by EPR analysis (Fig. S9†). In Fig. 3D, the peaks at 70.9 eV and 74.2 eV corresponded to the Pt 4f½ and Pt 4f½ of metallic Pt⁶⁺, respectively, indicating that the valence state of Pt was zero for Pt nanoparticles in the 0.5% Pt/TM-0.4 sample.†

3.4 Characterization of optical properties

The light absorption of TiO₂, MnO₂, and various TM-x samples was assessed through UV-vis-IR diffuse reflectance spectra. As shown in Fig. 4A, TiO₂ only absorbed light in the ultraviolet region, while all TM-x samples exhibited extended light absorption into the visible and infrared regions. In addition, the light absorption at all wavelengths strengthened with increasing Mn content. Interestingly, most TM-x also displayed stronger light absorption intensity than MnO₂, which can be attributed to the longer light path and lifetime within the IO porous structure. This strong absorption in the visible and infrared regions can efficiently elevate the temperature on the catalyst surface through both the heating effect and photothermal conversion effect. We measured surface temperature changes of TiO₂, TM-x, and MnO₂ under 300 W Xe lamp irradiation to confirm the mechanism discussed above. As illustrated in Fig. 4B, the surface temperature for all samples started to increase with increasing irradiation time, reaching a maximum value of 300°C at an irradiation time of 30 s for 0.5% Pt/TM-0.4. This suggests that the nanocomposites have the potential to be used as effective solar heaters.

Fig. 3  (A) Ti 2p, (B) Mn 2p, (C) O 1s, and (D) Pt 4f XPS spectra of TM-0.4 and 0.5% Pt/TM-0.4.

Fig. 4  (A) UV-Vis-IR diffuse reflectance spectra of TiO₂, MnO₂, and TM-x. (B) Surface temperature evolution of TiO₂, MnO₂, and TM-x under 300 W Xe lamp irradiation. (C) UV-Vis-IR diffuse reflectance spectra of TM-0.4 and Pt/TM-0.4 with different Pt loadings. (D) Surface temperature evolution of TM-0.4 and Pt/TM-0.4 with different Pt loadings.
reached equilibrium after 5 min of irradiation. The surface temperatures of all catalysts are listed in Table S2.† Notably, for TM-x samples, the trend in surface temperature agreed well with their light absorption ability in visible and infrared regions. Furthermore, Pt loading further enhanced the light absorption intensity and surface temperature, as demonstrated in Fig. 4C and D.

3.5 Characterization of photoelectrochemical properties

The photoelectrochemical properties of the as-prepared samples were then investigated using a series of techniques. As shown in Fig. 5A, the photocurrent response of the TM-x samples decreased with decreasing Ti-to-(Ti + Mn) ratio, while the MnO₂ barely generated any photocurrent. This is expected, since TiO₂ was the photocatalytic component while MnO₂ was the thermocatalytic component. In addition, this is also consistent with the EIS results (Fig. 5B) which showed that the electrochemical impedance of the TM-x samples increased with decreasing Ti-to-(Ti + Mn) ratio. Moreover, as shown in Fig. 5C and D, an increase of photocurrent response and a decrease of electrochemical impedance were observed for the TM-0.4 sample after the loading of Pt nanoparticles. Specifically, the photocurrent response increased in the order of TM-0.4, 0.1% Pt/TM-0.4, 0.5%Pt/TM-0.4, and 1.0%Pt/TM-0.4, while their electrochemical impedance decreased in the same order. In addition, we conducted the Mott–Schottky experiments for TM-0.4 and Pt/TM-0.4, as shown in Fig. 5E. All samples showed a positive slope in the Mott–Schottky plots. The Pt/TM-0.4 samples exhibited smaller slopes compared to the TM-0.4 sample, suggesting the higher charge transfer rate of photogenerated electrons. The flat band potential for TM-0.4 and Pt/TM-0.4, obtained from the intercept of the regression line, was −0.37 V. Since the flat band in n-type semiconductors is roughly 0.10 eV lower than the bottom of the conduction band (CB), the calculated CB of TM-0.4 was −0.47 eV. More importantly, as shown in Fig. 5F, the PL signals were also significantly suppressed after the loading of Pt nanoparticles, suggesting enhanced charger separation efficiency for the Pt/TM-0.4 samples compared to the TM-0.4 sample.

