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3D hierarchical structures MnO₂/C: A highly efficient catalyst for purification of volatile organic compounds with visible light irradiationJunli Zhou^a, Ming Wu^b, Yajun Zhang^a, Chenguang Zhu^a, Yiwen Fang^c, Yongfeng Li^a, Lin Yu^{a,*}^a Key Laboratory of Clean Chemistry Technology of Guangdong Higher Education Institutions, Faculty of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, Guangdong, China^b Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, Institute of Environmental Health and Pollution Control, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 51006, China^c Department of Chemistry, Shantou University, Shantou, Guangdong 515063, China

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ABSTRACT

This work mainly focuses on exploring carbon coated ϵ -MnO₂ (ϵ -MnO₂/C) with 3D hierarchical structures for degradation of gaseous toluene under visible light. Influence of C-coating on surface adsorption, visible-light activity and photocatalytic activities of C-coated MnO₂ have been investigated. The results indicate that the C-coating behave as the adsorption and electron-transfer system, and the resulting C-coated ϵ -MnO₂ could extend the optical response from UV to visible light region, which can generate more electron – hole pairs. The photocatalyst ϵ -MnO₂/0.45C exhibited excellent visible-light photocatalytic activities, with degradation rate of toluene up to 87.34% in 70 min, but no photocatalytic activity could be observed for the pure ϵ -MnO₂. The PL spectra and photocurrent response results indicate that the composite structure can not only enhance the utilization of visible light but also consequently reduce electron (e^-)-hole (h^+) pair recombination, which improve the photocatalytic efficiency of the composite photocatalyst. This work provides a facile and economic approach for fabricating photocatalysts with high efficiency for degradation of VOCs under visible light at room temperature.

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1. Introduction

Toluene is a major component of indoor air pollution and its potential hazards to health have been identified [1–3]. Hence, much efforts have been devoted to the degradation of toluene as liquid or gaseous pollutants [4–6]. Physical adsorption by activated carbon, microbial degradation, catalytic combustion and photocatalysis are common methods used for toluene removal. However, the application of these methods has many limitations, such as limited adsorption capacity, high energy consumption, high reaction temperature and low efficiency, etc. Therefore, it is still a challenge to remove indoor toluene at room temperature.

Room-temperature catalytic oxidation has been considered as promising strategy to remove toluene due to its mild reaction conditions and energy-saving properties [7–9]. Until now, most reported room-temperature photocatalysts for toluene degradation are the supported noble materials and they showed different removal, such as Ag-doping TiO₂ nanotubes achieved 98% after 6 h [10], 1%Ag-TiO₂ provided 75% after 7 h [11], 79% removal for

Pt-loaded TiO₂ catalyst [12]. As we known, the application of supported noble materials are limited by the high cost and their scarcity, and it is necessary to develop a new kind of cost-effective catalyst. Moreover, most reports on room temperature degradation of toluene are focus on the liquid-phase catalytic system, and there is few report on the degradation of toluene in the gas phase at visible light. Toluene occur in the urban ambient air and regarded as the air pollutant due to its toxic. Degradation of toxic toluene into harmless CO₂ by semiconductor photocatalyst would show a green and ideal route to remove the benzene pollution in air [13]. Various semiconductors materials such as ZnO [14] and TiO₂ [15] are typical visible-light photo-catalyst for toluene degradation. However, owing to the wide band gap (3.2 eV), UV-lights (2% of sunlight) are required for these pure TiO₂ or ZnO photocatalyst to initiate the catalytic reaction, which could help to separate the electron-hole pairs in the photocatalytic processes. Therefore, one of the challenges in the photocatalysis is to establish a photocatalytic process using solar energy as a clean and renewable energy [16]. Some problems still hinder the further enhancement of efficiency for the TiO₂ or ZnO photocatalyst, such as the weak absorption of visible light. The effective C coating has displayed promising results in photo-catalyst preparation, which could extend the light

* Corresponding author.

E-mail addresses: gych@gdut.edu.cn, zhoujunlees@163.com (L. Yu).

adsorption of TiO_2 or ZnO catalyst to visible light and increase utilization of visible light (49% of sunlight) [17,18]. In addition, some researchers suggest that the C coating could not only benefit to introduce the oxygen vacancies in TiO_2 or ZnO catalyst but also narrow the band gap of TiO_2 or ZnO , and thus hence the visible-light photocatalytic activity [19,20]. However, compared with that under UV light, the photocatalytic efficiency under visible light for current C coated catalyst is still not satisfactory and therefore the designs for high efficiency visible-light photocatalysts are required [21,22].

Manganese oxides have been attracted increasing attention in photocatalytic decompose for organic pollutants in liquid or gas phase due to its abundant morphologies and crystal structures (α -, β -, γ -, and δ - MnO_2), environment friendly and high efficiency [23,24]. For example, layered MnO_x with different water content reach HCHO conversion from 37.7% to 84.7% [25]. β - MnO_2 branchy structures show high efficiency to remove methyl blue as 80% in 120 min [26]. Recently, Wang et al. compared the α -, β -, γ -, and δ - MnO_2 catalysts for the catalytic oxidation of toluene in a combined plasma-catalytic process and supposed that α - MnO_2 catalyst showed the best activity yielding a toluene conversion of 78.1% [27]. The MnO_x with various crystal structure and morphology for toluene degradation by catalytic combustion at high temperatures are extensively investigated [28]. However, room temperature degradation of toluene by MnO_x under visible light was rarely reported, and the role of chemisorbed oxygen species (surface chemisorbed oxygen and lattice oxygen) has not been explored, which play an important role in the toluene oxidation reaction.

Recently, Wang et al. successfully developed an alternative MnO_2/C composite catalyst based on KMnO_4 and graphite using high energy electron beam (HEEB) irradiation, which possessed a high catalytic degradation efficiency for GP under sunlight [29]. It is well known that the deposition of amorphous carbon on the surface of nanostructures could greatly improve its photocatalytic activities by the high capture electron ability, which could inhibit the recombination of photo-generated electrons and holes [30,31]. Inspired by the above interesting works, in this work, the carbon coated ε - MnO_2 (ε - MnO_2/C) with 3D hierarchical structures reported in our previous work [32] are directly used as photocatalyst for degradation of toluene under visible light at room temperature and rapidly reach high efficiency for toluene removal. Most recently, the development of 3D hierarchical catalysts with the enhanced performance attracts great interest in various fields [33–35]. In this work, the 3D hierarchical structure, optical, photocatalytic performances and their photocatalytic mechanism of the composite are studied. We found that the C coating could promote toluene adsorption and enhance visible light utilization, followed by the oxidation by the rich surface oxygen species, and the oxygen gas could compensate the consumed oxygen species to maintain the efficient oxidation of toluene at room temperature.

