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Synergetic Effect between Photocatalysis on TiO2 and Thermocatalysis on CeO2 for Gas-Phase Oxidation of Benzene on TiO2/CeO2 Nanocomposites

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Abstract. TiO₂/CeO₂ nanocomposites of anatase TiO₂ nanoparticles supported on microsized mesoporous CeO₂ were prepared and characterized by SEM, TEM, BET, XRD, Raman, XPS, and diffuse reflectance UV-Vis absorption. The formation of the TiO₂/CeO₂ nanocomposites considerably enhances their catalytic activity for the gas-phase oxidation of benzene as one of hazardous volatile organic compounds (VOCs) under the irradiation of a Xe lamp compared to pure CeO₂ and TiO₂. A solar light driven thermocatalysis on CeO₂ is found for the TiO₂/CeO₂ nanocomposites. There is a synergetic effect between the photocatalysis on TiO₂ and the thermocatalysis on CeO₂ for the TiO₂/CeO₂ nanocomposites, which significantly increases their catalytic activity. The CO₂ formation rate (r_{CO2}) of the TiO₂/CeO₂ nanocomposite with the Ti/Ce molar ratio of 0.108 under the synergetic condition is 36.4 times higher than its r_{CO2} under the conventional photocatalytic condition at near room temperature. CO temperature-programmed reduction (CO-TPR) with the irradiation of the Xe lamp and in dark reveals that the synergetic effect, which occurs at the interface of the TiO₂/CeO₂ nanocomposite, is due to the considerable promotion of the CeO₂ reduction by the photocatalysis on TiO₂.

Keywords: TiO₂, TiO₂/CeO₂ nanocomposite, photocatalysis, thermocatalysis, photothermocatalysis, synergetic effect, VOCs

1. Introduction

Volatile organic compounds (VOCs) as major air pollutants in indoor air, polluted urban atmospheres, factories of petrochemical, fine chemical, paint, and so on are harmful to human health as well as the environment. It is highly desirable to develop efficient technology for the abatement of VOCs.^{1,2} Heterogeneous photocatalysis by nano semiconductors is a promising technology for the abatement of VOCs as it is energy-saving, and operates under mild conditions, such as ambient temperature, atmospheric pressure, and using oxygen (air) as the oxidizing agent. Among the various photocatalysts, nanostructured TiO₂ is one of the most prominent photocatalysts due to its excellent catalytic performance, chemical stability, low cost, and nontoxicity.³ However, there are three bottlenecks which greatly retard its extensive application for the removal of VOCs. One is its low quantum efficiency due to fast recombination of photogenerated electrons and holes.^{4,5} The other is that it is only photoactivated by UV, which accounts for ~ 5% of the sunlight, due to its wide band gap (3.2 eV for anatase, and 3.0 eV for rutile).⁶⁻⁸ The two disadvantages make the photocatalysis only efficient for the removal of low concentration VOCs. The third is that it is prone to deactivation mainly due to the deposition of less reactive byproducts on the TiO2 surface.9-11 Another efficient technology for the removal of VOCs is heterogeneous thermocatalysis that has been widely applied in industry. Expensive noble metals are conventionally used as the most efficient thermocatalysts.¹² The main advantages of thermocatalysis are that it is efficient for the removal of high concentration VOCs, and has good thermocatalytic durability. However, compared to the photocatalysis, thermocatalysis is energy-consuming, and must operate at higher temperature by using additional heater. Therefore, finding a novel strategy for the efficient abatement of VOCs with the advantages of both the photocatalysis and thermocatalysis, which could utilize renewable solar energy and avoid their disadvantages, would be scientifically and technologically significant.

Nanostructured CeO₂ is one of the efficient thermocatalysts besides the expensive noble metals for the removal of air pollutants including VOCs owing to its remarkable Ce^{4+}/Ce^{3+} redox properties.¹³⁻²⁰ Its thermocatalytic activity can be improved by controlling the size, exposed facets (e.g. {100}, {110}),¹⁴⁻¹⁶ and surface structure, such as oxygen vacancies,¹⁷⁻²⁰ etc. On the other hand, nanostructured CeO₂ as n-type semiconductor with band gap narrower than TiO₂ has photocatalytic activity under UV and/or visible irradiation,²¹⁻²⁴ and its photocatalytic activity can be improved by controlling its morphology, doping metal ions,^{25,26} and forming nanocomposite with TiO₂ to increase

