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# MOF-Templated Approach for Hollow $NiO_x/Co_3O_4$ Catalysts: Enhanced Light-Driven Thermocatalytic Degradation of Toluene

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Supporting Information

ABSTRACT: Catalysts with strong light absorption over a broad wavelength region and high catalytic performance are considered to be suitable materials for realizing efficient light-driven thermocatalytic environment purification. However, it still remains a challenge to acquire a highly efficient catalyst with tunable light absorption properties. In this report, structure management and secondary metal doping techniques were implemented to the catalysts for improving its solar-light utilization efficiency. We synthesized a series of hollow  $NiO_{x}/Co_{3}O_{4}$  composites derived from ZIF-67 by impregnation method and explored the light-driven catalytic activities on toluene oxidation under simulated sunlight. Remarkably, the prepared samples with strong light absorption and efficient photothermal conversion exhibit excellent catalytic activity under the full solar spectrum in toluene oxidation, which proceeds by a light-driven thermocatalysis. In terms of NiOx/Co3O4 composites, the 35- $NiO_x/Co_3O_4$  catalyst shows the highest thermocatalytic activity (ca. 95% for conversion and ca. 80% for mineralization) in toluene oxidation (210 ppm, gas



hourly space velocity =  $32\,000\,\text{mL/(g·h)}$ ). And the high light-driven catalytic performance over  $35\text{-NiO}_x/\text{Co}_3\text{O}_4$  catalyst can be mainly explained by its strong light absorption, lager surface area, low-temperature reducibility, more active oxygen species, and more active  $Co^{3+}$  sites. Furthermore, the in situ diffuse reflectance infrared Fourier transform spectroscopy study on 35-NiO<sub>x</sub>/  $Co_3O_4$  suggests that toluene is degraded via benzyl alcohol, benzaldehyde, and benzoate species as main intermediates and is finally decomposed to CO<sub>2</sub> and H<sub>2</sub>O.

KEYWORDS: ZIF-67, NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>, light absorption, light-driven thermocatalysis, photothermal conversion, VOCs degradation

# 1. INTRODUCTION

Volatile organic compounds (VOCs), as a large group of widely applied organic chemicals, are the major threat to the environment and human health.<sup>1,2</sup> Therefore, efficient technology is urgently required to eliminate VOCs. Over the past several decades, multiple technologies such as catalytic oxidation, low-temperature plasma technology, physical absorption, photocatalytic oxidation, etc., have been applied in VOCs abatement.<sup>3-6</sup> Among them, catalytic oxidation is widely used due to its high efficiency to remove VOCs and less harmful byproducts.<sup>3</sup> However, the external heat is necessary to supply operating temperature in this technology, which leads to a nonrenewable energy consumption such as electric energy. Solar energy, as an affordable, inexhaustible, and clean energy, is used in many applications.<sup>7</sup> The photocatalysis degradation of VOCs has been boomingly developed, while most photocatalysts only utilize the UV light or part of visible light that <sup>-10</sup> It is totally account for  $\sim 47\%$  of full solar spectrum energy.<sup>8</sup>

noted that there are relatively few studies devoted to utilizing full spectrum light including IR that constitutes 53% of the solar energy reaching earth's surface. Light-driven thermocatalysis provides a reasonable strategy to take full advantage of the whole solar spectrum energy to highly efficient degradation of VOCs such as benzene, toluene, and acetone,<sup>11</sup> which exhibits a combination of light-to-heat conversion and catalytic oxidation for VOCs destruction.

The development of the high-performance catalyst is a crucial issue for all oxidation technologies including light-driven thermocatalytic oxidation. In recent years, the search for catalytic materials with high activity, low cost, and high tolerability is attracting much effort.<sup>12</sup> Noble metal catalyst is a kind of low-temperature available catalyst, but the costly and

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# Scheme 1. Synthetic Process of NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> Catalysts



easily poisoned issue restricts its application.<sup>13,14</sup> The transition-metal oxides, usually featuring polymorphism and polyvalence, have exhibited remarkable activities in the removal of gaseous pollutants (CO, NOx, and VOCs), which are cheap and easily obtained.<sup>15-17</sup> And some of them also are the good candidates for light-driven thermocatalysis due to their excellent light absorption capacity, for example, MnO<sub>2</sub>,<sup>18</sup> Co<sub>3</sub>O<sub>4</sub>.<sup>19</sup> Additionally, it is well-known that the catalytic performance of catalyst is closely related to its morphology, crystal phase, average oxidation state, and specific surface area, which can be remarkably affected by preparation method. Metal-organic frameworks (MOFs) materials as sacrificial templates to prepare metal oxides have been investigated to work for catalytic oxidation by our previous study<sup>20</sup> and other reported papers.<sup>21-24</sup> For example, Pt@Cr<sub>2</sub>O<sub>3</sub> derived from MIL-101-Cr template with the high surface area displayed the good catalytic activities for toluene combustion;<sup>20</sup> Liu and coworkers recently reported well-dispersed and size-controlled supported CuO nanoparticles through the pyrolysis of Cu-BTC for CO oxidation.<sup>21</sup> For light-driven themocatalysis, the prerequisite is that the catalyst material possesses a strong light absorption over a broad wavelength region. Several researchers have found that the light absorption property of materials can be modulated by the shape and the structural variation or the secondary metal doping,<sup>9,25-27</sup> which is easy to implement through the modification of MOF precursors into sophisticated forms, such as hollow structure,<sup>28,29</sup> double shell,<sup>30,31</sup> and core–shell structure.<sup>32,33</sup> Hence, MOF-derived materials with adjustable light-absorption capacity seem to be promising catalysts for light-driven thermocatalytic degradation of VOCs by enhanced solar energy utilization.

