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Efficient infrared light promoted degradation of volatile organic compounds over photo-thermal responsive Pt-rGO-TiO₂ composites



Juan-Juan Li^{a,b}, Song-Cai Cai^{a,b,c}, En-Qi Yu^{a,b,c}, Bo Weng^{d,e}, Xi Chen^{a,b,c}, Jing Chen^f, Hong-Peng Jia^{a,b,c,*}, Yi-Jun Xu^{d,e,**}

^a CAS Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, PR China

b Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, PR China

^c University of Chinese Academy of Sciences, Beijing, 100049, PR China

^d State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, New Campus, Fuzhou University, Fuzhou, 350116, PR China

e College of Chemistry, New Campus, Fuzhou University, Fuzhou, 350116, PR China

^f Xiamen Institute of Rare-earth Materials, Haixi Institutes, Chinese Academy of Sciences, Xiamen, Fujian, 361021, PR China

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ABSTRACT

Infrared (IR) light photo-thermocatalysis has been motivated by the realization of prospects that sunlight is an inexhaustible energy source where infrared photons most strongly emitted in the solar spectrum are converted into thermal energy, which thus can drive different redox catalysis applications, e.g., oxidative degradation of volatile organic compounds (VOCs). Herein, we report that the hybrid nanomaterial Pt-rGO-TiO₂, featuring the broad light wavelength absorption (800–2500 nm), can be used as a highly active photo-thermal responsive catalyst for efficient VOCs decomposition under IR irradiation. The maximum photo-thermal conversion efficiency is able to reach 14.1% with a significant toluene conversion of 95% and CO₂ yield of 72% under infrared irradiation intensity of 116 mW/cm², along with retaining its stability for nearly 50 h. The comparison characterizations evidence that such excellent performance is predominantly attributed to the synergistic effects of efficient light-to-heat conversion, increased adsorption capacity and well dispersed supported Pt-TiO₂ catalyst on the 2D rGO sheet. This work highlights that graphene-based composites an alternative and feasible strategy for solar energy conversion.

1. Introduction

Volatile organic compounds (VOCs) emitted into the atmosphere from anthropogenic have led to photochemical smog and ground-level ozone [1]. The commercial heterogeneous catalytic reactions with oxides of transition metal are driven by thermal energy for complete oxidation of VOCs [2], but high operating temperatures involved in this process generally require external electrical heating and are characterized by low energy efficiencies and compromised durability of catalysts [3]. Since solar power is an inexhaustible energy source [4], researchers have long been infatuated with the idea of converting light into chemical energy via photocatalysis to generate highly reactive oxidative species (ROSs, e.g., holes or superoxide/hydroxyl radicals) to address air pollution problems [5]. For the most extensively studied semiconductor TiO₂ photocatalyst, the limited light absorption (only UV, 3% of solar light), high charge carriers recombination and lack of highly active sites on catalyst surface render such photochemical conversion inefficient [6]. Sunlight consists of about 44% visible light, and therefore multifarious strategies [7–9] such as doping with metals and/ or nonmetals, adopting organic sensitizers or coupling with other semiconductors, were developed in an attempt to extend the photoresponse toward improving the efficiency of TiO₂. However, many developed TiO₂-based or non-TiO₂-based photocatalysts [10,11] cannot be activated by the IR wavelength light that constitutes 53% of the solar energy reaching earth's surface [12].

In order to effectively utilize IR light, tremendous attempts have been made to develop IR-light-induced photocatalysts. Owing to the low photon energy and unsuitable band structure, small bandgap semiconductors with protruding NIR light adsorption, were generally deemed to lack photocatalytic activity [13]. Thus, many works have focused mainly on upconversion luminescence of rare-earth materials [14–17] through converting near infrared (NIR) excitation into UV or

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^{*} Corresponding author at: CAS Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, PR China. ** Corresponding author at: State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, New Campus, Fuzhou University, Fuzhou, 350116, PR China. *E-mail addresses*: hpjia@iue.ac.cn (H.-P. Jia), yjxu@fzu.edu.cn (Y.-J. Xu).

visible emission to trigger photocatalytic reaction. For instance, by assembling NaYF₄:Yb/Tm@NaYF₄ up-converting core-shell nanoparticles (NPs) with UV active ZnO NPs [18], organic molecules were photocatalytically degraded under NIR light. Although this work manifested the possibility of using NIR light for photocatalysis, the efficiency of NIR light energy transfer upconversion process was largely limited by its very narrow absorption band of light at 980 nm and the quick depletion of excitation energy [19,20]. In contrast to traditional rare-earth up-converting materials, carbon quantum dots (CQDs) are not limited to specific wavelength of light, and recent improvement has been made in using CQDs as up-conversion material in combination with developed UV- or visible-light-active NPs (i.e., CQDs/Cu₂O composites [21], CODs/H-TiO₂ nanobelt [22]) as NIR-responsive photocatalyst. Unfortunately, up-conversion efficiency of CQD was primarily restricted by the competition between up-conversion and down-conversion processes. Moreover, sparked by the discovery that the rare-earth cations are able to absorb IR light [23], BiErWO₆ solid solution [24], a regular stacking of BiErO₂ layers interleaved with WO₄ layers, was successfully constructed as an efficient NIR photocatalyst for the degradation of rhodamine B. Additionally, microcrystal of Cu₂(OH)PO₄ [25] was found to be a NIR-activated photocatalyst in which the hot electrons are generated at the CuO₄(OH) trigonal bipyramids and transfer to the neighboring CuO₄(OH)₂ octahedra for efficient electron-hole separation. Recently, Localized surface plasmon resonances (LSPR) also offer an exciting opportunity to design artificial materials with effective IR light harvesting for plasmonic photocatalysis applications [26–29]. For instance, Cu₇S₄ NPs utilized NIR photon through LSPR in which hot holes could be generated from the photoexcitation of Cu₇S₄ NPs under IR light illumination and quickly injected into Pd domain to render hole-rich Pd surface for photocatalytic oxidation of benzyl alcohol and for hydrogenation of nitrobenzene [30].