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e-h separation efficiency.²⁷⁻³⁹ Recently, a synergetic effect of photo/thermo-catalysis was reported by several groups. With the synergetic effect, significant enhancement in the catalytic activity was achieved on mesoporous CeO_2^{40} and Mn, Bi doped $CeO_2^{41, 42}$ for the abatement of VOCs such as benzene, formaldehyde, and on Y doped CeO_2 for the photodegradation of dye.⁴³

Recently, we developed a facile template-free approach to synthesize microsized mesoporous CeO_2 and we reported that the microsized mesoporous CeO_2 exhibited a significant enhancement of thermocatalytic activity as compared to CeO_2 nanoparticles and nanocubes without mesopores.²⁰ Herein, we load TiO₂ nanoparticles on the microsized mesoporous CeO_2 to form TiO₂/CeO₂ nanocomposites. We achieve a perfect combination of photocatalysis and thermocatalysis on the TiO₂/CeO₂ nanocomposites. They exhibit efficient catalytic activity for the gas-phase benzene oxidation under the full solar spectrum irradiation and visible-infrared irradiation. A solar light driven thermocatalysis on CeO_2 is found for the TiO₂/CeO₂ nanocomposites. We find a novel synergetic effect between the light driven thermocatalysis on CeO_2 and the photocatalysis on TiO₂ for the TiO₂/CeO₂ nanocomposites, which considerably increases their catalytic activity. We reveal that the synergetic effect, occurring at the interface of the TiO₂/CeO₂ nanocomposites, is due to the considerable promotion of the CeO₂ reduction by the photocatalysis on TiO₂.

2. Experimental

Preparation. Microsized mesoporous CeO₂ was prepared according to the procedure reported in our previous work:²⁰ 60.000 g of Ce(NO₃)₃·6H₂O and 24.896 g of urea were added into 160 ml of distilled water under magnetic stirring until they were dissolved. Then, the solution was added to a 200 mL Teflon bottle, which was sealed tightly in a stainless-steel autoclave. The autoclave was put in an electric oven, heated to 180 °C and kept at 180 °C for 16 h. After the autoclave cooled to ambient temperature, the precipitate was thoroughly washed with distilled water and dried at 90 °C for 12 h. The power obtained was the uncalcined ceria. Finally, the powder was calcined at 400 °C for 4 h in a Muffle furnace.

 TiO_2/CeO_2 samples with different Ti/Ce molar ratio were prepared according to the following procedure: A known amount of titanium butoxide (e.g. 0, 0.341, 0.852, 1.705 g) was dissolved to 70 mL of ethanol in a beaker. 4.742 g of the uncalcined ceria was added to the titanium butoxide solution. The beaker was placed into a water bath at 70 °C. The mixture was magnetically stirred until the

ethanol was evaporated. The product was thoroughly washed with distilled water, dried at 90 °C for 12 h in an electric oven, and finally calcined at 400 °C for 4 h in a Muffle furnace. The obtained TiO₂/CeO₂ samples with Ti/Ce molar ratio of 0.043, 0.108, 0.216 in reactants are denoted as TiO₂/CeO₂-A, TiO₂/CeO₂-B, TiO₂/CeO₂-C, respectively.

Pure nano TiO_2 was prepared by the same procedure as the TiO_2/CeO_2 samples except for no addition of the uncalcined ceria.

Characterization. SEM images and energy dispersive X-ray spectroscopy (EDX) were obtained with a ULTRA PLUS-43-13 scanning electron microscope. Transmission electron microscopy (TEM) images were obtained on a JEM-100CX electron microscope. The measurement of surface area was conducted by using N₂ adsorption at -196 °C on ASAP2020. X-ray diffraction (XRD) was taken on a Rigaku Dmax X-ray diffractometer with Cu Ka radiation. Raman spectra were recorded on a Renishaw inVia Raman microscope with the excitation of 514.5 nm laser light. X-ray photoelectron spectroscopy (XPS) analysis was taken on a VG Multilab 2000 X-ray photoelectron spectrometer with Mg Kα radiation. Diffuse reflectance UV-Vis absorption was measured on a UV-3600 spectrophotometer.

CO temperature-programmed reduction (CO-TPR) was performed on a TP-5080 multifunctional adsorption apparatus equipped with a TCD detector. The sample was put in a tubular quartz reactor. A quartz window was connected to one of the end of the quartz reactor. A Xe lamp (CHF-XM500) was put in the front of the quartz window. The samples were pre-treated in 5 vol% O_2 /He at 200 °C for 1 h. CO-TPR was conducted by heating the pre-treated samples in the flow of 5 vol% CO/He with the irradiation of the Xe lamp or in dark.