Herein, we synthesized a series of  $NiO_r/Co_3O_4$  composites derived from ZIF-67 template (Scheme 1), as described in two steps: (1)  $Ni(NO_3)_2$  was first preabsorbed on the ZIF-67 to form  $Ni(NO_3)_2/ZIF-67$  precursor; and then (2) the asobtained precursor was pyrolyzed in air at 350 °C to obtain hollow  $NiO_x/Co_3O_4$  composite by burning off the organic ligands of ZIF-67. The light-driven catalytic activities of the  $NiO_{x}/Co_{3}O_{4}$  catalysts on toluene oxidation were explored by using simulated sunlight. The physicochemical properties of the catalysts were studied by X-ray diffraction (XRD), Raman, Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS), diffuse reflectance spectroscopy (DRS), hydrogen temperature-programmed reduction (H2-TPR), oxygen temperature-programmed desorption (O2-TPD), etc. It was found that this synthetic strategy not only boosted the light utilization of materials in the full solar spectrum but also improved the catalytic activity on toluene oxidation. The as-prepared NiO<sub>x</sub>/ Co<sub>3</sub>O<sub>4</sub> catalysts possess well hollow structure, excellent light absorption, more active sites, and good low-temperature reducibility, boosting the VOCs light-driven thermocatalytic combustion. This provides a new approach to the design of light-driven environmental purification catalyst with high efficiency.

## 2. EXPERIMENTAL SECTION

**2.1. Chemicals and Materials.** All the reagents were analytical reagent (A.R.) grade and used directly without further purification. Nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), cobalt nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), commercial cobalt oxide (Co<sub>3</sub>O<sub>4</sub>-Com), commercial nickel oxide (NiO), concentrated NH<sub>3</sub>·H<sub>2</sub>O solution, methanol (CH<sub>3</sub>OH), and ethanol (C<sub>2</sub>H<sub>5</sub>OH) were purchased from Sinopharm Chemical Reagent Co., Ltd. 2-Methylimidazole (C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>) was purchased from Aladin.

**2.2. Catalyst Preparation.**  $Co_3O_4$ -MOF sample was synthesized by calcination of ZIF-67. The ZIF-67 precursor was prepared by a reported precipitation method with slight modification.<sup>34</sup> The 75 mL of methanol containing 5.46 g of  $Co(NO_3)_2$ · $6H_2O$  and 6.16 g of 2-methylimidazole was stirred at room temperature for 6 h. The purple precipitate ZIF-67 was collected by filter and washed with methanol three times. Finally, the obtained purple solid was dried at 80 °C overnight and calcined in air at 350 °C for 4 h to get  $Co_3O_4$ -MOF.

The NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> composites were prepared via impregnation method (Scheme 1). The as-prepared ZIF-67 (500 mg) was added to a 100 mL ethanol solution containing 10 mmol/L Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and stirred at room temperature for 6 h. After they were washed with ethanol three times and dried at 80 °C overnight, the indigo solids were obtained and then calcined in air at 350 °C for 4 h. The as-prepared catalyst was donated as 10-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>. The 20-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>, 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>, and 50-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> composites were prepared with the same procedure, except that the dosage of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was changed to 20, 35, and 50 mmol/L, respectively.

The Mix-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> catalyst was prepared by physically mixing commercial-Co<sub>3</sub>O<sub>4</sub> and commercial-NiO with a 3:5 molar ratio of Co/Ni and then calcined at 350  $^{\circ}$ C for 4 h.

2.3. Catalyst Characterization. XRD was tested on X'pert Pro instrument equipped with a radiation source of Cu K  $\!\alpha$  over the  $2\theta$ angle range of  $15^{\circ}$  - 90° at a speed rate of  $12^{\circ}$ /min. The microstructure was analyzed by scanning electronic microscopy (SEM, S-4800) and transmission electronic microscopy (TEM, JEM 2100F). The elemental distribution of the sample was detected by using energydispersive spectroscopy (EDS) of Oxford Instrument. Raman spectra were obtained on LabRAM Aramis using a green laser as the excitation source (wavelength 532 nm). X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI Quantum 2000 Scanning ESCA Microprobe. Diffuse reflectance spectra (DRS) were measured using a Shimadzu UV-2550 spectrophotometer. The spectra were recorded in the region of 200-2500 nm with a data point distance of 1 nm at room temperature. White standard BaSO<sub>4</sub> was filled in a sample cell with a depth of 3 mm to take a baseline. The powder samples ( $\sim 80-$ 100 mg) were loaded into a sample cell and pressed to ensure the surface was smoothed. And the thickness of the sample was controlled to 3 mm. Nitrogen adsorption-desorption measurements were characterized on a Quantachrome Autosorb IQ instrument and calculated using the BET and Barrett-Joyner-Halenda (BJH) methods. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to detect the metal content of the catalysts. H<sub>2</sub>-TPR and O2-TPD were tested on a Quantachrome chemisorption instrument. H2-TPR was tested as follows: the sample was pretreated in pure helium stream at 300 °C for 1 h, then the sample was reduced by 5% H<sub>2</sub>/He mixed gas (20 mL/min) via elevating temperature from 50 to 800  $^\circ\text{C}$  with 5  $^\circ\text{C}/\text{min}$  and the  $H_2$  consumption was detected by TCD. O2-TPD was performed with designed program: first, the sample was pretreated by 5% O<sub>2</sub>/He gas mixture (70 mL/min) from



Figure 1. XRD patterns (a) and Raman spectra (b) of the catalysts, enlargement of Raman spectra from 120 to 770 cm<sup>-1</sup> (c).

room temperature to 300 °C for 1 h. The sample was cooled to 50 °C at flowing stream of 20%  $O_2$ /He (30 mL/min), then the pure He gas flew through the sample for 30 min. Finally, the temperature was elevated from 50 to 800 °C at He stream (70 mL/min), and the signal of  $O_2$  molecule was collected by an online mass spectroscopy (Tilon, LC-200M). In situ diffuse reflection infrared Fourier transform spectroscopy (in situ DRIFTS) was performed on Thermo Fisher is50 instrument. Toluene (1000 ppm) balanced with  $N_2$  was first introduced to the sample 35-Ni $O_x$ /Co<sub>3</sub> $O_4$  for 20 min, and then the temperature was raised step by step to observe the reactivity of preadsorbed toluene with pure air at 200, 250, and 290 °C.