Despite the recent progress in searching strategies for effective exploitation of IR light, the IR-light-induced photocatalysis efficiency is still not satisfactory to date due to the limited utilization of photogenerated charge carriers, which impedes its practical application. In contrast, the strong thermal effect induced by IR photon energy, especially on the IR-induced photo-thermocatalysis for environmental pollutants purification, has been significantly overlooked. Drawing inspiration from near-IR light photosensitizers largely exploited in photothermal cancer therapy [31-33], there has been a resurgence of research interest in an exploration of IR photo-thermal responsive materials. For example, Hu and co-workers recently have reported that photo-thermal effect is utilized in core-shell Fe₃O₄@SiO₂ to capture the energy of IR light for photo-thermal catalytic oxidation of NO [34]. Therefore, IR-driven photo-thermocatalysis provides an alternative approach to solar energy utilization and opens the possibility of substituting light-driven photo-thermocatalysis reactions for conventional thermal-based catalytic redox reactions.

In principle, to achieve high photo-thermal energy conversion efficiency, an ideal material must satisfy several functional requirements: robust harvesting of IR light, forceful coupling of the harvested photons into thermal energy and effective catalytic active sites. Graphene, a single-layer carbon sheet with a hexagonal packed lattice structure, has inspired tremendous interest due to its unique physic-chemical properties such as high thermal conductivity, excellent carriers mobility, and good optical transparency [35,36]. So far, the main focus of interest has been on electronic properties, i.e., photoelectron mediator and acceptor in graphene-based composite photocatalysts. Due to its high optical absorption in the NIR region, a new direction for graphenebased composites is photo-thermal effect [37], and one remarkable application is its potential use in photo-thermal therapy for the ablation of cancerous cells whereby NIR light is absorbed and converted into heat [38,39]. In addition, the photo-thermal effect of reduced graphene oxide (rGO) sheets can make the electrons obtain more energy and move faster on the hot rGO sheet to promote the degradation of methyl blue over the rGO-P25 composites [40].

With these motivations, we report that the photo-thermal responsive hybrid nanomaterial of Pt-rGO-TiO₂ can be used for efficient degradation of VOCs under IR light. The results showed that photo-thermal responsive 1% Pt-rGO-TiO₂ composites exhibited high catalytic performance with 95% of toluene conversion, 72% of CO₂ yield and long term stability of nearly 50 h toward degradation of VOCs under IR light. The comparative characterizations revealed that such photo-thermal catalytic activity enhancement results from the restacking-in-hibited 2D rGO sheet, by which the synergistic effects of efficient light-to-heat conversion, increased adsorption capacity and supported active Pt NPs can be achieved. This work highlights that graphene-based composites, featuring the broad IR light absorption, show promise for redox catalysis applications through photo-thermal effect, which would open a new promising route to using graphene-based composite materials as IR light photon absorber for solar energy conversion.

2. Experimental section

2.1. Preparation of graphene oxide

Graphene oxide (GO) was synthesized from natural graphite powder by a modified Hummers method [37,41]. In detail, 2 g of graphite powder (Alfa Aesar) was put into a mixture of 50 mL of concentrated H_2SO_4 and 1 g of NaNO₃ in an ice water bath and 8 g of KMnO₄ was added gradually for 120 min under vigorous stirring. Then, the solution was heated to 35 °C in an oil-bath and kept stirring for 2 h. Successively, 50 ml of deionized (DI) water was added into the above mixture, followed by stirring at 95 °C for 0.5 h. Then, to the resulting mixture were added 50 ml of DI water and 20 mL of 30% H_2O_2 to remove unreacted KMnO₄. When cooled to room temperature, the supernatant then underwent two more high-speed centrifugation steps at 8000 rpm for 10 min, then washed with 5% HCl aqueous solution to remove metal ions followed by DI water to remove the acid. The product was ultrasonicated for 1.5 h, then stirred under ambient condition overnight. The mixture was then carefully diluted with deionized (DI) water, filtered, and washed until the pH of rinse water became neutral. Finally, a homogeneous GO aqueous solution (4 mg/mL) was obtained.

2.2. Preparation of Pt-rGO-TiO₂ composites

To synthesize the Pt-reduced graphene oxide-TiO₂ (x% Pt-rGO-TiO₂) composites with various ratios of Pt, a simple solvothermal method using ethanol-water as solvent was used as the following [42], where titanium dioxide (TiO₂) nanopowder is the commercial P25 (Degussa). 7.5 mL of GO aqueous solution (4 mg/mL) was ultrasonicated in a 15 mL of deionized water and 11.25 mL of anhydrous ethanol solution to disperse it well; after that, 0.6 g of TiO₂ first, then certain amount of H₂PtCl₆ (3.8 mg/mL) aqueous solution was then rapidly injected into the above GO solution by pipet to prepare 0.1, 0.5, 1 and 2 wt% Pt-rGO-TiO2 nanocomposite catalysts. The mixing solution was aged with vigorous stirring for 2h to obtain a homogeneous suspension. Then, this suspension was transferred to a 50 mL teflon-sealed autoclave and maintained at 120 °C for 24 h. Under such a solvothermal condition, the solvent of ethanol-water has the strong power to simultaneously reduce Pt⁴⁺ and GO into Pt and rGO [43]. The resulting composites were filtered and washed with deionized water, and fully dried at 60 °C in vacuum oven to get the final x% Pt-rGO-TiO₂ composites.

For comparison, the preparation procedure of TiO_2 , rGO- TiO_2 and 1% Pt- TiO_2 was similar to that of x% Pt-rGO- TiO_2 without addition of rGO and/or Pt solution.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) characterization was carried out on a X'Pert Pro automatic powder diffractometer operated at $40 \, \text{kV}$ and



Fig. 1. XRD patterns (A); Raman spectra (B) and the enlarged view in (C) and (D); XPS spectra of the C 1s (E), Ti 2p (F), O 1s (G), and Pt 4f (H) of the samples.