2. Experimental section

2.1. Preparation of ε - MnO_2/C samples

All the chemicals are analytical grade and used without further purification. The ε - MnO_2/C samples are prepared as the previous report [32]. Typically, tetrabutylammonium bromide (TBAB, 0.12 mol/L), urea (0.33 mol/L), 50% $\text{Mn}(\text{NO}_3)_2$ (8 mL) and glucose (0.15–0.45 g) are added to ethylene glycol (50 mL), and then the homogeneous mixture is transferred into the autoclave and kept at 160 °C for 1 h. After the autoclave is cooled down, the precipitate is centrifuged, washed and then dried at 60 °C. Finally, the

as-obtained powers are calcined at annealed at 400 °C for 3 h in air to obtain the ε - MnO_2/C structures. The amount of glucose is controlled at 0.15 g, 0.25 g and 0.45 g. The samples prepared with different amount of glucose are denoted as ε - $\text{MnO}_2/0.15\text{C}$, ε - $\text{MnO}_2/0.25\text{C}$ and ε - $\text{MnO}_2/0.45\text{C}$, respectively.

2.2. Characterizations

Scanning electron microscopy (SEM) is performed by a Digital Scanning Microscope S-3400N at 15 kV. Transmission electron microscopic (TEM) images are carried out on a JEOL 2100F transmission electron microscope at a voltage of 200 kV. N_2 adsorption/desorption isotherms and BET specific area are measured using a Micromeritics ASAP 2020 Analyzer (USA). The pore size distributions are calculated by the Barrett, Joyner and Halenda (BJH) method. The UV/vis diffuse reflectance spectra are measured at a UV-vis spectrophotometer (TU-1901, China), using BaSO_4 as reference sample. (Electron Paramagnetic Resonance) EPR spectra are measured using a Bruker EMXplus10-12 EPR electron paramagnetic resonance spectrometer equipped with a quanta-Ray Nd: YAG laser system as their radiation light source (266 nm). The settings are the center field at 3480.00 G, microwave frequency at 9.83 GHz, and power at 6.35 mW.

2.3. Visible-light photocatalytic activity measurement

The photocatalytic activities of ε - MnO_2/C are evaluated by degradation of gaseous toluene under visible light irradiation at room temperature. Typically, 0.3 g of samples are placed in a fixed-bed continuous flow quartz reactor (9 mm i.d.), which is operated in a down-flow mode at atmospheric pressure. A 6 W ordinary light pipe is used as the visible light source. A flow of N_2 (5 mL/min) is used as carrier gas for toluene. The toluene taken out by N_2 is mixed with the diluted gas N_2 (25 mL/min) and O_2 (5 mL/min) through a three-way valve and then flow into the reactor. Prior to visible light irradiation, the toluene is allowed to reach the adsorption equilibrium. The initial concentration of toluene is controlled at 56 mmol/L. The gas compositions in the outlet and inlet are analyzed using Agilent 7820A on-line gas chromatograph. The whole schematic illustration of visible-light photocatalytic system for toluene degradation are shown in Fig. 1.

2.4. Detection of CO_2 produced by photocatalytic reaction

The detection of CO_2 is carried out by Micromeritics AutoChem 2920 II. The fresh catalyst is (about 300 mg) is loaded in a U-shaped quartz micro-reactor. After being pretreated in flowing He at 300 °C for 30 min and cooled to room temperature. The toluene taken out by N_2 is mixed with the diluted gas N_2 (25 mL/min) and O_2 (5 mL/min) through a three-way valve and then flow into the reactor. A 6 W ordinary light pipe is used as the visible light source. The photocatalytic reaction products are observed

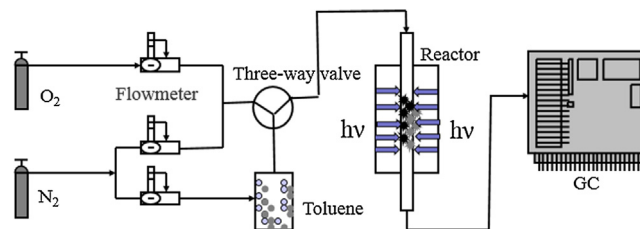


Fig. 1. Schematic illustration of visible-light photocatalytic system for toluene degradation.

by a mass spectrometer (Quadstar 32-bit) directly connected to the outlet of the reactor. The mass spectrometer scanned the ions peaks, $m/z = 44$ within 1 s.

2.5. Photocurrent response measurement

Photocurrent measurements are carried out under Xe lamp (300 w) irradiation with the UV light cut off and recorded with an CHI electrochemical workstation. The photo-electrochemical cell is designed as a three-electrode system. The prepared samples mixed with some ethanol to form a slurry. The prepared sample slurry is uniformly spread on an FTO glass substrate ($1\text{ cm} \times 1.2\text{ cm}$), which would act as the working electrode. The saturated calomel and platinum electrodes act as the reference and counter electrodes, respectively. The photoinduced current with time ($I-t$) are measured with the light on and off. The gap between the light with switching on and turning off is 20 s. The measurements are performed in a 1 M Na_2SO_4 solution at ambient temperature.

3. Results

3.1. Structures and morphologies of $\epsilon\text{-MnO}_2/\text{C}$ samples

The $\epsilon\text{-MnO}_2/\text{C}$ samples applied in this work has been studied for decolorization of methyl orange in our previous report [32]. However, this work mainly focuses on exploring $\epsilon\text{-MnO}_2/\text{C}$ for degradation of gaseous toluene under ordinary light pipe (6W) at room temperature and its photocatalytic mechanism. In this work, the XRD patterns and SEM images for $\epsilon\text{-MnO}_2/\text{C}$ samples are obtained again and shown in Fig. 2.