2.4. Catalytic Tests. A 300 W xenon lamp (PLS-SXE300/300UV, PerfectLight) and an infrared lamp (PHILIPS IR 375 CH IR2) were used for catalytic oxidation of the toluene. Before the catalytic test, the 0.1 g catalyst was dispersed in an appropriate amount of ethanol, then coated on a fiberglass-membrane of 50 mm diameter and dried at 80 °C. An aluminum silicate fiber with a diameter of 50 mm was placed on the bottom of the reactor to reduce energy loss. A thermocouple was put on the center of the catalyst layer to measure the temperature under irradiation. The adsorption-desorption equilibrium of toluene on the catalyst was performed before light irradiation. The concentration of toluene was ~210 ppm using an air stream bubbling through a liquid toluene. The flow rate of the air stream is 53 mL/min. The reactants and products were determined by a GC 9160 gas chromatograph (GC) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The toluene conversion and the CO<sub>2</sub> yield were calculated by using the following eqs:

toluene conversion(%)

 $= 100 \times ([toluene]_{in} - [toluene]_{out})/[toluene]_{in}$ 

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

The irradiation intensities of the xenon lamp and the infrared (IR) lamp were measured with an optical power meter (CEL-NP2000–2).

The photocatalytic activity of the catalyst (0.1 g) for toluene oxidation was measured in the same reactor with an ice–water bath to keep the reaction temperature at low temperature (58 °C) under the irradiation with the 500 mW/cm<sup>2</sup> xenon lamp.

To measure light-driven catalytic activity of ultraviolet–visible or infrared, the appropriate cutoff filter was placed between the lamp and the quartz window of the reactor. The light intensity of xenon lamp used on the catalysts was 500 mW/cm<sup>2</sup>. And the intensity of UV–vis light (265 mW/cm<sup>2</sup>) was acquired by using the cutoff filter to block the wavelengths above 800 nm of the xenon lamp. In addition, the total light intensity of the infrared lamp was fixed at 225 mW/cm<sup>2</sup> after filtering out the wavelengths below 800 nm.

To compare the catalytic performance of 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> at the heating condition and illuminating condition, the temperatures at different regions of the catalyst layer were measured under the irradiation of simulated sunlight with a light intensity of 500 mW/cm<sup>2</sup>. To measure the actual temperature, four points were set up from the center to the edge of the catalyst layer with separation distance of 8.3 mm.

# 3. RESULTS AND DISCUSSION

3.1. Catalysts Characterizations. XRD patterns of the samples are shown in Figure 1a. The Mix-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> shows a simple addition of well diffraction peaks for typical Co<sub>3</sub>O<sub>4</sub> (PDF No. 01-076-1802) and NiO (PDF No. 01-078-0423). The diffraction peaks for Co<sub>3</sub>O<sub>4</sub>-MOF can be well-indexed to standard Co<sub>3</sub>O<sub>4</sub> phase (PDF No. 01-076-1802), and no impurity peaks corresponding to CoO and Co2O3 were clearly detected, where the weaker and broader peaks confirm the occurrence of disordered structure due to vast nanoscaled crystals. With the increasing of Ni element, the peaks for  $NiO_x/$ Co<sub>3</sub>O<sub>4</sub> composites are further broadened and weakened, which indicates the formation of NiO species simultaneously accompanying the more amorphization of materials.<sup>33</sup> Especially for the Ni-riched samples (20-NiOx/Co3O4, 35- $NiO_x/Co_3O_4$ , and  $50-NiO_x/Co_3O_4$ ), this tendency is more apparent. The gradual increasing of Ni amount in samples was verified by ICP analysis with the significant decreasing of the Co/Ni molar ratio (Table 1). It is generally accepted that poor

Table 1. Element Composition and Physical Properties ofSamples

samples	$\binom{S_{\rm BET}}{(m^2/g)}$	total pore volume (cm³/g)	average pore size (nm)	Co/Ni molar ratios by ICP
Co <sub>3</sub> O <sub>4</sub> - MOF	45.4	0.50	44.18	
10-NiO <sub>x</sub> / Co <sub>3</sub> O <sub>4</sub>	80.0	0.66	32.76	3.06
20-NiO <sub>x</sub> / Co <sub>3</sub> O <sub>4</sub>	112.2	0.83	29.63	1.26
35-NiO <sub>x</sub> / Co <sub>3</sub> O <sub>4</sub>	132.3	0.73	22.01	0.65
50-NiO <sub>x</sub> / Co <sub>3</sub> O <sub>4</sub>	146.6	0.75	20.47	0.45
Mix-NiO <sub>x</sub> / Co <sub>3</sub> O <sub>4</sub>	1.8	0.02	47.86	0.62

crystallinity of the sample results in the absence of peaks and the attenuation of intensity.<sup>36</sup> Thus, Ni doping leads to the poor crystalline phase, encourages the occurrence of the lattice defects and the exposure of inner atoms, and enlarges the surface area of materials, which are believed to be closely related to the catalytic oxidation of VOCs.<sup>37</sup>

To further confirm the structural transformation of the oxides, Raman spectra of the samples were investigated and are shown in Figures 1b,c. The  $Co_3O_4$ -MOF sample shows five peaks (690, 479, 618, 519, and 194 cm<sup>-1</sup>) of a typical Ramanactive phonon modes ( $A_{1g} + E_g + 3F_{2g}$ ) of an ideal spinel structure.<sup>35,38</sup> The most intense peak at  $A_{1g}$  (690 cm<sup>-1</sup>) can be ascribed to the vibration of  $CoO_6$  sites of the spinel  $Co_3O_4$ ,<sup>39</sup> which is more sensitive to lattice defect. The Raman spectrum



Figure 2. SEM images of ZIF-67 (a),  $Co_3O_4$ -MOF (b), 10-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (c), 20-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (d), 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (e), 50-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (f); TEM images of  $Co_3O_4$ -MOF (g), 10-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (h), 20-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (i), 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (j), 50-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (k); TEM element mapping images of 10-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (l), 20-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (m), 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (o).