40 mA using Cu Ka monochromatized radiation. Raman spectroscopy was carried out on LabRAM Aramis using a green laser of 532 nm wavelength. The actual loading content of noble -metal was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian, VISTAMPX-ICP). Nitrogen adsorption-desorption measurements of the catalysts were performed on a Quantachrome autosorb iQ2 adsorption automatic instrument at liquid nitrogen temperature. All samples were degassed under vacuum at 60 °C for 24 h before the measurement. The specific surface area and pore volume of the catalysts were calculated from the nitrogen adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. Diffuse reflectance spectra were recorded using a Varian Cary 5000 UV-vis spectrophotometer in the 200-2500 nm range at room temperature using BaSO₄ as a reference. XPS analysis was conducted on a Thermo Scientific ESCALAB 250 with a monochromatised microfocused Al X-ray source. Transmission electron microscopy (TEM) was analyzed using a JEOL model JEM 2100 EX instrument at an acceleration voltage of 200 kV. Temperature-programmed desorption (TPD) measurement was performed on a Quantachrome Chemstar instrument. 200 mg catalyst sample was filled in an adsorption vessel and pretreated in a He flow (50 ml/min) at 300 °C for 60 min then cooled to 35 °C and kept at this temperature for 60 min in a flow of 5 vol% O₂/He or gaseous toluene (30 ml/min). Then, the sample was swept with He for 120 min and heated to 800 °C at a rate of 10 °C/min in a He flow of 30 ml/min. The desorbed products were monitored simultaneously by thermal conductivity detector and mass spectroscopy equipment. The enthalpy of samples was obtained by using differential scanning calorimeter (Netzsch STA 449 F3, Thermal Analysis Corporation, Germany) from 30 to 300 °C at a heating rate of 5 °C/min in a N₂ flow of 50 ml/min. Electron paramagnetic resonance (EPR) spectra were taken from Bruker A300 spectrometer by applying an X-band (9.43 GHz, 1.5 mW) microwave and sweeping magnetic field at room temperature. In situ DRIFTS was performed on a FTIR spectrometer (Nicolet Nexus 670) equipped with a smart collector and a MCT/A detector. Prior to experiment, the sample was pretreated at 150 °C for 1.5 h in a N2 flow to remove adsorbed impurities. The background spectrum was collected under N2 and automatically deducted from the sample spectra. Afterward, 1000 ppm toluene/N2 was introduced to the cell at a flow rate of 50 mL/min at 150 °C, and then DRIFTS spectra were recorded. Subsequently, the flow of N₂ was introduced to investigate the reactivity at 150 °C.

2.4. Photo-thermocatalytic activity

The photo-thermocatalytic activity of the samples for toluene oxidation was evaluated in a cylindrical stainless steel reactor with a quartz window under IR light irradiation (375 W, Philips) with a 800 nm cut-off filter. In the experiments, an ethanol suspension containing 0.1 g of the catalyst was prepared, and then coated on a fiberglass membrane of 50 mm diameter, dried at 40 °C and finally placed on the photoreactor. Prior to irradiation, the adsorption-desorption equilibrium of toluene on the photocatalyst was carried out. The equilibrium concentration of toluene was about 200 ppm produced by an air stream bubbling through a liquid toluene. The flow rate of the gas was 52.2 mL min^{-1} . The concentration of toluene and the evolution of CO_2 were monitored by an on-line gas chromatograph equipped with two flame ionization detectors (FID) and a nickel-based methanizer. The toluene conversion and CO_2 yield for the photocatalytic reaction were calculated by using by using Eqs. (1) and (2), respectively.

Toluene conversion (%) = $100 \times ([Toluene]_{in} - [Toluene]_{out})/[Toluene]_{in}$ (1)

 CO_2 yield (%) = $100 \times [CO_2]_{produced} / [CO_2]_{theoretical}$ (2)

2.5. Photocatalytic activity

The photocatalytic activity of the catalyst for toluene oxidation was measured in a cylindrical quartz reactor (5 cm \times 5 cm \times 1 cm) with a glycerol-water bath of ultralow temperature (-20 °C) to keep the reaction temperature at room temperature (28 °C) under the irradiation of IR lamp.

2.6. Thermocatalytic activity

The thermocatalytic activity of the catalyst for toluene oxidation was carried out in a cylindrical stainless steel reactor on an online gasphase reaction apparatus at different temperature by external electrical heating.

3. Results and discussion

Fig. 1(A) displays the XRD patterns of the bare TiO₂, rGO-TiO₂ and Pt-rGO-TiO₂ composites with various loading amounts of Pt NPs. All of identified peaks of the samples are perfectly in accordance with anatase TiO₂ (JCPDS card no. 01-084-1286) and rutile TiO₂ (JCPDS card no. 01-089-0554). Moreover, no typical diffraction peaks assigned to Pt NPs have been observed in x% Pt-rGO-TiO₂ composites (x = 0.0.1, 0.5 and 1), which could be ascribed to the low content of small sized Pt [44], whereas a small peak at 41° for Pt NPs was observed in 1% Pt-TiO2 and 2% Pt-rGO-TiO₂ samples, which might be attributed to high loading or Pt with large particle size. Likewise, no diffraction peaks for rGO were detected in rGO-TiO2 and x% Pt-rGO-TiO2 composites due to the small amount and weak intensity of rGO which might be shielded by the peak of TiO₂ at 25.3° [45]. Raman spectroscopy has been applied to further distinguish the sp² and sp³ hybridization in the carbon-based materials [46]. As shown in Fig. 1(B), the bare TiO_2 exhibits five intensive peaks of anatase $TiO_2(A)$ where the peaks at 144, 196 and 636 cm⁻¹ are assigned to the E_g mode of TiO₂(A), and the peaks at 396 cm⁻¹ and 517 cm⁻¹ correspond to the B_{1g} mode of TiO₂(A) and doublet of A_{1g} / $B_{1\sigma}$ [47]. No obvious peaks corresponding to rutile TiO₂(R) are observed, presumably since the peaks are too weak to be clearly observed. These peaks are also observed in 1% Pt-TiO2, rGO-TiO2, 1% Pt-rGO-TiO₂ composites, but their intensities decrease significantly, and even shift to a high wavenumber (Fig. 1(C) and (D)), thereby indicating that the symmetric stretching vibration of O-Ti-O in TiO₂ has been destroyed to some extent after combination with Pt or/and rGO [48]. The peak shift can be attributed to a change of surface strain stemming from the introduction of Pt or/and rGO which shows a strong interaction with oxygen in TiO₂ [49]. For the rGO-TiO₂ and 1% Pt-rGO-TiO₂ composites, two typical features (D and G bands) of rGO at 1335 cm^{-1} and 1591 cm⁻¹ (Fig. 1 (D)), respectively, are observed, where the D band corresponds to ring breathing modes of sp² carbon atoms adjacent to a defect or an edge and the G band is associated with sp² carbon atoms in