The three sharp peaks (1 0 0, 1 0 1 and 1 0 2) could be indexed to the hexagonal $\epsilon\text{-MnO}_2$ (JCPDS No. 30-0820). The low and

broadened peak is attributed to amorphous carbon coating (Fig. 2e). Interestingly, it is found that the morphology of $\epsilon\text{-MnO}_2/\text{C}$ samples can be controlled simply by the addition of glucose. As shown in Fig. 2, all the $\epsilon\text{-MnO}_2/\text{C}$ samples show 3D hierarchical structures. Especially, the $\epsilon\text{-MnO}_2/0.15\text{C}$ show hierarchical micro-flower morphology with 0.15 g glucose added in the reaction system (Fig. 2b). No obvious carbon layer is observed on the surface of $\epsilon\text{-MnO}_2/0.15\text{C}$ (Fig. 2i). When the glucose is added to 0.25 g, the $\epsilon\text{-MnO}_2/0.25\text{C}$ exhibit uniform micro-dumbbells morphology (Fig. 2d). However, the carbon layer is still not found now (Fig. 2ii). When the amount of glucose further added to 0.45 g, the uniform twin micro-spheres morphology is formed (Fig. 2f). Moreover, an amorphous carbon layer with 5 nm thickness is observed on surface of $\epsilon\text{-MnO}_2/0.45\text{C}$ (Fig. 2iii). Moreover, the Raman spectra are also applied to characterize the carbon layer structure for $\epsilon\text{-MnO}_2/\text{C}$ and shown in Fig. S1. The peak at 1333 cm^{-1} corresponded to the D-band attributing to the vibrations of carbon bonds at the edges of disordered graphite defects. The peak at 1605 cm^{-1} (G-band) corresponded to the E_{2g} mode of graphite and is related to the vibration of sp^2 -bonded carbon atoms in a two-dimensional (2D) hexagonal lattice in graphite layer. The measured intensity I_D/I_G ratio for $\epsilon\text{-MnO}_2/0.45\text{C}$ is about 1.21, suggesting that the carbon exists in a disordered/amorphous form. No carbon signal could be observed for the pure $\epsilon\text{-MnO}_2$ [36]. The EDS images (Fig. 3) show uniform distribution of Mn. The C element are detected for all the $\epsilon\text{-MnO}_2/\text{C}$ samples and the carbon content increase with the adding glucose. The element distribution of Mn and C for $\epsilon\text{-MnO}_2/0.45\text{C}$ are uniform and well-matched with each other (Fig. 3ii, iii). The formation mechanism for different morphologies is studied by a series of time-dependent experiments and proposed as “rod-to-dumbbell-to sphere” theory [37] (Fig. S2). The formation reactions for the synthesis of MnO_2/C are also proposed as follows:

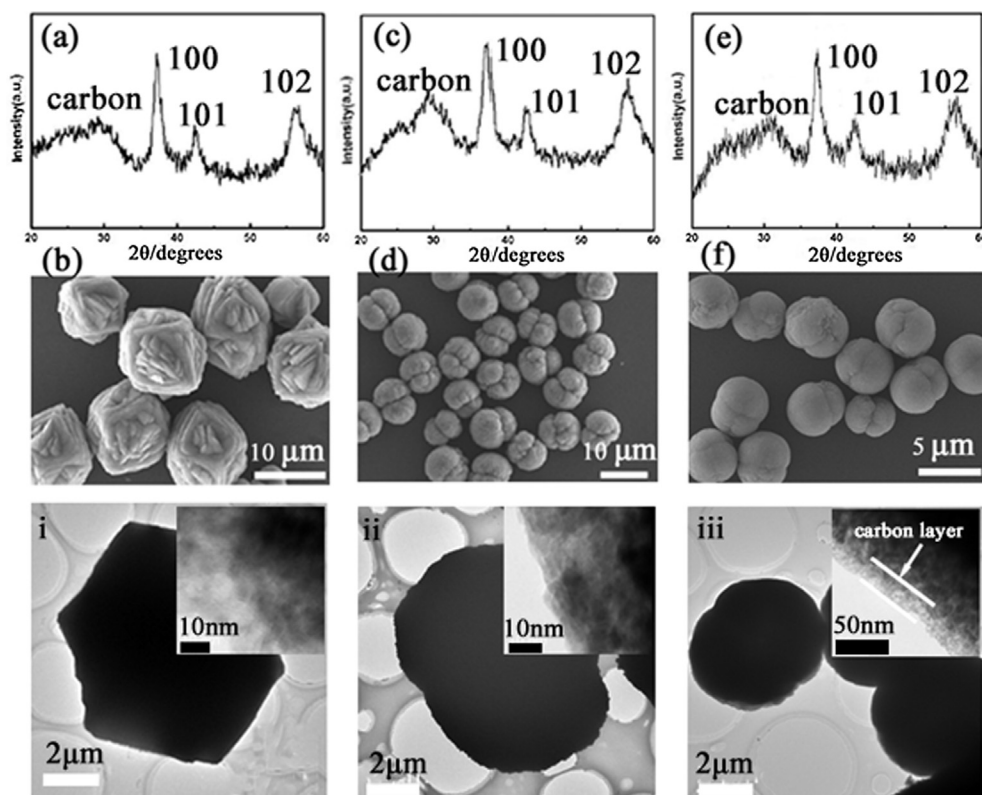


Fig. 2. XRD patterns, SEM images and TEM images for (a, b, i) $\epsilon\text{-MnO}_2/0.15\text{C}$, (c, d, ii) $\epsilon\text{-MnO}_2/0.25\text{C}$ and (e, f, iii) $\epsilon\text{-MnO}_2/0.45\text{C}$.