of Mix-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> exhibits the superposition of NiO<sub>x</sub> and  $Co_3O_4$  peaks, where five obvious peaks of NiO<sub>x</sub> can be assigned to three vibration modes: one-phonon (1P, 487 cm<sup>-1</sup>), twophonon (2P, 724, 891, and 1082 cm<sup>-1</sup>), and two-magnon (2M, 1448 cm<sup>-1</sup>).<sup>40</sup> For NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> composites, no obvious peaks corresponding to NiO<sub>x</sub> can be observed even for the sample with high Ni content  $(50-NiO_x/Co_3O_4)$ , suggesting the existence of highly dispersed NiO<sub>x</sub>. The  $A_{1g}$  peak of  $Co_3O_4$ displays an obvious redshift from 690 cm<sup>-1°</sup> (Co<sub>3</sub>O<sub>4</sub>) to 672  $cm^{-1}$  (10-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>, 20-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>) and further to 658  $cm^{-1}$  (35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>, 50-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>), which indicates the occurrence of lattice defects caused by residual stress or lattice distortion.<sup>41</sup> Simultaneously, all the peaks of  $\text{Co}_3\text{O}_4$  are gradually broadening and weakening with the increasing of Ni content, which proves the continuous accumulation of the disordered structure due to more lattice defects. Raman results are coincided with the XRD analysis, where Ni doping can lead to more lattice defects. Generally, more lattice defects are helpful to produce more active oxygen species, which is beneficial for the catalytic combustion of VOCs.

The morphology and structure of the samples are investigated by SEM and TEM. ZIF-67 precursor shows the well-defined polyhedron structure with the size in the range of 500-1500 nm, as seen in Figure 2a for SEM image. After calcination, the obtained Co<sub>3</sub>O<sub>4</sub>-MOF exhibits shrinking structure composed by aggregation of Co<sub>3</sub>O<sub>4</sub> nanocrystallites, which results in the formation of numerous irregular mesopores on the surface of Co<sub>3</sub>O<sub>4</sub>-MOF (Figure 2b). TEM image of Co<sub>3</sub>O<sub>4</sub>-MOF (Figure 2g) further confirms that these mesopores exist not only on the surface but also within the bulk. With Ni doping, it is obvious to observe the evolution of

the shells of particles (Figures 2c,f). At low content of Ni doping, it starts to form the incomplete shells (for  $10-\text{NiO}_x/$  $Co_3O_4$ , Figure 2c) and then thicken to obtain complete shells (for 20-NiOx/Co3O4, Figure 2d). The TEM images of 10- $NiO_r/Co_3O_4$  (Figure 2h) and 20- $NiO_r/Co_3O_4$  (Figure 2i) confirm the formation of core-shell structures with the NiO<sub>x</sub> shell and  $Co_3O_4$  core, where the element distribution by EDS verifies that  $NiO_x$  is the main component for the shell and  $Co_3O_4$  largely composes the core (Figure 21,m). With moderate Ni doping, the shells are further thickened and form the apparent wrinkles on the surface, as observed for 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (Figure 2e). TEM image of 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> displays the hollow structure with the shells composed by homogeneous Ni and Co elements (Figure 2j,n and Figure S1), where the Ni-Co binary shells are constructed possibly due to a combination of nonequilibrium interdiffusion effect (the Kirkendall effect) and generated gas release process.<sup>42,43</sup> During the calcination process, the Ni/Co shells act as the reaction interface of the oxygen in the air and the inner Co species, since the inner Co species diffused quicker than the outside oxygen, a hollow structure was eventually formed. When the high Ni content was doped, the hollow structure was broken (Figure 2f,k). Therefore, it can be concluded that the addition amount of Ni is the main factor in the determination of morphology and structure, and the appropriate addition is in favor of the formation of strong interaction between NiO<sub>x</sub> and Co<sub>3</sub>O<sub>4</sub>.

 $\rm N_2$  adsorption–desorption isotherms for all samples exhibit the features of type III isotherm with H3 hysteresis loop, demonstrating the irregular mesoporous characteristic (Figure S2). According to desorption curve, the pore size distribution was calculated by means of BJH method. All the samples have



Figure 3. Degradation of gaseous toluene over the catalysts under the irradiation of simulated sunlight with a light intensity of 500 mW/cm<sup>2</sup> (a, b) and degradation of gaseous toluene over 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> under the irradiation of simulated sunlight with different intensities (c, d).

the porous structure that are from inherent pores and/or the stacking pores of nanoparticles. For NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> composites, with increasing of Ni doping content, the values of major pore size can be gradually decreased from 11.39 to 6.77 nm, which can be reasonably explained by the metal oxides accumulation on the thickened shell blocks the mesoporous channels. The BET surface area, total pore volume, and average pore size of all the samples are listed in Table 1. The  $S_{\text{BET}}$  value and total pore volume are improved by introduction of Ni, especially for  $S_{\text{BET}}$ values (132.3 m<sup>2</sup>/g for 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> and 146.6 m<sup>2</sup>/g for 50- $NiO_x/Co_3O_4$ ), which can maximally reach to ~3 times of pure  $Co_3O_4$ -MOF (45.4 m<sup>2</sup>/g). Although Mix-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> has the largest average pore size, low BET surface area and small total pore volume extremely restrain the catalytic performance in heterogeneous catalysis. In general, the large specific surface area and high total pore volume are believed to be advantageous to the catalytic performance for VOCs oxidation, which accelerates the diffusion of toluene molecules in the pore channel and improves the contact between toluene molecules and active sites.