a planar and conjugated structure [50].

X-ray photoelectron spectroscopy (XPS) was employed to inspect the interactions among Pt, TiO₂ and rGO as well as the chemical states of elements. The peak deconvolutions of C 1s, Ti 2p, O 1s and Pt 4f are shown in Fig. 1(E)-(H). The deconvoluted C1s peaks located at 284.7, 286.7 and 288.6 eV are characteristic of C-C, C-O and COOH, respectively, indicating a significant deoxygenation of oxygen-containing functional groups of GO and effective reduction of GO to rGO [51,52]. The two deconvoluted Ti 2p peaks centered at 459.7 and 465.4 eV are assigned to the core levels of $Ti^{4+} 2p_{3/2}$ and $Ti^{4+} 2p_{1/2}$ [53], which are slightly shifted toward a higher binding energy compared with those in TiO₂, revealing the change in the chemical environment of Ti in 1% PtrGO-TiO₂ composites due to the formation of Ti-O-C bond [45], since oxygen is highly electronegative and it removes the electron density from the Ti of the 1% Pt-rGO-TiO₂ composites [53]. The three deconvoluted O 1s bands located at 530.8, 532.1 and 533.8 eV correspond to Ti-O-Ti (lattice O), Ti-O-C and C-O groups, respectively [45]. where the existence of the Ti-O-C bond demonstrates that rGO is intensively attracted to TiO₂. The characteristic peaks of Pt 4f_{5/2} and Pt 4f_{7/2} located at 71.4 eV and 74.7 eV are assigned to the core levels of Pt° [54]. The XPS results further convince the incorporation of Pt and rGO into TiO₂, and the presence of the interaction between the Pt/rGO and TiO₂, which is consistent with the Raman analysis.

UV-vis diffuse reflectance spectra (DRS) measurement was performed to evaluate the optical response of the catalysts. Fig. 2 plots the absorption spectra of the x% Pt-rGO-TiO₂ (x = 0, 0.1, 0.5, 1 and 2) composites as compared with those of bare TiO₂ and 1% Pt-TiO₂. The bare TiO_2 looks pale white (inset in Fig. 2) and displays a typical absorption with an intense transition in the UV region, as a result of the electron transitions from the valence band to the conduction band $(O_{2p} \rightarrow Ti_{3d})$ in the intrinsic band gap absorption of TiO₂ [55], but with almost no absorption in the Vis-IR. Compared with TiO₂, all Pt-rGO-TiO₂ composites exhibit an enhanced absorption in the Vis-IR region with no obvious red shift at the absorption. For the TiO₂ that is loaded only with Pt NPs, it shows a color of grey white. Unlike Ag and Au NPs with strong surface plasmon bands in the UV-vis region [56,57], TiO₂ supported Pt NPs exhibits increased and quite flat absorption of 68% over the whole range of 800-2500 nm, arising from the damping effect of the d-d transitions in Pt NPs which tends to wash out the free electron contribution to the dielectric function [58]. For the rGO-TiO₂, the absorption significantly rises up to 94% for the long wavelength part of Vis-IR region, suggesting that the introduction of rGO into the matrix of rGO-TiO₂ is able to effectively promote the IR response of rGO-TiO₂ composites, which can be attributed to electronic interactions between rGO and TiO₂ [42] as well as reduced reflection of light [59]. For the hybrid Pt-rGO-TiO₂ of our research focus, its color becomes blue black and the absorption coefficient is further enhanced to 97% over IR light region due to the integrated effect of Pt NPs and rGO sheet. It is worth noting that all of the rGO-TiO₂ composites with different ratios of Pt



Fig. 2. UV–vis DRS of x% Pt-rGO-TiO₂ composites (x = 0, 0.1, 0.5, 1 and 2). 1% Pt-TiO₂ and TiO₂ is used for comparison.



Fig. 3. Time course of toluene conversion (A) and CO₂ yield (B) over TiO₂, 1% Pt-TiO₂ and x% Pt-rGO-TiO₂ (x = 0, 0.1, 0.5, 1 and 2) under IR irradiation with various light intensities (95, 106 and 116 mW/cm²); the temperature curve of the samples with their irradiation of IR lamp (C); the durability of 1% Pt-rGO-TiO₂ composites for toluene oxidation with IR irradiation of 116 mW/cm² under steady state conditions (D).

show high absorption with no significant difference, since the light absorption intensity of rGO is much stronger than Pt NPs. An ideal light absorber that a dark material absorbs radiation at all angles and polarizations [60], which demonstrates its possible potential as a suitable catalyst that efficiently absorbs light and releases the absorbed light energy in the form of heat (photo-thermal effect), resulting in a considerable increase of temperature, enough to stimulate thermocatalytic process. Thereby, Pt-rGO-TiO₂ catalysts can be expected to be as an efficient IR-light photon absorber to drive photo-thermal catalysis for a given reaction. This hypothesis is confirmed by the following gas-phase degradation of toluene over the Pt-rGO-TiO₂ composites under IR irradiation.