3.6 Investigation of photothermocatalytic activity

The PTC activity of the prepared catalysts was evaluated using toluene as a typical VOC pollutant and a 300 W Xe lamp as the light source. Fig. 6A and B show the change of concentration for CO₂ (product) and toluene (reactant) for TiO₂, MnO₂, and TM-x. As shown in Fig. 6B, initial adsorption of toluene on the catalyst surface led to a drop in toluene concentration even before light irradiation. However, since the surface temperature of these catalysts was increased upon light irradiation, an increase of CO₂ concentration was observed. This is consistent with the results shown in Fig. 6C and D, where the concentration of CO₂ increased with increasing Pt loading. In addition, we conducted the PTC experiments for TM-0.4 and 0.5% Pt/TM-0.4, as shown in Fig. 6E and F. The concentration of CO₂ under the PTC, TC, and PC conditions for (E) TM-0.4 and (F) 0.5% Pt/TM-0.4.
toluene concentration was observed for catalysts with low activity, due to the fact that adsorption and desorption of toluene on the catalyst surface needed to reach a new equilibrium at an elevated temperature. From Fig. 6A and B, it is clear that TM-0.4 exhibited the highest catalytic activity among all the samples. After 60 min of light irradiation, the degradation rate of toluene for TM-0.4 reached 97.1%, while those for TiO2 and MnO2 were only 16.1% and 18.0%, respectively. As shown in Fig. S10A,† the kinetic curves exhibited good linearity, indicating that the catalytic degradation of toluene on TM-x followed the quasi-first-order kinetics. The reaction rate constant of TM-0.4 was 0.03812 min⁻¹, which was 11.3 times and 12.1 times higher than that of TiO2 and MnO2, respectively. Upon complete degradation of toluene, the final CO2 concentration (∼8000 ppm) was nearly seven times the initial concentration of toluene, approaching its stoichiometric yield of toluene combustion ($C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$). This suggests that toluene was completely mineralized into CO2 and H2O after reaction.

We further investigated the influence of Pt loading on the catalytic activity by employing the optimal TM-0.4 as the model catalyst. As shown in Fig. 6C and D, the CO2 production rate (or the toluene degradation rate) increased with increasing Pt loading. 97.4% of toluene was degraded after 30 min of light irradiation for 0.5% Pt/TM-0.4. This value was 1.49 times higher than that achieved for TM-0.4 (65.5%). As shown in Fig. S10B,† the reaction rate constant for the 0.5% Pt/TM-0.4 catalyst was 0.076 min⁻¹, which was 1.7 times higher than that of TM-0.4 and higher than that of most of the state-of-the-art catalysts reported in the literature (Table S3†). Given that 1.0% Pt/TM-0.4 and 0.5% Pt/TM-0.4 exhibited almost the same catalytic activity for toluene degradation, further investigation was performed on 0.5% Pt/TM-0.4 due to its lower operational cost. The stability of TM-0.4 and 0.5% Pt/TM-0.4 was investigated through cyclic experiments of toluene degradation. As shown in Fig. S11 and S12,† the conversion rates of toluene for both TM-0.4 and 0.5% Pt/TM-0.4 showed a negligible decrease after 10 runs, indicating that they possessed excellent stability.

For comparison, we also performed control experiments under the PC and TC conditions. The reaction temperature under the TC conditions was kept the same as the surface temperature of the catalyst using an electrical heating system. As shown in Fig. S15,† the ignition temperature (denoted by $T_{ign}$, expressed by the temperature at 10% conversion) of 0.5% Pt/TM-0.4 was 160 °C, which was significantly lower than that of TM-0.4 (200 °C), indicating that Pt loading can enhance toluene degradation efficiency by effectively reducing the ignition temperature of toluene. 60 To further understand the contribution of Pt under the PC conditions, we also investigated the active species generated during the PC reaction processes for TM-0.4 and 0.5% Pt/TM-0.4 using the ESR spin-trap technique with DMPO as the trapping agent. 57 In methanol solution, six peaks with similar intensity corresponding to the characteristic peaks of DMPO−⋅O2− were observed (Fig. 7A). 58 In aqueous solution (Fig. 7B), four peaks with intensity ratios of 1:2:2:1 were attributed to DMPO−⋅OH. 59 These results confirm the formation of $\cdot O_2^-$ and $\cdot OH$ (e$^-$ + $O_2 \rightarrow O_2^-$; h$^+$ + $OH^-$ → $\cdot OH$) under Xe lamp irradiation. Notably, the peak intensities of these characteristic peaks generated in the 0.5% Pt/TM-0.4 catalyst were stronger than those produced in TM-0.4 alone, indicating that Pt loading can enhance the production of active species by forming a Schottky junction with TiO2. 60 To assess the contribution of these active species to toluene degradation, we conducted toluene degradation experiments in the presence of various scavengers, namely, $K_2Cr_2O_7$ [Cr(VI)] for e$^-$, EDTA-2Na for h$^+$, mannitol for $\cdot OH$ and p-benzoquinone (p-BQ) for $\cdot O_2^-$, 61−63 As shown in Fig. 7C, D and S16, S17,† all scavengers exhibited an inhibitory effect on toluene degradation, suggesting that all these active species contributed to toluene degradation. On the other hand, given that the oxidation potential of toluene (1.276 V vs. NHE) is lower than that of h$^+$ (2.53 V vs. NHE), toluene was first oxidized