**3.2. Catalytic Performance.** Catalytic activities of catalysts were first evaluated with respect to conversion and mineralization of toluene under irradiation of simulated sunlight with a light intensity of 500 mW/cm<sup>2</sup>, as shown in Figure 3a,b. The  $Co_3O_4$ -MOF possesses a moderate catalytic activity with maximum toluene conversion of ca. 80% and  $CO_2$  yield of ca. 60%, which are significantly superior to that of  $Co_3O_4$ -Com (ca. 19% for both toluene conversion and  $CO_2$  yield). It is found that the Ni-doped  $Co_3O_4$  samples exhibit enhanced catalytic performance compared to pure  $Co_3O_4$ -MOF. With the appropriate amount of Ni doping, the 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> catalyst gives the best conversion of ~95% and mineralization of ~80% at least for 90 min. It is noted that the  $CO_2$  yields based on 20-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>, 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>, and 50-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> are much higher the theoretical amount at the beginning several minutes,

which suggests these catalysts with large  $S_{\text{BET}}$  and high total pore volume have the good toluene adsorptivity, and the adsorbed toluene is rapidly decomposed to form CO<sub>2</sub>. The Mix-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> shows the lowest catalytic activity of toluene oxidation (ca.10% for conversion and ca. 8% for mineralization), ascribing to its lowest  $S_{\text{BET}}$  value. Thus, from the primary activity investigation of catalysts, it can be summarized that strong metal oxide interaction and structure are crucial factors for toluene degradation, and an appropriate Ni doping is helpful to enhance the catalytic activity of catalyst.

Furthermore, the influence of different light intensities on the catalytic activity of the 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> was also investigated, as shown in Figure 3c,d. Obviously, the catalytic performance of toluene oxidation over 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> is highly dependent on the light intensity. Under irradiation with light intensity of 500  $mW/cm^2$ , the toluene conversion can quickly reach to 95% in 10 min, and then the catalytic activity (conversion and mineralization) can be almost maintained at least for 90 min. However, when the light intensities are decreased from 400 to  $200 \text{ mW/cm}^2$ , the toluene conversions first reach to the high values (77%-90%) and then reduce with reaction time. It indicates that more intermediates produced from incomplete oxidation of toluene accumulate on the active sites of catalyst and further restrain catalytic reaction, especially for low light intensity, which is also confirmed by extremely low CO<sub>2</sub> yields under irradiation of 200 and 300 mW/cm<sup>2</sup> light intensities. When the light intensity is further decreased to below 100 mW/cm<sup>2</sup>, the conversion is dramatically reduced to less than ca. 20%, and no  $CO_2$  is produced. Therefore, the light intensity plays an important role in light-driven catalytic oxidation of toluene.

**3.3. Photothermal Conversion.** As we know, photoinduced catalysis is intimately associated with light absorption. Thus, the UV–vis–IR diffuse reflectance spectroscopy was first applied to investigate the absorption properties of the catalysts.



Figure 4. UV-Vis-IR spectra of the catalysts.

As shown in Figure 4, a commercial reference  $Co_3O_4$  ( $Co_3O_4$ -Com) exhibits the relatively weak absorption in the entire spectrum region. Two obviously enhanced absorption regions at ~230-800 nm and 1200-1700 nm are clearly observed for Co<sub>3</sub>O<sub>4</sub>-MOF compared with that of Co<sub>3</sub>O<sub>4</sub>-Com, which results from morphology variation (interfacial electronic coupling effect) or particle size (quantum confinement).<sup>25,26</sup> After Ni doping, the DRS spectra of the obtained  $NiO_x/Co_3O_4$ composites show remarkable enhancement in the full spectrum (190-2500 nm). This enhanced absorption in the full spectrum is presumably attributed to the metal-to-metal charge transfer (MMCT),<sup>27</sup> which is from the very close contact between different metals. Moreover, the light absorption property of transition-metal oxide mainly related to the d-d indirect transition of different metal ions; thus, the different Co/Ni molar ratio of catalyst leads to the slight difference of light absorption in some regions of the full spectrum. As observed for TEM and elemental mapping images of catalysts,  $10-\text{NiO}_x/\text{Co}_3\text{O}_4$  and  $20-\text{NiO}_x/\text{Co}_3\text{O}_4$  with low Ni doping contents display the core-shell structure with inhomogeneous elemental distribution; thus, slightly decreased absorption intensities in the UV and Vis regions can be obviously observed. 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> with hollow structure shows the homogeneous Ni/Co distribution and tight contact of NiO<sub>r</sub> and Co<sub>3</sub>O<sub>4</sub> in the shells (high-resolution (HR) TEM images in Figure S3), which presents the strong absorption in the full spectrum. The 50-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> displays a slightly lower light absorbance than other  $NiO_x/Co_3O_4$  samples in the vis-NIR (NIR = near-infrared) region, which is caused by the collapse of the hollow structure to result in an inferior light absorption capacity of the sample. The hollow structure allows multiple reflections of light within the interior cavity, which promotes the efficient contact between photon and matter.<sup>26,27</sup> As a reference, the Mix-NiO<sub>v</sub>/Co<sub>3</sub>O<sub>4</sub> with negligible interaction between Ni and Co species brings about the weak light absorption in the entire spectrum region and even less than that of  $Co_3O_4$ -Com in most of spectrum region. Consequently, an approximate order based on light absorption intensity in the full spectrum is listed as follows: Mix-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> < Co<sub>3</sub>O<sub>4</sub>-Com

<  $Co_3O_4$ -MOF < x-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>, which is in accordance with the catalytic activities of catalysts. It can be regarded as that the strong absorbance of catalyst is helpful to toluene oxidation.