To confirm whether the broad IR absorption identified for Pt-rGO-TiO₂ composites is capable of driving solar energy conversion, we tested the catalytic activity of hybrid nanomaterial Pt-rGO-TiO₂ in the catalytic oxidation of gaseous toluene under IR light irradiation. The catalytic performance of the Pt-rGO-TiO₂ composites under IR lamp with different light intensities as a function of irradiation time is illustrated in Fig. 3(A) and (B). Remarkably, the conversion of toluene and the yield of CO₂ over Pt-rGO-TiO₂ composites increase with elevated light intensity from 95, 106 to 116 mW/cm^2 . The positive relationship between reaction conversions/CO2 yields and light intensity can be explained by a photo-thermal effect, as a stronger light intensity results in a higher reaction temperature (Fig. 3(C) and Fig. S1), which is extremely favorable for endothermic reactions, i.e., catalytic oxidation of toluene. Under identical irradiation intensity, the photo-thermal catalytic performance for Pt-rGO-TiO₂ composites closely depends on the loading of Pt NPs. Specifically, the photo-thermal activity of these samples follows the sequence 1% Pt-rGO-TiO₂ > 2% Pt-rGO- $\text{TiO}_2 \geq 0.5\%~\text{Pt-rGO-TiO}_2 > 0.1\%~\text{Pt-rGO-TiO}_2.$ Within 90 min of IR irradiation of 116 mW/cm^2 , the 1% Pt-rGO-TiO₂ composites shows the most active for photo-thermal catalytic degradation of toluene with the maximum conversion of 95% and CO₂ yield of 72%, which is obviously

higher than that achieved over 0.1% Pt-rGO-TiO₂, 0.5% Pt-rGO-TiO₂ and 2% Pt-rGO-TiO₂ counterparts. In addition, it should be noted that among the 0.1% Pt-rGO-TiO₂, 0.5% Pt-rGO-TiO₂, 1% Pt-rGO-TiO₂ and 2% Pt-rGO-TiO₂ composites with uniform addition ratios of rGO, the reaction temperature for the photo-thermal activity is identical, that is, around 120, 135 and 150 °C when irradiated by IR light at the same intensity of 95, 106 and 116 mW/cm², respectively. To get insight into the influence of Pt loading, the surface area analysis over Pt-rGO-TiO₂ composites has been performed and the results of N2 adsorption-desorption isotherms are shown in Fig. S2. The BET surface areas of 0.1% Pt $rGO\text{-}TiO_2$ composite is ca. $67.910\,m^2\,g^{-1}$ and slightly decreases to $66.460 \text{ m}^2 \text{g}^{-1}$ and $65.615 \text{ m}^2 \text{g}^{-1}$ when the Pt loading is further increased from 0.1% to 0.5% and 1%, which are much higher than 57.485 m² g⁻¹ of 2% Pt-rGO-TiO₂ composite. The large specific surface area, in most case, could afford abundant active sites for gas absorption and behave as an important reason for the enhanced catalytic activities [61], but in this work, it is not a decisive factor, since the results of specific surface area are inconsistent with photo-thermal catalytic activities. In the previous study of Zhang's group [62] that the MnCeW/m- ${\rm TiO}_2$ catalyst had the smallest specific surface area of $96\,m^2\,g^{-1}$ in comparison with MnCe/m-TiO₂, MnW/m-TiO₂ and Mn/m-TiO₂ counterparts, but exhibited the best catalytic performance for NO_x reduction owing to the promotional effects of W. Furthermore, the toluene adsorption experiment was performed and the result in Fig. S3 shows that the 1% Pt-rGO-TiO₂ composite exhibits the strongest adsorption capability toward reactant, possibly being associated with well dispersed Pt NPs on the 2D rGO sheet and large amount of exposed active Pt sites. Because the heterogeneous photo-thermal catalysis is a surface-based redox process [63], the high adsorption capacity over 1% Pt-rGO-TiO₂ enables the surface lattice oxygen to effectively react with toluene adsorbed on the surface of catalyst, which, in turn, contributes to the catalytic activity enhancement. The synergistic effects of these factors would lead to the higher photo-thermal efficiency of 1% Pt-rGO-TiO₂ composite than that of the 0.1% Pt-rGO-TiO₂, 0.5% Pt-rGO-TiO₂ and 2% Pt-rGO-TiO2 counterparts. To further demonstrate the advantages of the 1% Pt-rGO-TiO₂ composites in photo-thermal catalysis, the contrast reactions over TiO₂, rGO-TiO₂ and 1% Pt-TiO₂ were also performed. The results show that no observable catalytic activities for either the bare TiO₂ or the rGO-TiO₂ composites under IR irradiation are demonstrated, because neither IR light can be absorbed in pure TiO₂ nor active sites can be provided in rGO-TiO₂ composites. Remarkably, under IR irradiation, the 1% Pt-rGO-TiO2 catalyst shows almost complete conversion of toluene at light intensity of 116 mW/cm^2 , while that of 1% Pt-TiO₂ decreased by 7% under identical reaction conditions. It should be noted especially that the stability of 1% Pt-TiO₂ catalyst. which gave a gradual climbing curve of toluene conversion and CO₂ yield, and reaching to maximum at ca. 88% and 45% for about 90 min, then gradually decreased to 44% and 9% with the irradiation time further increased to 150 min. More significantly, the stability experiment of 1% Pt-rGO-TiO₂ composite clearly shows that the toluene conversion and CO2 yield are close to 95% and 72% over consecutive irradiation of 50 h in Fig. 3(D).