3.7 Investigation of the contribution of Pt
To understand the contribution of Pt under the TC conditions, we measured the thermocatalytic degradation rates of toluene for TM-0.4 and 0.5% Pt/TM-0.4 at different temperatures by controlling the surface temperature of the catalysts using an electrical heating system. As shown in Fig. S15,† the ignition temperature (denoted by $T_{ign}$, expressed by the temperature at 10% conversion) of 0.5% Pt/TM-0.4 was 160 °C, which was significantly lower than that of TM-0.4 (200 °C), indicating that Pt loading can enhance toluene degradation efficiency by effectively reducing the ignition temperature of toluene. 60

![Fig. 7](image-url)
into C₂H₄⁺, which was more easily oxidized into CO₂ and H₂O as the electron number in the bonding molecular orbital of C₂H₄⁺ is less than that of toluene.⁶⁴,⁶⁵

3.8 ¹⁸O₂ isotope labeling experiments and H₂-TPR tests

It is widely acknowledged that the catalytic combustion of organic compounds typically proceeds via the MvK mechanism. This mechanism entails the initial oxidation of adsorbed organic molecules by lattice oxygen present in metal oxide catalysts, followed by the subsequent re-oxidation of the catalysts by the gaseous oxygen.⁶⁶,⁶⁷ To elucidate the degradation mechanism of toluene on TM-0.4 and 0.5% Pt/TM-0.4, isotopic labelling experiments were carried out using ¹⁸O₂ as the oxidant instead of ¹⁶O₂.⁶⁸ In Fig. 8A and B, FTIR spectra revealed three peaks at 2310 cm⁻¹, 2322 cm⁻¹, and 2343 cm⁻¹. The peak at 2310 cm⁻¹ was attributed to the C–O stretching vibrations of ¹²C¹⁸O₂, while the peak at 2322 cm⁻¹ and 2343 cm⁻¹ were assigned to the C–O stretching vibrations of ¹²C¹⁶O¹⁸O, as per previous references.⁶⁹–⁷¹ The formation of ¹²C¹⁸O₂ and ¹²C¹⁶O¹⁸O was further corroborated by the appearance of molecular ion peaks at 48 and 46 in the GC-MS spectra (Fig. S18†). As the ¹⁸O within the lattice is consumed, the ¹⁸O in the reactor would replenish the ¹⁶O vacancy and become incorporated into the lattice ¹⁸O of the catalyst.⁷²–⁷⁴ Both ¹⁶O and ¹⁸O participated in the oxidation of C₂H₈, resulting in the formation of ¹²C¹⁸O₂ and ¹²C¹⁶O¹⁸O. The above results indicate that the degradation of toluene on TM-0.4 and 0.5% Pt/TM-0.4 followed the MvK mechanism.

Given the close correlation between the catalytic activity of metal oxide catalysts and their redox properties, we examined the redox characteristics of the TM-x and Pt/TM-0.4 samples through the H₂-TPR test (Fig. 8C and D) conducted over a temperature range of 40–800 °C. In Fig. 8C, TiO₂ only exhibited a single peak around 650 °C, which was attributed to the transition from Ti⁴⁺ to Ti³⁺ characteristic of anatase TiO₂.⁷²–⁷⁴ MnO₃ displayed two peaks at 310 °C and 650 °C, which was ascribed to the transitions of MnO₃–Mn₂O₃ and MnO₂–MnO, respectively.⁷⁶ All TM-x samples showed two primary reduction peaks, in which TM-0.4 displayed two lowest reduction temperature points at 390 °C for MnO₂–MnO and 515 °C for MnO₃–MnO, consistent with its extraordinary catalytic activity of TM-0.4.⁷⁷ After the loading of Pt nanoparticles, all catalysts showed a prominent single reduction peak at 100–300 °C (Fig. 8D), corresponding to the reduction of Pt related oxidation species and active oxygen species.⁷⁸ With increasing Pt loading, the reduction temperature decreased slightly, indicating further improvement of redox ability.⁷⁹ These findings showed that Pt loading can effectively enhance the redox ability of TM-0.4, consequently improving its catalytic activity for toluene oxidation.