To understand how photoinduced thermocatalysis plays a decisive role in the catalytic oxidation of toluene, a control experiment was initially performed by studying the lowtemperature activity of toluene oxidation over 35-NiO<sub>x</sub>/ Co<sub>3</sub>O<sub>4</sub> under irradiation with a light intensity of 500 mW/  $cm^2$  (Figure S4). It was found that no activity of 35-NiO<sub>x</sub>/  $Co_3O_4$  (0% for toluene conversion and  $CO_2$  yield) can be observed at 58 °C (controlled by an ice-water bath); thus, it indicates that there is nonexistence of traditional photocatalysis associated with photogenerated charge carriers and/or reactive oxidative species. Another energy supply by light to thermal conversion is further considered in this catalysis, which has been proved that can trigger some reactions such as CO<sub>2</sub> reduction<sup>44,45</sup> and environmental purification.<sup>46</sup> The absorbed light is converted efficiently into heat through the nonradiative recombination process.<sup>47</sup> It is a loss process in the conversion of charges in semiconductors; charge carriers recombine without releasing photons. A phonon is released instead, which contributes to the temperature rise on a macroscopic scale. To measure the heat production capacity of the materials, the temperature evolution on the catalyst layer surface was monitored, as shown in Figure S5. Under irradiation of 500 mW/cm<sup>2</sup> light intensity, the surface center temperature of the membrane with catalyst layer can be rapidly raised to more than 250 °C (Figure S5a-g) and reaches a plateau temperature when the balance is built between the energy absorption and dissipation, which is much higher than that of blank membrane (Figure S5h). When the light is turned off, the plateau temperature quickly goes back to room temperature. This result demonstrates direct evidence for an efficient photothermal conversion based on catalysts. A comparison of plateau temperatures on the surface of different samples validates that there exists a relation between thermal effect and light absorbance, giving the order as follows: Mix-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> <  $Co_3O_4-Com < Co_3O_4-MOF < 10-NiO_x/Co_3O_4$ , 20-NiO<sub>x</sub>/  $Co_3O_4 < 35-NiO_x/Co_3O_4$ , 50-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> (Figure S5). This is



Figure 5. Co  $2p_{3/2}$  (a), Ni  $2p_{3/2}$  (b), and O 1s (c) XPS spectra; O<sub>2</sub>-TPD (d), H<sub>2</sub>-TPR (e), and initial H<sub>2</sub> consumption rate profiles (f) of the catalysts.

well coincided with the results of DRS analysis and catalytic activities of toluene oxidation. Therefore, it can be deduced that the catalytic performance of toluene oxidation over these catalysts is driven by photothermal catalysis using solar energy to thermal conversion. The thermocatalytic behavior over 35- $NiO_{r}/Co_{3}O_{4}$  is further verified by investigating catalytic performance of toluene degradation under heating condition and illuminating condition (Figure S6). Because of the defect of the light source, it is difficult to obtain the uniform light intensity on whole catalyst layer (50 mm diameter). The light intensity at the central point of 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> is 500 mW/ cm<sup>2</sup> and decreased from the center to the edge, which results in the different actual temperatures at different regions (Figure S6a). The catalytic performance of  $35-NiO_x/Co_3O_4$  under heating condition and illuminating condition obeys the order as 295 °C > 247 °C > 500 mW/cm<sup>2</sup> > 198 °C > 157 °C. The catalytic performance of the edge region of the catalyst layer is much lower than the central region under the irradiation of simulated sunlight; thus, the whole catalytic performance under the irradiation of simulated sunlight is slightly lower than under heating at 295 and 247 °C. It also confirms that the thermocatalytic process plays a key role in the catalytic performance over 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> under light irradiation.

In view of the strong absorption in the full spectrum for  $NiO_{x}/Co_{3}O_{4}$  samples, it is necessary to examine which region of full spectrum is dominant in the photothermal oxidation. Toluene oxidation over 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> was investigated by comparing the catalytic activities under full spectrum (500 mW/cm<sup>2</sup>), UV-vis (265 mW/cm<sup>2</sup>), and IR (225 mW/cm<sup>2</sup>). As shown in Figure S7, the toluene conversion under the irradiation of UV-vis light is increased at the early stage and then decreased gradually, and CO<sub>2</sub> yield is almost to be 0 within the time of irradiation, which manifests that the temperature (178 °C) converted by UV-vis is not enough to oxidize the formed intermediate products. Conversely, under the irradiation of IR light, toluene conversion and CO<sub>2</sub> yield have obvious improvement in catalytic activity, which are closer to that under the full spectrum irradiation, indicating that IR light is the main contribution to the photothermocatalytic

activity due to noticeable temperature enhancement of catalyst layer (228  $^{\circ}\mathrm{C}).$ 

**3.4. Origin of the Thermocatalytic Activity.** It is wellknown that the catalytic activity of the catalyst in VOCs combustion is closely associated with components, oxygen species, and reducibility. XPS analysis was used to study the surface elemental compositions and chemical states of catalysts (Figure 5). The two deconvoluted Co 2p peaks centered at 780.9 and 779.6 eV are assigned to the core levels of  $Co^{2+} 2p_{3/2}$ and  $Co^{3+} 2p_{3/2}$  for all samples.<sup>48,49</sup> The Ni 2p XPS spectra show two deconvoluted peaks at 853.8 and 855.47 eV, which can be assigned to Ni<sup>2+</sup> and Ni<sup>3+</sup> species, respectively.<sup>50,51</sup> The O 1s XPS peaks around 529.5, 531, and 532.5 eV can be assigned to lattice oxygen (O<sub>latt</sub>), absorbed oxygen (O<sub>ads</sub>), and oxygen species in surface-absorbed water (O<sub>H2O</sub>), respectively.<sup>52</sup> The deconvolution results of surface elemental state are listed in Table 2. The highest ratio of  $Co^{3+}/Co^{2+}$  in 35-

Table 2. Summary of Surface Elemental ComponentsCalculated by XPS Spectrum

	molar ratios by XPS		
samples	Co <sup>3+</sup> /Co <sup>2+</sup>	Ni <sup>3+</sup> /Ni <sup>2+</sup>	$O_{ads}/(O_{latt}+O_{H2O})$
Co <sub>3</sub> O <sub>4</sub> -MOF	0.5		0.3
$10-\text{NiO}_x/\text{Co}_3\text{O}_4$	0.8	5.0	0.3
20-NiO <sub>x</sub> /Co <sub>3</sub> O <sub>4</sub>	0.8	5.1	0.4
$35-NiO_x/Co_3O_4$	1.3	4.6	0.4
$50-NiO_x/Co_3O_4$	1.2	3.8	0.3
Mix-NiO <sub>x</sub> /Co <sub>3</sub> O <sub>4</sub>	0.7	2.0	0.3