Severe deactivation of 1% Pt-TiO₂ catalyst during the catalytic oxidation of toluene was also reported in previous literatures [64,65], where the inactivation mainly originates from the accumulation of partially oxidized intermediates, such as benzyl alcohol, benzaldehyde and benzoic acid, which more strongly adsorbs on TiO2 surface than toluene to occupy the active sites on the catalyst surface. The activity experiment result in Fig. 3(B) displays that the mineralization of toluene on 1% Pt-TiO $_2$ catalyst occurs slowly with accumulating recalcitrant intermediates, which is closely related to deactivation, whereas the oxidation reaction efficiently boosts the mineralization efficiency of toluene over the 1% Pt-rGO-TiO₂ composite to inhibit the deposition of recalcitrant intermediates on the catalyst surface, which consequently increases the durability of catalyst. The significant difference of reaction durability between 1% Pt-TiO₂ and 1% Pt-rGO-TiO₂ composites can be attributed to a promotional effect of rGO nanosheet. The BET surface area of 1% $Pt-rGO-TiO_2$ composite is ca. $65.615 \text{ m}^2 \text{g}^{-1}$, which is higher than $58.545 \text{ m}^2 \text{g}^{-1}$ of 1% Pt-TiO₂, since the rGO sheets contribute to increase the specific surface area of rGO-based composites. Moreover, the toluene-TPD experiment result in Fig. 4 shows that 1% Pt-rGO-TiO₂ exhibits stronger adsorption capability toward reactant than 1% Pt-TiO₂, because rGO has a strong affinity to toluene molecules involving the increased intermolecular π - π interaction with expanding π -conjugation [66,67]. Furthermore, the well-dispersed Pt NPs in 1% Pt-rGO-TiO2 leads to higher density of chemisorbed reactant and larger amount of exposed active sites for the quick surface toluene mineralization over 1% Pt-rGO-TiO₂ than those over 1% Pt-TiO₂ [68], as well as its strong photo-thermal effect giving rise to the unique ability against catalyst deactivation and the excellent reaction stability of 1% Pt-rGO-TiO2 composite for toluene oxidation.

Furthermore, the microscopic structure of Pt, TiO_2 NPs with rGO in



Fig. 4. Toluene-TPD of TiO₂, rGO-TiO₂, 1% Pt-TiO₂ and 1% Pt-rGO-TiO₂.

Pt-rGO-TiO₂ was characterized by HR-TEM. As shown in Fig. 5(D) and Fig. S4, rGO sheet exhibits extremely thin morphology with ripples, which could increase the surface area to support Pt-TiO₂ NPs and provide good potential for light absorption (Table 1) [71]. Additionally, Pt NPs are either uniformly dispersed on the surface of rGO sheet in isolation or stuck with TiO₂ on rGO sheet. The fast Fourier transform (FFT) patterns of the selected area (marked by the green and yellow frame) shown in Fig. 5(D) authenticate the anatase nanocrystals with 0.351 nm lattice spacing of (101) facet and rutile nanocrystals with 0.325 nm lattice spacing of (110) facet. HAADF-STEM was further performed to confirm the distribution and configuration of Pt. The STEM and HR-TEM images of 2% Pt-rGO-TiO₂ and 1% Pt-TiO₂ (Fig. 5(E, F) and Fig. S4) show the severe agglomeration of Pt NPs, with the identity of these agglomerates confirmed by strong signals of Pt in a EDS line scan of Fig. 5(G, H) and EDS spectrum of Fig. S4(G, H). This reveals that the rGO sheet protects Pt NPs to maintain their original size/morphology when the Pt NPs with 1 wt % loading or below. That is, the introduction of rGO sheet efficiently inhibits the agglomeration of Pt NPs in Pt-rGO-TiO₂ composites, which can improve the utilization efficiency of Pt NPs, light absorption and reactant adsorptivity to accelerate the photo-thermal catalytic reaction. By the way, the aforementioned comparison characterizations evidence that (1) the optical property as well as the crystal phase of the catalysts almost kept unchanged after different amount of Pt loading, confirmed by the DRS and XRD observations; (2) the synergistic effects of high adsorption capacity, well dispersed supported Pt-TiO2 catalyst on the 2D rGO sheet and large amount of exposed active Pt sites are the decisive factors for the excellent performance of Pt-rGO-TiO2 composites rather than the slight change in specific surface area.

To understand if the high catalytic activity of 1% Pt-rGO-TiO₂ under IR irradiation arises from the photocatalysis and/or photo-thermocatalysis, the photocatalytic activity of 1% Pt-rGO-TiO₂ composite for toluene oxidation was carried out. 100 mg of 1% Pt-rGO-TiO₂ was coated on a cylindrical quartz reactor (5 cm \times 5 cm \times 1 cm) and then the reactor was placed in a glycerol-water bath of ultralow temperature $(-20 \,^{\circ}\text{C})$ to ensure the photocatalytic reaction at near room temperature (28 °C) under IR irradiation of 116 mW/cm². However, in this case, neither distinct photo-degradation of toluene nor the discernable generation of CO_2 can be clearly observed in Fig. S5(A). This indicates that the 1% Pt-rGO-TiO₂ composite is photocatalytically inert toward the oxidation of toluene under IR light at room temperature, which can be attributed mainly to (1) wide-bandgap TiO₂(A) and TiO₂(R) [72], not being able to be activated by the inadequate excitation energy of IR photon, (2) the zero bandgap of grapheme [73] (Fig. S5(B)) endowed the holes in the composites with inadequate oxidation capacity and ineffective transfer to the VB of either TiO₂(A) or TiO₂(R) due to the stringent valence-band position requirement of semiconductor catalysts, and (3) inexistence of energetic hot holes injection from the excitation of Pt NPs with broad light absorption without recognizable peaks (Fig. S5(C)) [74]. Notably, the strong and anisotropic bonding and the low mass of the carbon atoms give graphene and graphenebased materials unique thermal properties, where graphene as nanometer-sized heaters can strongly absorb NIR light and effectively convert it into thermal energy to raise the temperature of composites [75-79]. Impressively, the temperature of rGO-TiO₂ and x% Pt-rGO-TiO₂ composites quickly increases from room temperature to 120 °C, 135 °C and 150 °C with the lamp on the light intensity of 95, 106, 116 mW/cm², respectively. When the temperature reaches a plateau, an equilibrium is established between the absorption of light energy and the energy dissipation from the catalyst to the surroundings [80]. The plateau temperatures of the catalysts demonstrate direct evidence for their efficient photo-thermal conversion. For high photo-thermal energy conversion efficiency, it is a prerequisite for an ideal material to markedly absorb IR light, efficiently convert the harvested photon into heat thermal energy and provide effective catalytic active sites. The 1% Pt-rGO-TiO2 composite, featuring the broad light wavelength