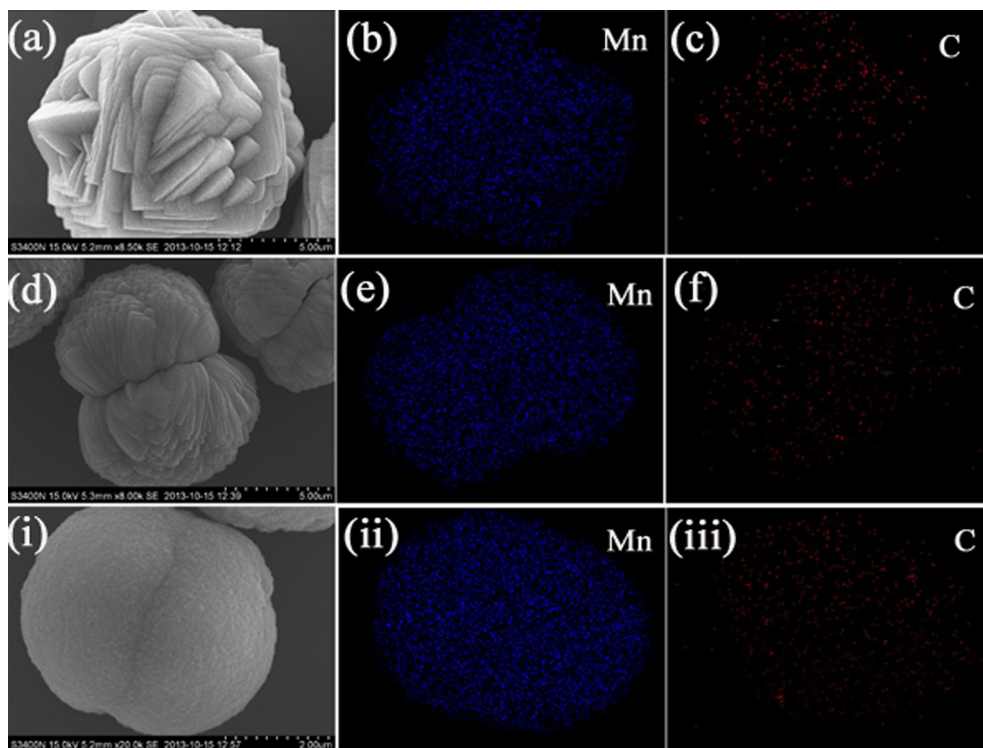
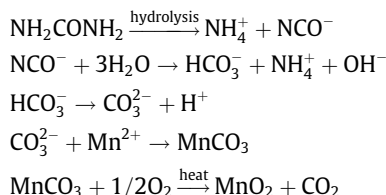


Fig. 3. SEM images and EDS images for (a, b, c) ϵ -MnO₂/0.15C, (d, e, f) ϵ -MnO₂/0.25C and (i, ii, iii) ϵ -MnO₂/0.45C.



Urea is used to provide a steady CO_3^{2-} ion through urea hydrolysis. In a typical experiment, when no urea is added under the same reaction conditions, no precipitate could be collected. We introduce TBAB as a stabilizer for preventing the aggregation of particles as previous report [38]. In addition, the ethylene glycol solvent is found to play an important role in the formation of ϵ -MnO₂/C samples with 3D hierarchical structures. SEM images of the product prepared in water solvent is also obtained. Without the assistance of ethylene glycol solvent, no distinct flowerlike architectures could be observed (Fig. 4a). The glucose is used as carbon source and morphological controller in our synthetic route. Without glucose, only the micro-flower morphology could be obtained (Fig. 4b). The micro-dumbbells and micro-spheres are failed to produced.

3.2. Study of visible light photocatalytic activities

MnO₂ has been considered as a visible light photocatalysts [39] and its photocatalytic activities are investigated [40,41]. Here, the photocatalytic activities of various ϵ -MnO₂/C samples are examined by degradation of gaseous toluene under visible light irradiation and compared with that of pure ϵ -MnO₂. As shown in Fig. 5, the pure ϵ -MnO₂ samples are almost inactive for toluene degradation under visible light. However, with different amount of C-doping, all the ϵ -MnO₂/C samples show greatly enhanced degradation performance. The ϵ -MnO₂/0.45C possesses the highest degradation efficiencies (up to 87.34% in 70 min) compared with ϵ -MnO₂/0.25C (44.51%) and ϵ -MnO₂/0.15C (45.48%). Moreover, the ϵ -MnO₂/0.45C samples obtained in this work display much higher degradation efficiencies than that of previous reports, such as the three-component nanojunction system Pt/C-coated TiO₂/PtCl₄ (87.4% in 120 min) [42], nitrogen coated Ta₂O₅ and Nb₂O₅ Nanoparticles (about 70% in 90 min) [43] and NH₂-MIL-101 (Fe) metal-organic frameworks (79.4% after 10 h) [44]. These results indicate that C coating on the surface of ϵ -MnO₂ could significantly promote the visible light photocatalytic activity in degradation of

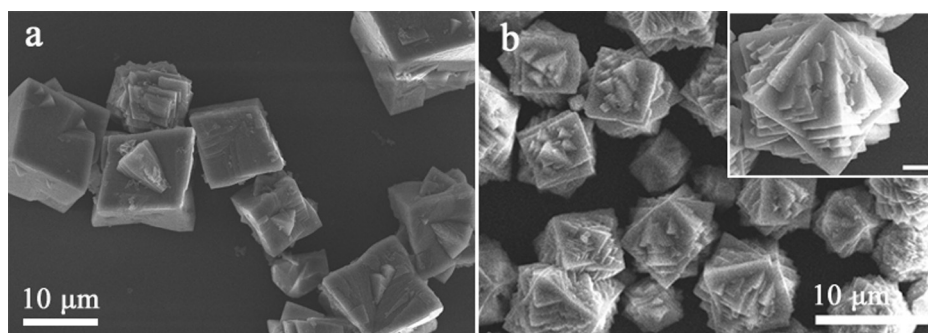


Fig. 4. SEM images for the products prepared (a) in water solvent and (b) without glucose assistance.

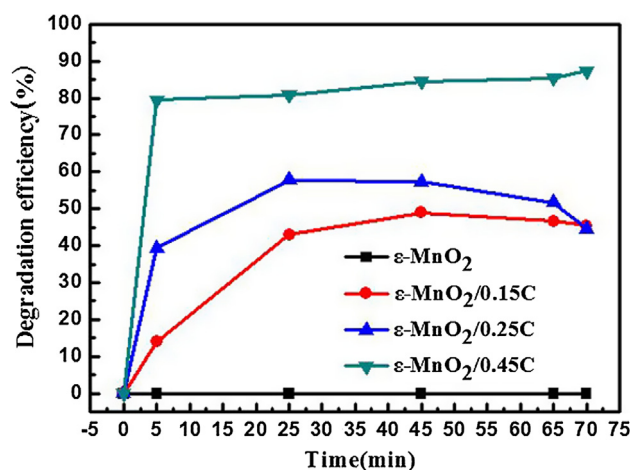


Fig. 5. Photocatalytic activities of ϵ -MnO₂/C samples under visible light irradiation.

toluene. Moreover, the formation of CO₂ produced by photocatalytic removal of toluene over ϵ -MnO₂/C samples are detected by the mass spectrometer. Few CO₂ can be observed for pure ϵ -MnO₂ (Fig. 6a). By comparison, the concentration of CO₂ reached a high steady-state value for ϵ -MnO₂/C samples, indicating the toluene could be removed by photocatalytic reaction over ϵ -MnO₂/C samples to give CO₂. The CO₂ concentrations are in the order of ϵ -MnO₂/0.45C > ϵ -MnO₂/0.25C > ϵ -MnO₂/0.15C, which agree well with the photocatalytic activities results.