 $NiO_x/Co_3O_4$  is observed, which indicates the presence of rich surface  $Co^{3+}$  species. Generally, the  $Co^{3+}$  species was proved to be active sites in VOCs oxidation.<sup>39</sup> Wang and co-workers have recently reported that  $Co^{3+}$  accounts for the formation of carboxylate species, which are the main intermediate byproducts in benzene oxidation.<sup>17</sup> Furthermore, the surfaceadsorbed oxygen ( $O_{ads}$ ) could play an important role in the part of VOCs oxidation.<sup>50</sup> As observed, Ni doping is helpful to promote the percentage of  $O_{ads}$  compared to pure  $Co_3O_4$ -MOF, where the highest value is obtained for 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>. With more  $Co^{3+}$  species and  $O_{ads}$  as well as appropriate Ni<sup>3+</sup>/Ni<sup>2+</sup>, it leads to the better catalytic activity for toluene oxidation on 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>. Thus, the incorporation of Ni ions into Co<sub>3</sub>O<sub>4</sub> by this MOF-template method results in the binary oxides with special morphology, more active sites, and more absorbed oxygen species, which exhibits the synergistic effect to improve photothermal catalytic performance for toluene oxidation.

To deeply investigate the activation of oxygen species, O2-TPD measurements of catalysts were performed. The oxygen species changed in the O<sub>2</sub>-TPD program are as follows process:  $\dot{O}_2(ad) \rightarrow \dot{O}_2^-(ad) \rightarrow \dot{O}^-(ad) \rightarrow O^{2-}(lattice).^{53}$  Thereinto, O<sub>2</sub>(ad) is a kind of physically absorbed oxygen and can be easily wiped off by pretreatment of helium.  $O_2^{-}(ad)$  and O<sup>-</sup>(ad) species refer to chemically absorbed oxygen, and O<sup>2-</sup>(lattice) belongs to the lattice oxygen. As shown in Figure 5d, the profiles of  $O_2$ -TPD show four distinguishable peaks defined as peaks  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ . The peak  $\alpha$  and peak  $\beta$  are attributed to the desorption of  $O_2^{-}(ad)$  and  $O^{-}(ad)$  species, respectively. The peak  $\gamma$  can be assigned to the desorption of labile surface lattice oxygen, and the peak  $\delta$  refers to the desorption of lattice oxygen from the bulk oxides. After Ni doping, the  $O_2$ -TPD patterns of x-Ni $O_x$ /Co<sub>3</sub> $O_4$  are enhanced and display the similar peaks compared to Co<sub>3</sub>O<sub>4</sub>-MOF. Especially, 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> and 50-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> with higher Ni content show the much stronger  $\beta$  and  $\gamma$  peaks, suggesting that there are more easily extracted oxygen species to take part in oxidation. Therefore, the addition of Ni enhances surfaceactive oxygen species, which can make a great contribution to the catalytic activity.

To investigate the reducibility of catalysts, H2-TPR experiments were performed, and the profiles are shown in Figure 5e. For Co<sub>3</sub>O<sub>4</sub>-MOF, two obvious differentiable reduction peaks centered at 302 and 400 °C, corresponding to the reduction of  $\mathrm{Co}^{3+}$  to  $\mathrm{Co}^{2+}$  and  $\mathrm{Co}^{2+}$  to  $\mathrm{Co}^{\bar{0}},$  respectively, are clearly observed.<sup>54</sup> In TPR spectrum of Mix-Ni $O_x/Co_3O_4$ , it displays a very broad peak from 260 to 700 °C containing a series of reductions of Co3+-Co2+-Co0 and Ni3+-Ni2+-Ni0, which is possibly because the compacted particles of sample restrain the reduction process to some degree. With Ni doping, the x- $NiO_x/Co_3O_4$  catalysts show the low-temperature shift of all reduction peaks compared to  $Co_3O_4$ -MOF, indicating that the electronic interaction between NiO<sub>x</sub> and Co<sub>3</sub>O<sub>4</sub> will promote the redox cycle of Ni<sup>3+</sup> and Co<sup>2+</sup>, which contributes to their low-temperature reducibility.<sup>55</sup> As observed in TEM, the 35- $NiO_{x}/Co_{3}O_{4}$  with homogeneously dispersed metal oxides and well hollow structure gives the lowest-temperature reducibility, where the first small peak (205 °C) probably represents the reduction from Co<sup>3+</sup> to Co<sup>2+</sup> and from Ni<sup>3+</sup> to Ni<sup>2+</sup>, and the other broad peak can be characteristic of the reduction from Co<sup>2+</sup> to Co<sup>0</sup> and from Ni<sup>2+</sup> to Ni<sup>0</sup>. For all catalysts, the lowtemperature reducibility obeys the order as Co<sub>3</sub>O<sub>4</sub>-MOF < 10- $NiO_{x}/Co_{3}O_{4} < 20-NiO_{x}/Co_{3}O_{4} < 50-NiO_{x}/Co_{3}O_{4} < 35 NiO_x/Co_3O_4$ . The initial H<sub>2</sub> consumption rate at low temperature (Figure 5f) is applied to further estimate the difference of reducibility, which is in line with the trend of the low-temperature reducibilities for catalysts. In general, the higher initial H<sub>2</sub> consumption rate, the better the lowtemperature reducibility. Therefore, the  $35-NiO_x/Co_3O_4$ shows the best low-temperature reducibility. Normally, the reducibility of the catalyst is closely related to its catalytic activity, and the catalyst with a reduced reduction temperature usually shows higher catalytic activity. Therefore, the order of low-temperature reducibilities has a good accordance with the catalytic activities, where the 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> sample displays the best catalytic activity under the photothermal conditions.