Fig. 5. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and HRTEM of x% Pt-rGO-TiO₂ (x = 0.1 (A), 0.5 (B), 1 (C–D) and 2 (E)) and 1% Pt-TiO₂ (F), (the right side of (D) is the fast Fourier transform (FFT) pattern of the area marked by the green and yellow square box and the corresponding intensity profiles); Energy dispersive X-ray spectroscopy (EDS) line scan line mapping profiles of (G) 2% Pt-rGO-TiO₂ and (H) 1% Pt-TiO₂ along the directions marked by the orange lines in (E) and (F), respectively (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 1

Physical structura	parameters of va	arious samples.
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Entry	Absorptance (%) ^a	$S_{BET} (m^2 g^{-1})$	Pore volume ($cm^3 g^{-1}$)	Mean size of Pt NPs (nm) ^b	Pt loading (wt%) ^c
	IR (800 $\leq \lambda \leq 2500$ nm)				
TiO ₂	0	53.476	0.433	/	/
1% Pt-TiO ₂	67.672	58.545	0.480	part aggregated	1.10
rGO-TiO ₂	93.985	72.510	0.481	/	/
0.1% Pt-rGO-TiO ₂	97.116	67.910	0.463	3.6	0.09
0.5% Pt-rGO-TiO ₂	96.701	66.460	0.459	4.1	0.44
1% Pt-rGO-TiO ₂	96.934	<mark>65.615</mark>	0.457	4.8	0.91
2% Pt-rGO-TiO ₂	97.091	57.485	0.486	part aggregated	1.86

^a Absorptance (a = $\int (1-R(\lambda))*E_{IR})/\int E_{IR}$ [69,70].

^b Mean size of Pt NPs was analyse from STEM.

^c Bulk composition was measured by ICP-OES.



Fig. 6. The toluene conversion and CO_2 yield over 1% Pt-rGO-TiO₂ composites under IR irradiation with different light intensities at 90 min or upon heating at corresponding temperatures (A); photo-thermal conversion efficiency of 1% Pt-rGO-TiO₂ composites under IR irradiation of 116 mW/cm² (B).

absorption, exhibits a strong IR heating effect with a considerable increase of local temperature in the catalyst and surrounding medium, which was expected to trigger and accelerate chemical reactions nearby. To further determine whether the high catalytic activity observed with 1% Pt-rGO-TiO₂ composite is induced by the photo-thermal effect, the thermocatalytic activity for toluene oxidation was performed in a cylindrical stainless steel reactor at different temperatures by external electrical heating and monitored on an online gas-phase chromatograph. As shown in Fig. 6(A), the toluene conversion and the CO_2 yield of 1% Pt-rGO-TiO₂ composite achieved by heating at the temperatures of 120, 135 and 150 °C are similar to those obtained by IR irradiation of 95, 106 and 116 mW/cm², respectively. These results imply that the efficient infrared light promoted degradation of toluene over photo-thermal responsive 1% Pt-rGO-TiO₂ composite should be closely associated with the photo-thermocatalysis. The photo-thermal conversion efficiency (η) is defined as the ratio of the converted thermal energy to the incident light energy [81] where the maximum efficiency and equilibrium efficiency reach 14.1% and 8.4% for 1% Pt-rGO-TiO₂ composite under IR irradiation of 116 mW/cm², respectively, which is shown in Fig. 6(B).

The mechanism that the oxidation of a given VOCs depends on activated forms of oxygen, *i.e.*, lattice oxygen and adsorbed oxygen [82]. To further investigate the adsorption and activation of oxygen on 1% Pt-rGO-TiO₂ composite, as well as the lattice oxygen mobility of the catalyst, O₂-TPD measurement was performed. As shown in Fig. 7(A), 1% Pt-rGO-TiO₂ composite displays a large intense peak at around 490 °C and a small sharp peak centered at around 679 °C, corresponding to the surface lattice oxygen species O₂⁻, while the peaks below 400 °C and above 700 °C are assigned to surface adsorbed peroxy species O₂⁻/monatomic species O⁻ and bulk lattice oxygen, respectively [83,84]. Notably, for the O₂⁻ lattice desorption, 1% Pt-rGO-TiO₂ composites

revealed a much stronger intensity than either hybrid 1% Pt-TiO₂ or TiO₂ NPs, indicating that the desorption amount of surface lattice oxygen species of the 1% Pt-rGO-TiO₂ catalyst are greatly enhanced. Morales et al. [85] previously suggested that the adsorbed oxygen on the catalyst surface released at low temperature participates in the surface oxidation reaction via a Rideal-Eley mechanism, while lattice oxygen of the catalyst with high oxygen mobility is desorbed at high temperature (> 400 °C) and proceeds the redox cycle via a Mars-van Krevelen mechanism. Meanwhile, it has been widely believed that VOC oxidation over reducible transition-metal oxides such as TiO₂, WO₃, CeO₂, etc, follows a Mars-van Krevelen mechanism [86]. The key characteristic feature of this mechanism is that the oxide surface is directly involved via its most reactive surface lattice oxygen atoms, rather than just a spectator of the reaction. In the research of Li and coworkers [87], the experimental data strongly support a typical Marsvan Krevelen type mechanism for benzene oxidation reaction by investigating the evolution of CO₂ concentration in the atmosphere of highly pure Ar after the injection of benzene into the reactor with the TiO₂ catalyst during either photo-thermal or thermal catalytic process. Recently, DRIFTS experiment performed by Maier's research group [88] also support this mechanism that the formation of carboxylates in oxygen-free feed gas manifests that propane is not activated by preadsorbed oxygen, but by the TiCrO_x catalyst itself. To further validate whether or not a similar dynamic adatom mechanism is also feasible on 1% Pt-rGO-TiO₂ composite, in situ DRIFTS spectroscopy was applied to look into the effect of surface lattice oxygen on toluene oxidation reactivity [89]. Prior to toluene adsorption and reaction experiments, the sample was flushed with pure N2 at 150 °C for 1.5 h to remove adsorbed impurities. The background spectrum was collected under N2 and automatically deducted from the sample spectra. Afterward, 1000 ppm toluene/N2 was introduced to the cell at a flow rate of 50 mL/min at