4. Discussion

4.1. The influence of specific surface area on activity

In general, the catalytic activities for catalysts are related to their specific surface area. As shown in Table 1, the specific surface area for all the ϵ -MnO₂/C samples are larger than that of pure ϵ -MnO₂ samples (79.83 m² g⁻¹), ranging from 88.28 to 105.49 m² g⁻¹. The degradation efficiencies are in the order of ϵ -MnO₂/0.45C > ϵ -MnO₂/0.25C $\approx$ ϵ -MnO₂/0.15C > pure ϵ -MnO₂. Among these catalysts, the ϵ -MnO₂/0.45C possess the largest specific surface area, resulting the higher degradation efficiency. In addition, the pore size distributions are calculated and shown in Fig. 7. Compared with the pure ϵ -MnO₂, a distinct type IV hysteresis loop in the P/P₀ range of 0.6–0.99 and a pore size distribution centered at 10 nm are observed for ϵ -MnO₂/0.45C (Fig. 7b), which indicate a fingerprint of a mesoporous feature [45,46]. Therefore, the greatly enhanced degradation efficiency for gaseous toluene could be attributed to the mesoporous structure and the large specific surface area (105.49 m² g⁻¹), which results in more active sites on the surface.

Table 1
Surface area and pore volume (V_B) of samples.

Sample	S _{BET} (m ² g ⁻¹)	V _B (cm ³ g ⁻¹)	Degradation efficiency (%)
ϵ -MnO ₂	79.83	0.15	0
ϵ -MnO ₂ /0.15C	88.28	0.17	45.48
ϵ -MnO ₂ /0.25C	94.33	0.17	44.51
ϵ -MnO ₂ /0.45C	105.49	0.20	87.34

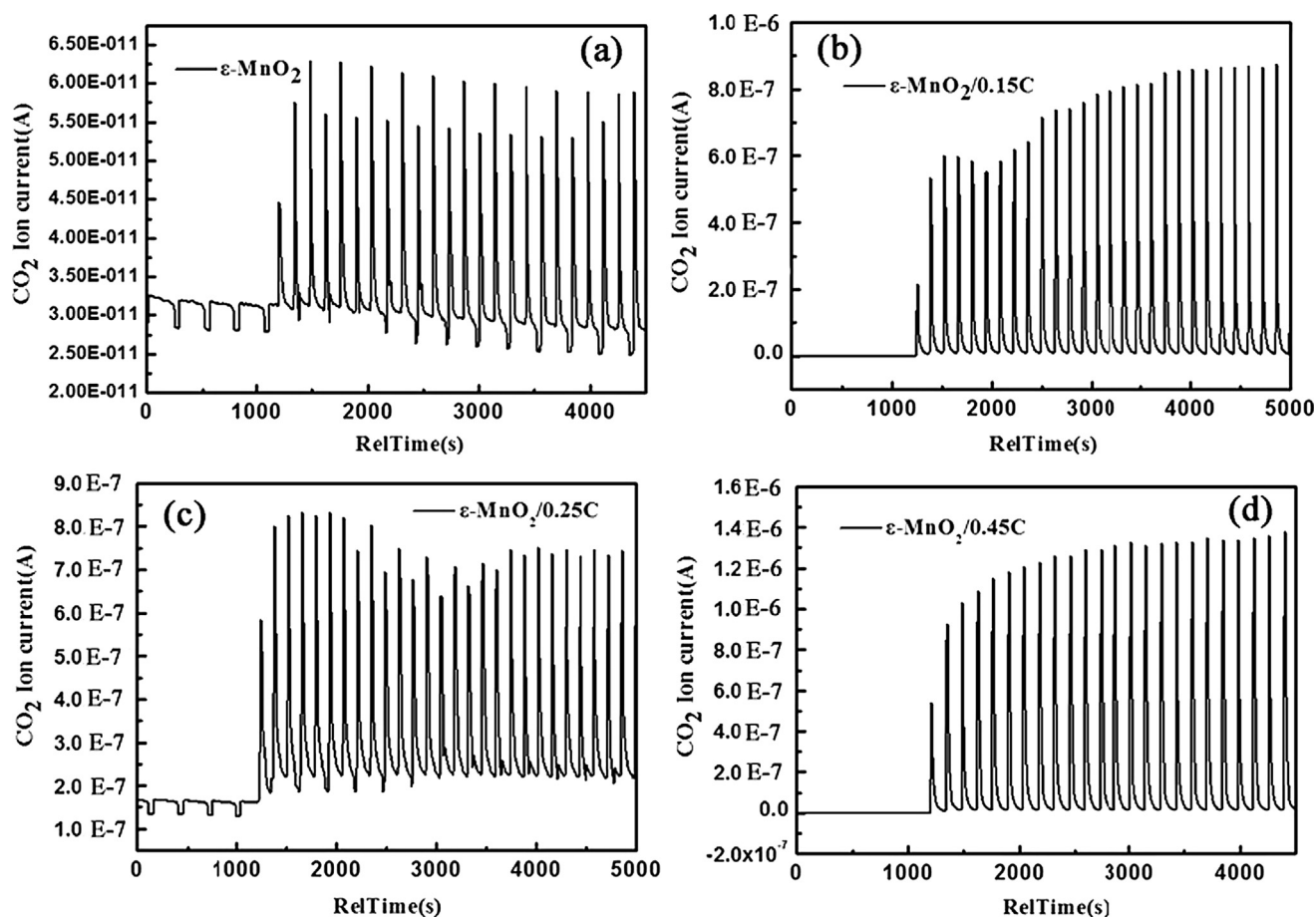


Fig. 6. The formation of CO₂ produced by photocatalytic removal of toluene over ϵ -MnO₂/C samples.