3.9 Investigation of the contribution of the IO structure

To explore the impact of the IO structure on catalytic performance, we prepared TM-0.4 without adding the PS template (referred to as TM-0.4-NPs) and compared its microstructures, light absorption properties and catalytic activities with those of TM-0.4. As shown in Fig. 9A, TM-0.4-NPs took the form of small nanoparticles (NPs) instead of the IO structure. Its specific surface area was determined to be 24.02 m² g⁻¹, markedly lower than that of TM-0.4 (97.1%) is 2.26 times that of TM-0.4-NPs (42.9%), underscoring the beneficial role of the IO structure. The enhancement of catalytic activity by the IO structure can be attributed to the following mechanisms: firstly, the IO structure...
provided a larger specific surface area and more active sites. Secondly, the IO structure enhanced light absorption, leading to higher surface temperatures under light irradiation. Finally, the interconnected ordered pore structure promoted the transport of reactants and products.

3.10 Investigation of the mechanism via in situ DRIFTS analysis

The in situ DRIFTS technique was employed to investigate intermediate products for 0.5% Pt/TM-0.4 under the PTC, TC, and PC conditions, as shown in Fig. 10. The peaks at 3070 and 1598 cm\(^{-1}\) can be attributed to the stretching vibration of the aromatic ring, and the peak at 1490 cm\(^{-1}\) can be attributed to skeleton C\(=\)C bond vibration of aromatic rings.\(^{81-83}\) The peak at 3043 cm\(^{-1}\) was associated with C-H bond stretching vibrations of the aromatic ring and the peaks at 2937 and 2884 cm\(^{-1}\) belonged to asymmetric and symmetric C-H bond stretching vibrations of the methyl group, indicating the adsorption of toluene on the catalyst surface.\(^{84}\) Notably, the peak at 3070 cm\(^{-1}\) was similar in intensity under all conditions, but the peak at 3043 cm\(^{-1}\) was significantly lower in intensity under the PTC conditions compared to those observed under the PC and TC conditions, indicating that the methyl group on the benzene ring was quickly oxidized before the benzene ring under the PTC conditions.

This can also be confirmed by the observation of peaks at 1024 and 1175 cm\(^{-1}\) which correspond to the C-O bond stretching vibration of benzyl alcohol.\(^{85}\) Additionally, peaks at 1445 and 1248 cm\(^{-1}\) were also observed which were characteristic of the C=O bond vibrations and skeleton C-C bond vibration of benzaldehyde.\(^{86}\) Furthermore, the peaks at 1516 and 1416 cm\(^{-1}\) were associated with the anti-symmetric vibration of the COO- group and C-O bond symmetric stretching vibration, respectively, indicating the formation of benzoate species.\(^{87,88}\) It should be noted that the intensity of all these peaks was higher under the PTC conditions compared to the TC and PC conditions, indicating faster oxidation of toluene under the PTC conditions. More direct evidence of this is the observation of doublet peaks at 2364 and 2342 cm\(^{-1}\) which can be attributed to the asymmetric O==C==O stretching vibration of CO\(_2\) molecules under the PTC conditions.\(^{87}\) The intensity of these two peaks was significantly lower under the TC and PC conditions compared to the PTC conditions. Acid anhydride species (1966 and 1920 cm\(^{-1}\)) and carbonate species (1473 cm\(^{-1}\)) were also observed under the PTC and TC conditions but were barely detected under the PC conditions.\(^{88,89}\) This is consistent with the toluene degradation results in which toluene was most efficiently degraded under the PTC conditions, followed by the TC conditions, and then by the PC conditions.