Fig. 7. O_2 -TPD profiles of the TiO₂, 1% Pt-TiO₂ and 1% Pt-rGO-TiO₂ composites (A); *in situ* DRIFTS spectra of species on 1% Pt-rGO-TiO₂ composites for the adsorption of toluene in N₂ upon heating at 150 °C (B), the right side of (B) is the enlarged view at 1750–1350 cm⁻¹; schematic diagram of the proposed Pt-assisted Mars-van Krevelen mechanism of photo-thermal catalysis (C).

150 °C, and then DRIFTS spectra were recorded. The DRIFTS spectra of 1% Pt-rGO-TiO₂ composite in Fig. 7(B) show that the broad peaks at 3078 and 3036 cm⁻¹ are characteristic of C–H stretching vibrations of the aromatic ring. The strong peaks located at 2948, 2934, 2884 cm⁻¹ and 1602, 1499 cm⁻¹ are associated with asymmetric/symmetric C-H stretching vibrations of methyl group and in-plane skeletal vibration of the aromatic ring [90], respectively, which originates from the adsorbed toluene. Noticeably, the new weak bands at 1630 and 1383 cm⁻¹ assigned to various vibrations of the aromatic ring/methyl/ carboxyl groups and the asymmetric/symmetric vibrations of COO group observably appear, resulting from the oxidation of the breaking methyl or ring [90]. These band intensities monotonically increase with time on stream, revealing that organic byproducts are accumulated on the catalyst surface. Moreover, the new doublet peaks attributable to asymmetric O=C=O stretching vibrations at 2367 and 2339 cm⁻¹ are clearly observed [91,92], while the generated CO₂ arises from the deep oxidation of the carboxylate species. Obviously, the intensity of the bands assigned to CO₂ linearly increases with time on stream during the first 20 min, which implies that the oxidation of toluene proceeds even in oxygen-free feed gas. Moreover, the involvement of adsorbed oxygen or gaseous oxygen in the activation of toluene is completely excluded,

which confirms that lattice oxygen is involved in the deep catalytic oxidation of toluene on 1% Pt-rGO-TiO2 composite. Furthermore, adsorbed toluene could be oxidized on the catalyst surface, thereby giving rise to carboxylate intermediates [93]. The formation of carboxylate intermediates and CO₂ end-product in oxygen-free feed gas suggest that toluene is activated by the 1% Pt-rGO-TiO₂ catalyst itself. Additionally, the flow of N₂ was introduced to replace 1000 ppm toluene/N₂ to further investigate the reactivity at 150 °C. The adsorbed toluene reactant and accumulated intermediate carbonate species at extended reaction times continue to react with lattice oxygen, thereby these bands assigned to toluene and carbonate species disappear and the bands corresponding to CO2 still exist. Based on the O2-TPD and DRIFTS observations, we can conclude that under oxygen free condition, the surface lattice oxygen from 1% Pt-rGO-TiO₂ composite can actively react with adsorbed toluene via a Mars-van Krevelen mechanism to generate intermediate carboxylate species and end-product CO2. Upon IR irradiation, photo-thermal responsive 1% Pt-rGO-TiO₂ composite achieves broad spectrum utilization for thermalization and then rGO via phonon-phonon coupling resulting in heat dissipation into the surrounding medium. The heat generated is used to increase the local temperature of the system, thereby driving the toluene catalytic oxidation reaction via a Pt-assisted Mars-van Krevelen mechanism. On the 1% Pt-rGO-TiO₂ catalyst, the adsorbed toluene can pick up surface lattice oxygen atoms located at low-coordinated sites on the TiO₂ surface to form the oxygenated compound (i.e. CO_2 , H_2O), simultaneously leaving behind oxygen vacancies on the surface where metal oxide TiO₂ lose oxygen atoms and donate them to the adsorbed toluene in the process [86]. In order to realize the persistent catalytic activity, the reaction must take place under oxygen pressure so that molecular oxygen dissociatively adsorbed onto the Pt NPs to give surface oxygen adatoms then followed a spillover of the oxygen adatoms from Pt NPs to the surface of the TiO₂ to refill the vacancies created in the oxidative process [94], which resulted in the efficient catalytic oxidation of toluene. The schematic of the proposed Pt-assisted Mars-van Krevelen mechanism of the photo-thermal catalysis is shown in Fig. 7(C).

4. Conclusions

In summary, the utilization of renewable solar energy via infrared light photo-thermocatalysis is seen to offer a potential alternative strategy for environmental remediation. The restacking-inhibited 2D rGO sheet, featuring the broad IR light absorption, results in efficient light-to-heat conversion, enhanced adsorption capacity and well dispersed supported Pt-TiO₂ catalyst, thereby increasing reaction temperature above light-off temperature for driving photo-thermocatalytic redox reactions. Under infrared irradiation with low power density (116 mW/cm²), photo-thermal responsive 1% Pt-rGO-TiO₂ composite demonstrates excellent catalytic activity with 95% of toluene conversion and 72% of CO₂ yield, along with retaining its stability for nearly 50 h, in which the maximum photo-thermal conversion efficiency is able to reach 14.1%. These results highlight the achievement of graphene-based composites as IR light photon absorber to trigger redox reactions, which will open an attractive avenue to harvesting solar light through photo-thermal effect. It is anticipated that this work may enable the wide development of graphene-based composites photo-thermocatalysis for solar energy conversion.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2018.04.011.

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