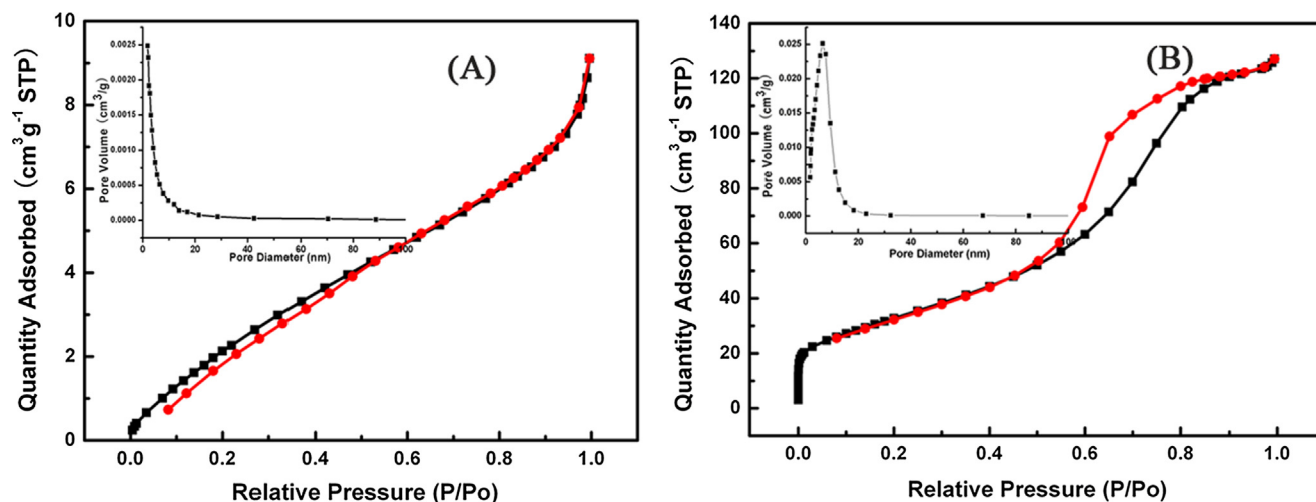


Fig. 7. N_2 adsorption-desorption isotherm and pore size distribution of (a) ϵ - MnO_2 and (b) ϵ - $MnO_2/0.45C$ samples.

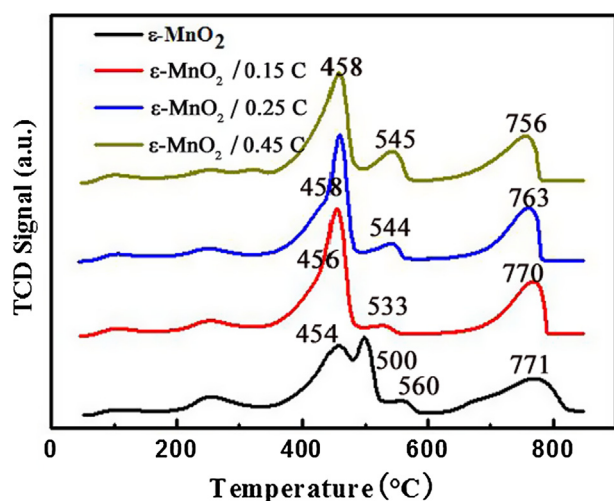


Fig. 8. O_2 -TPD profiles for ϵ - MnO_2/C samples and pure ϵ - MnO_2 .

4.2. Investigation of oxygen species on activity

The oxygen temperature programmed desorption (O_2 -TPD) for ϵ - MnO_2/C samples and pure ϵ - MnO_2 are shown in Fig. 8 and the calculated results are listed in Table 2. The chemisorbed oxygen species are divided into three types according to temperatures: the chemisorbed oxygen (O^{2-} , O^- or OH) on the catalyst surface located at LT (low temperature, 400–510 °C), the lattice oxygen (O_2^{2-}) close to the surface located at MT (middle temperature, 510–670 °C) and the HT (high temperature, 670–800 °C) oxygen species [47,48]. Table 2 lists the peak temperature, the peak area and the composition of LT, MT and HT oxygen species of pure ϵ - MnO_2 and ϵ - MnO_2/C catalysts. Compared with pure ϵ - MnO_2 , all

the ϵ - MnO_2/C possess much rich surface oxygen species (LT% + MT%), ranging from 66.96% to 72.80%, indicating that the C doping could promote the mobility of the reactive oxygen species. It is well known that both the LT and the MT oxygen species play an important role in improving the catalytic activity [49]. In this work, the amount of surface oxygen species follows the order ϵ - $MnO_2/0.45C > \epsilon$ - $MnO_2/0.25C > \epsilon$ - $MnO_2/0.15C > \text{pure } \epsilon$ - MnO_2 , which is quite in accord with the degradation efficiency for all the catalysts.

4.3. Influence of C-doping on visible-light activity

Fig. 9 displays the UV/Vis DRS for pure ϵ - MnO_2 and ϵ - $MnO_2/0.45C$. Compared with the pure ϵ - MnO_2 , the ϵ - $MnO_2/0.45C$ shows greatly enhanced visible light adsorption. Significant increase in visible light adsorption of ϵ - MnO_2/C is caused by excitation of electrons from modified valence band in the band gap due to carbon doping [42]. In general, the photocatalytic activities are in proportional to $(I_{\alpha}\phi)^n$ ($n = 1$ for low light intensity, $n = 1/2$ for high light intensity), where I_{α} is the photon-numbers absorbed by photocatalyst per second and ϕ is the efficiency of the band gap transition [50]. In this work, the greatly enhanced visible light absorbance could contribute to the increase of $I_{\alpha}\phi$, and thus improving the photocatalytic activities. Therefore, the enhanced photocatalytic activities for ϵ - MnO_2/C samples could be partly explained by the increasing visible light absorbance.