Based on the above experimental results, the possible toluene degradation mechanism under the PTC conditions for TM-0.4 and Pt/TM-0.4 were proposed. Generally, the TC degradation of toluene follows the MvK mechanism.\(^{90}\) The pore structure of TM-0.4 enhanced the adsorption of reactants (C\(_7\)H\(_8\) and \(\text{O}_2\)) and offered more reaction sites for toluene degradation. As illustrated in Fig. 11A, under light irradiation, the catalyst surface was gradually heated to the ignition temperature, initiating the oxidation of toluene by the lattice oxygen on the MnO\(_2\) surface, while MnO\(_2\) was reduced to MnO\(_{2-x}\). In the absence of TiO\(_2\), the reduced MnO\(_{2-x}\) can be re-oxidized by adsorbed \(\text{O}_2\) via the MvK mechanism. However, when TiO\(_2\) was present, photogenerated electrons (\(e^-\)) and holes (\(h^+\)) would react with C\(_7\)H\(_8\), O\(_2\) and H\(_2\)O (or OH\(^-\)) to produce C\(_7\)H\(_8\)\(^+\), \(\cdot\text{O}_2\), and \(\cdot\text{OH}\) radicals.\(^{93}\) Since C\(_7\)H\(_8\)\(^+\) has fewer electrons in the bonding molecular orbital compared to C\(_7\)H\(_8\), it is much easier to be oxidized by the lattice oxygen. More importantly, \(\cdot\text{O}_2\) and \(\cdot\text{OH}\) radicals are more active than the adsorbed O\(_2\) for oxidation of the reduced MnO\(_{2-x}\) by promoting the re-generation of lattice oxygen species.\(^{94}\) Such a synergy is the reason why toluene degradation under PTC conditions could outperform that under PC and TC conditions. Pt loading improved the catalytic activity of TM-0.4 by the following mechanisms (Fig. 11B): on one hand, Pt nanoparticles loaded on TM-0.4 can effectively absorb toluene and \(\text{O}_2\) due to their quantum size effect;\(^{95}\) on the other hand, Pt nanoparticles could activate \(\text{O}_2\) via hot electrons to form reactive oxygen species.\(^{45,93}\) Thus, toluene (C\(_7\)H\(_8\) and C\(_7\)H\(_8\)\(^+\)) can be oxidized by Pt-induced oxygen species and the lattice oxygen of MnO\(_2\) accompanied by the cyclic conversion of Pt\(^{4+}\) to Pt and MnO\(_2\) to MnO\(_{2-x}\). The reduced catalyst was re-oxidized by O\(_2\) and active oxygen species (\(\cdot\text{OH}, \cdot\text{O}_2\)) to participate in the next cycle of reaction, which conformed to the MvK mechanism.\(^{94}\) Moreover, during PC processes, Pt nanoparticles can effectively separate the photogenerated electrons and holes of TiO\(_2\) by forming a Schottky barrier, promoting the formation of \(h^+, \cdot\text{O}_2\) and \(\cdot\text{OH}\) radicals.\(^{95}\) As a result, Pt loading
significantly enhanced the catalytic activity for toluene degradation for the TM-0.4 catalyst.

4. Conclusions

In this study, IO structured TM-\(x\) photothermocatalysts with varying Ti-to-(Ti + Mn) ratios were constructed using a well-arranged PS template. The macroporous IO structure not only enhanced light absorption of catalysts in the visible and near infrared regions but also increased their surface area for adsorption of gaseous reactants. Amongst the TM-\(x\) samples, TM-0.4 displayed the highest PTC activity for toluene degradation. Specifically, 1150 ppm of toluene could be completely mineralized into CO\(_2\) within 60 min, which was 6.0 times and 5.4 times the activity of TiO\(_2\) and MnO\(_y\), respectively. Further enhancement of PTC activity was achieved by loading of Pt nanoparticles, with 97.4% of toluene being degraded after 30 min of light irradiation for 0.5% Pt/TM-0.4. A synergistic effect between PC and TC was observed, where the degradation rate of toluene under PTC conditions far exceeded that under either PC or TC conditions. EPR and radical trapping experiments confirmed that e\(^-\), h\(^+\), -OH, and -O\(_2\)\(^-\) were active species produced under light irradiation. The \(^{18}\)O\(_2\) isotope labeling, GC-MS, and H\(_2\)-TPR analyses revealed that degradation of toluene under the PTC conditions followed the MvK redox mechanism. The active species produced in the photocatalytic reaction not only activated toluene but also accelerated the oxidation of oxygen vacancies in TM-0.4. Pt loading improved catalytic activity by promoting the adsorption of toluene and O\(_2\) as well as activating O\(_2\) to form reactive oxygen species. We believe that this study would provide a reference for fabricating new photothermocatalytic materials with high sunlight-driven activity to solve the VOC pollution issue.

Data availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the ESL. Additional data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of interest

The authors declare no conflict of interest.

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