3.5. Proposed Mechanism of Photo-Thermocatalysis. On the basis of above results, a conclusion can be drawn that toluene degradation on  $x-NiO_x/Co_3O_4$  catalysts under irradiation is mainly via the light-driven thermocatalysis, where the thermal energy is provided by converting photo to heat to promote reaction temperature. Two important factors are crucial to meet with the light-off temperature for toluene oxidation in this system: illumination intensity and strong light absorption capacity. As mentioned in the DRS analysis, x- $NiO_r/Co_3O_4$  catalysts show the strong light absorption in the full spectrum, leading to the better catalytic performance than that of Mix-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>. The Co<sub>3</sub>O<sub>4</sub>-MOF owns the stronger light absorption in some region of spectrum than that of Co<sub>3</sub>O<sub>4</sub>-Com, thus giving the better catalytic activity. These results indicate that the strong light absorption is beneficial to efficient photothermal conversion. Furthermore, the lightdriven catalytic performance of catalyst is affected by other various factors such as surface areas, compositions, metal oxide distributions, morphologies, structures, and so on. According to characterization analyses, the MOF-templated catalysts possess much larger  $S_{\text{BET}}$  than Mix-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>. With the increasing of Ni doping content, the morphology and structure of  $x-NiO_x/$ Co<sub>3</sub>O<sub>4</sub> are gradually varied, which results in the change of elemental distribution, active species, and reducibility of the catalysts. Thus, the high light-driven catalytic performance over  $35-NiO_x/Co_3O_4$  catalyst can be mainly explained by its strong light absorption, low-temperature reducibility, homogeneous metal oxides distribution, more active species and active sites, hollow structure, and lager surface area.

Moreover, the in situ DRIFTS analysis is further applied to investigate the possible reaction pathway of toluene oxidation on  $35\text{-NiO}_x/\text{Co}_3\text{O}_4$  by direct electric heating, which can be fulfilled by photothermal conversion in this system. As shown in Figure 6, it can be clearly seen that toluene is adsorbed on



Figure 6. In situ DRIFTS spectra for 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> catalyst under exposure to toluene in air at different temperatures.

the surface of 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> at room temperature due to the characteristic absorbance bands of toluene (at ~3100–3000 cm<sup>-1</sup> domain) and the typical aromatic ring vibrations at 1600 and 1494 cm<sup>-1.56</sup> The bands 2875 and 2934 cm<sup>-1</sup> are associated with symmetric/asymmetric C–H stretching of methylene ( $-CH_2$ ).<sup>57</sup> With the increase of temperature, the bands of toluene rapidly decrease and finally disappear, which indicates toluene oxidation occurs on the 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub>. When the temperature is above 150 °C, the obvious new band

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appears at 1583 cm<sup>-1</sup>, which is assignable to benzyl alcohol.<sup>56</sup> And the band at 1653 due to adsorbed benzaldehyde is also present.<sup>56</sup> In addition, the bands at 1558, 1542, 1507, and 1392 cm<sup>-1</sup> are the characteristic of typical carboxylate group, indicating the formation of benzoate species that have been identified as key intermediates in the toluene oxidation.<sup>17,20,56</sup> With increase of temperature, most of these bands have an obvious increase in intensity, demonstrating the toluene oxidation is further accelerated to form more intermediates. Thus, the reaction pathway of toluene oxidation on 35-NiO<sub>x</sub>/  $Co_3O_4$  may proceed in consecutive steps: toluene  $\rightarrow$  benzyl alcohol  $\rightarrow$  benzaldehyde  $\rightarrow$  benzoate species  $\rightarrow$  H<sub>2</sub>O and CO<sub>2</sub>.

**3.6. Durability.** The durability test was investigated on the light-driven thermal oxidation of toluene under the irradiation of simulated sunlight with a light intensity of  $500 \text{ mW/cm}^2$  for 10 cycles, where each cycle lasted for 90 min. As depicted in Figure 7, the catalytic activity for toluene conversion is



Figure 7. Durability of 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> under irradiation of  $500 \text{ mW}/\text{cm}^2$  simulated sunlight.

decreased at the first four cycles from 95% to 82% and then is stable for the rest of the cycles, which is possibly ascribed to the small amount deposit of the formed intermediates at the beginning stage and then reach to reaction equilibrium. The  $CO_2$  yield is flapping at ~70%. The results confirm that the 35- $NiO_x/Co_3O_4$  catalyst is durable and stable at least in 900 min under the irradiation of simulated sunlight.

# 4. CONCLUSIONS

To summarize, the utilization of renewable solar energy via light-driven thermocatalysis offers a potential alternative strategy for VOCs remediation. The NiOx/Co3O4 composites with well-shaped morphologies prepared by MOF-templated method show the efficient light utilization due to their strong absorption in the full solar spectrum and high solar heating effect. The 35-NiO<sub>x</sub>/Co<sub>3</sub>O<sub>4</sub> with Co/Ni molar ratio 3:5 shows the best catalytic activity with 95% of toluene conversion and 80% of CO<sub>2</sub> yield, and the better catalytic durability in the 10cycle experiment under irradiation, which is attributed to the synergic effect of the strong light absorption, strong interaction of different metal oxides, more active sites, low-temperature reducibility, and hollow structure. Furthermore, the investigation of in situ DRIFTS on 35-NiOx/Co3O4 indicates the mechanism of toluene oxidation is finally decomposed to CO<sub>2</sub> and H<sub>2</sub>O via benzyl alcohol, benzaldehyde, and benzoate species as main intermediates. Therefore, on the basis of this work, it highlights a new strategy of material design for lighttriggered VOCs oxidation reaction, which will provide an

efficient avenue to harvesting solar light through photothermal effect in VOCs control.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.8b00587.

Detailed linear scanning element distribution; BET results and HRTEM images; low-temperature catalytic performance of toluene oxidation, and temporal temperature evolution of the catalysts layer under the irradiation of simulated sunlight (light intensity of 500 mW/cm<sup>2</sup>); surface temperature monitoring of  $35\text{-NiO}_x/\text{Co}_3\text{O}_4$  catalyst layer under the irradiation of simulated sunlight with the light intensity of 500 mW/cm<sup>2</sup> and toluene degradation under external heat; toluene degradation under the irradiation of simulated sunlight ( $500 \text{ mW/cm}^2$ , 295 °C), UV–vis light ( $265 \text{ mW/cm}^2$ , 178 °C), and infrared light ( $225 \text{ mW/cm}^2$ , 228 °C) (PDF)

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