4.4. Photocatalytic mechanism of ϵ - MnO_2/C system

The photocatalytic mechanism for toluene degradation have been investigated on various metal oxide-based catalyst system [11,51]. In this work, the greatly enhanced photocatalytic efficiency could be attributed to the adsorption-catalyst reaction coupling mechanism. Generally, the photocatalytic activities are

Table 2
 O_2 -TPD results of ϵ - MnO_2/C samples.

Sample	Peak temperature θ (°C)			Peak area A (mol g ⁻¹)			Surface Chemisorb ALT%	Bulk		Surface % ALT% + AMT%
	θ LT	θ MT	θ HT	ALT	AMT	AHT		Lattice AMT%	Lattice AHT%	
ϵ - MnO_2	454/500	560	771	2.0	0.15	1.10	62.22	4.65	33.13	66.86
ϵ - $MnO_2/0.15C$	456	533	770	1.94	0.12	1.02	63.04	3.91	33.04	66.96
ϵ - $MnO_2/0.25C$	458	544	763	1.85	0.46	1.02	55.56	13.81	30.63	69.37
ϵ - $MnO_2/0.45C$	458	545	756	2.01	0.64	0.99	55.22	17.58	27.20	72.80

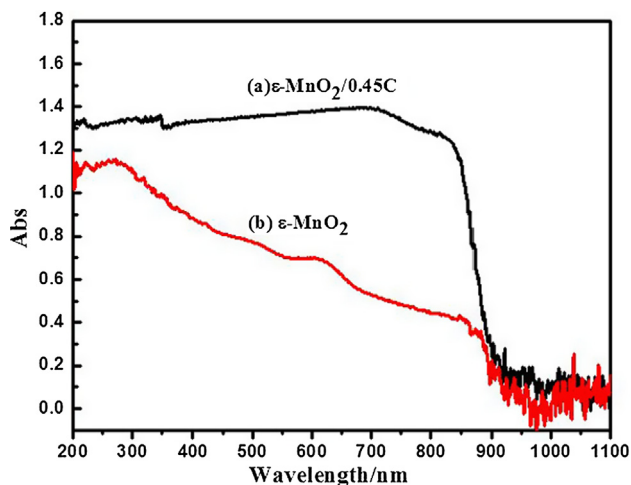


Fig. 9. UV/Vis diffuse reflectance spectroscopy (DRS) of (a) pure ϵ - MnO_2 and (b) ϵ - $\text{MnO}_2/0.45\text{C}$.

related to its adsorptive capacity. Fig. 10a shows the FT-IR study for the adsorption process of toluene by the ϵ - MnO_2/C samples. After 3 h adsorption, no characteristic peaks of toluene can be observed for the pure ϵ - MnO_2 . However, after 3 h adsorption for ϵ - $\text{MnO}_2/0.45\text{C}$, two obvious peaks display at 1366 and 1630 cm^{-1} , which can be attributed to the vibration of aromatic rings [44]. These results indicate that, compared with pure ϵ - MnO_2 , the adsorption capacity for ϵ - $\text{MnO}_2/0.45\text{C}$ is greatly enhanced due to the amorphous C coating. Therefore, the toluene molecules could be absorbed well on the surface of ϵ - $\text{MnO}_2/0.45\text{C}$, and hence

the photocatalytic efficiency is accelerated [52]. In addition, as shown in Fig. 9, the ϵ - $\text{MnO}_2/0.45\text{C}$ show significant absorption in the visible-light region, which can generate more electron-hole pairs. And then the C coating could capture photo-generated electrons of the conduction band more efficiently and thus restrain the photo-generated electron-hole pair recombination. Here, the separation efficiency of photo-generated electron-hole pairs in the photocatalytic process is studied by the PL analysis, as shown in Fig. 10b. It is accepted that the lower intensity of the PL accounted for the higher separation efficiency for the electron-hole pairs, which gives long-lived photo-generated charge carriers. In our work, the PL intensity of ϵ - MnO_2 is significantly higher than that of ϵ - $\text{MnO}_2/0.45\text{C}$, which indicate that the ϵ - $\text{MnO}_2/0.45\text{C}$ might decrease the recombination rate of electron-hole pairs and hence enhance the separation efficiency of electron-hole pairs during photocatalysis process. To further investigate the photo-generated electrons excited from the valence band to the conduction band under visible light irradiation, the photocurrent response experiments are designed and the results are shown in Fig. 10c. The photocurrent for different samples are in the order of ϵ - $\text{MnO}_2/0.45\text{C} > \epsilon$ - $\text{MnO}_2/0.25\text{C} > \epsilon$ - $\text{MnO}_2/0.15\text{C} > \epsilon$ - MnO_2 . The higher photocurrent rise indicates much more electron-hole pairs are generated under visible light irradiation and more importantly, the higher separation efficiency for electron-hole pairs.

Based on the above results, the whole photocatalytic mechanisms for ϵ - MnO_2/C photocatalysts under visible light irradiation is illustrated in Fig. 10d and proposed as the following reactions. The band gap of ϵ - $\text{MnO}_2/0.45\text{C}$ (1.29 eV) as calculated from the UV-Vis spectra (Fig. S3) is much smaller than that of pure TiO_2 or ZnO photo-catalyst (3.2 eV), and hence a large amount of the electron (e_{CB}^-)-hole (h_{VB}^+) pairs could be easily generated by ϵ - MnO_2/C under visible light irradiation (reaction 1). Then the

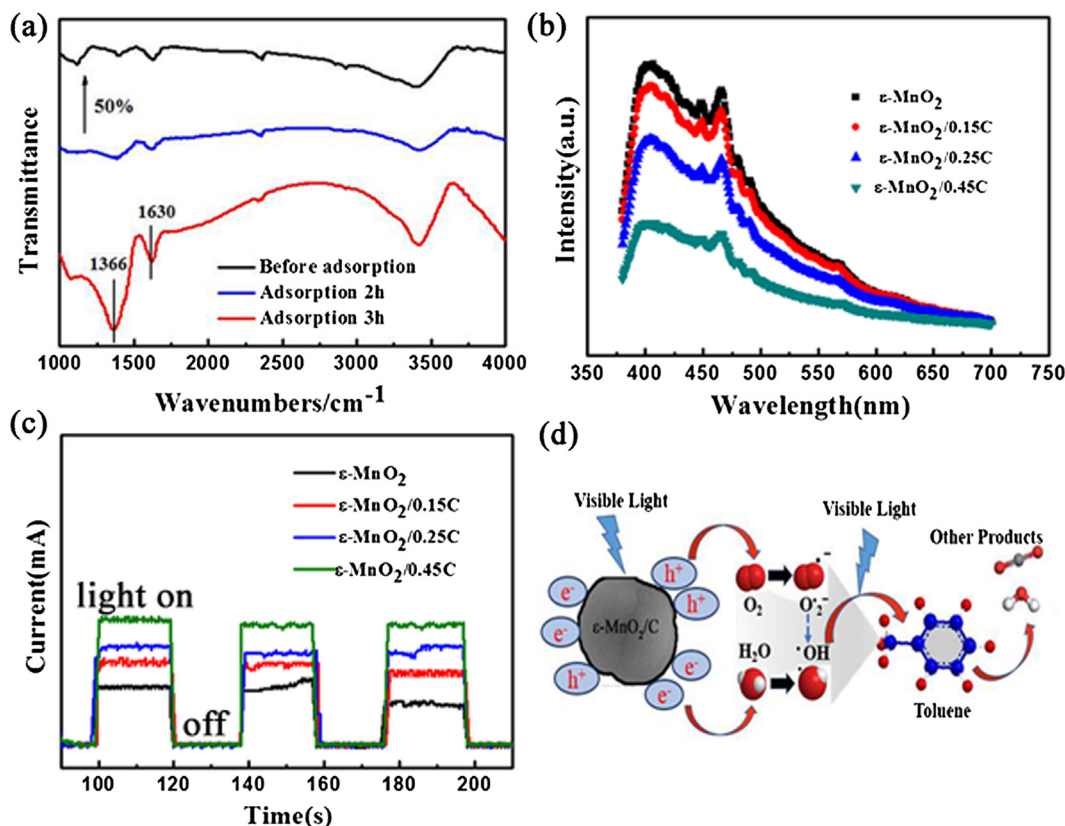


Fig. 10. (a) FT-IR studies for the adsorption process of toluene, (b) PL spectra and (c) the photocurrent response for different samples, (d) photocatalytic mechanisms for ϵ - MnO_2/C photocatalysts under visible light irradiation.

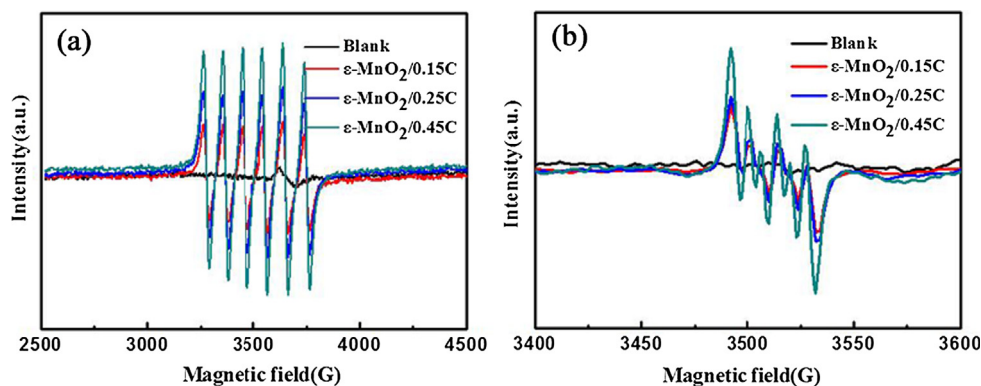
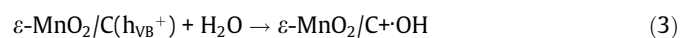
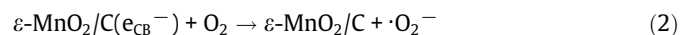
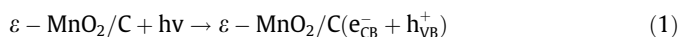


Fig. 11. ESR spectra of radical adducts trapped by DMPO in ϵ -MnO₂/C dispersions: (a) DMPO-OH formed in irradiated aqueous dispersions; (b) DMPO-O₂ formed in irradiated methanol dispersions.

generated electron (e_{CB}^-)-hole (h_{VB}^+) could be migrated rapidly from the amorphous carbon coating to the surfaces of catalyst particles, where they are finally trapped and carried out redox reaction. The resulting electron (e_{CB}^-) could reduce the absorbed O₂ to $\cdot O_2^-$ (reaction (2)), and the hole (h_{VB}^+) could transform H₂O or OH⁻ into $\cdot OH$ through oxidation process (reaction (3)). Moreover, as proved the O₂-TPD results in Fig. 7, the ϵ -MnO₂/0.45C also possess much rich surface oxygen species (O²⁻, O⁻ or OH). Finally, these reactive species $\cdot O_2^-$ and $\cdot OH$ with strong oxidation ability are responsible for the high degradation efficiency of ϵ -MnO₂/0.45C (reaction 4). This hypothesis is further confirmed by the (Electron Paramagnetic Resonance) EPR spectra analysis. As shown in Fig. 11, no $\cdot OH$ and O₂^{*} are formed for the aqueous solution without the catalysts. Moreover, the intensity signal of the formed $\cdot OH$ and O₂^{*} radical species in ϵ -MnO₂/C dispersions follows the order ϵ -MnO₂/0.45C > ϵ -MnO₂/0.25C > ϵ -MnO₂/0.15C, thus accounting for a higher photocatalytic performance of ϵ -MnO₂/0.45C than ϵ -MnO₂/0.25C and ϵ -MnO₂/0.15C toward the degradation of toluene pollutants.



5. Conclusion

This work mainly focuses on exploring carbon coated ϵ -MnO₂ (ϵ -MnO₂/C) with 3D hierarchical structures for degradation of toluene under visible light irradiation at room temperature. It is found that sample ϵ -MnO₂/0.45C exhibits excellent visible-light photocatalytic activities, with degradation rate of toluene up to 87.34% in 70 min, but no photocatalytic activity could be observed for the pure ϵ -MnO₂. The enhancement of photocatalytic activity could be attributed to the increased adsorption capacity, the enhanced utilization of visible light and the reduced electron (e^-)-hole (h^+) pair recombination. This work provides a facile and economic approach for fabricating photo-catalysts with high efficiency for degradation of gaseous toluene under natural light at room temperature.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apsusc.2018.03.183>.

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