Photothermocatalytic activity. The photothermocatalytic activity of the samples for benzene oxidation was measured on a closed cylindrical stainless steel gas-phase reactor with a quartz window under the irradiation of a Xe lamp (CHF-XM500) as schematically illustrated in Scheme 1. To reduce energy loss during the irradiation, 0.1000 g of the sample was coated on a thermal insulation slice. To measure the photothermocatalytic activity under the visible-infrared irradiation from the Xe lamp, a cutoff filter that can filter out the irradiation with wavelength less than 420 or 480 nm was placed between the Xe lamp and the quartz window. The products and reactants were analyzed by gas chromatograph. The experimental procedure and the light intensity from the Xe lamp were detailed in our recently published work.⁴⁴



Scheme 1. The schematic diagram of the photothermocatalytic set-up.

Photocatalytic activity. The photocatalytic activity of the samples for the oxidation of benzene under the Xe lamp irradiation at near ambient temperature was measured according to the procedure described in our recent publications.⁴⁴

Thermocatalytic activity. The thermocatalytic activity of the samples for the oxidation of benzene was tested in a continuous flow fixed-bed quartz tubular reactor at different temperature. The experimental procedure was detailed in our previous publication.²

3. Results and Discussion

3.1. Characterization. The TiO₂/CeO₂ nanocomposites with different Ti/Ce molar ratio were prepared by loading different amount of TiO₂ nanoparticles on the microsized mesoporous CeO₂. Figure 1 shows SEM images with the distribution of elements and energy dispersive X-ray spectroscopy of the TiO₂/CeO₂ samples. It can be seen from Figure 1, titanium is well distributed on the microsized CeO₂ for all the TiO₂/CeO₂ samples (Figure 1A, 1B, and 1C). This is confirmed by the SEM images with the separate distribution of Ti, Ce, and O for the TiO₂/CeO₂ samples (Figure S1, Supporting information). Ce, O, Ti, and adventitious carbon are detected by EDX (Figure 1D, IE, and 1F). The Ti/Ce molar ratio of TiO₂/CeO₂-A, TiO₂/CeO₂-B, and TiO₂/CeO₂-C is 0.021, 0.068, 0.174, respectively (Table 1), which is slightly lower than the corresponding data in reactants (0.043, 0.108, 0.216). This is due to the diffusion of titanium butoxide into the pores of the microsized mesoporous CeO₂ during the preparation (see Experimental). Figure 2 shows TEM images of the TiO₂/CeO₂ samples. TiO₂ nanoparticles are observed. When the Ti/Ce molar ratio increases to 0.216

(TiO₂/CeO₂-C, Figure 2C), there is observed a thin layer of TiO₂ nanoparticles formed on microsized CeO₂. The size of TiO₂ nanoparticles in the TiO₂/CeO₂ samples is estimated by TEM to be $2\sim17$ nm. In this case, mesopores cannot be observed on microsized CeO₂ as they are blocked by TiO₂ nanoparticles. HRTEM shows that TiO₂ nanoparticles with {101} planes of anatase for all the TiO₂/CeO₂ samples are closely contacted to CeO₂ with {111} planes. This result indicates the formation of TiO₂/CeO₂ nanocomposites of anatase TiO₂ nanoparticles supported on microsized mesoporous CeO₂.

Table 1. Ti/Ce molar ratio, BET surface area, pore volume, dominant pore size, and Ce³⁺ fraction of the samples.

Sample	Ti/Ce molar ratio		BET surface	Pore volume	Dominant	Ce ³⁺ /(Ce ³⁺ +Ce ⁴⁺)
	in reactants	by EDX	area (m ² g ⁻¹)	(cm^3g^{-1})	pore size (nm)	molar ratio by XPS
CeO ₂			84.0	0.055	3.8	0.30
TiO ₂ /CeO ₂ -A	0.043	0.021	71.6	0.059	1.5	0.31
TiO ₂ /CeO ₂ -B	0.108	0.068	70.3	0.057	1.5	0.33
TiO ₂ /CeO ₂ -C	0.216	0.174	73.1	0.061	1.3	0.35



Figure 1. SEM images with the distribution of elements and EDX of $TiO_2/CeO_2 - A$ (A, D), $TiO_2/CeO_2 - B$ (B, E), and $TiO_2/CeO_2 - C$ (C, F): Ti (red), Ce (cyan), and O (green).



Figure 2. TEM images of TiO₂/CeO₂-A (A, D), TiO₂/CeO₂-B (B, E), and TiO₂/CeO₂-C (C, F).

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The N₂ adsorption–desorption isotherm indicates that the TiO₂/CeO₂ samples have a desorption hysteresis due to the capillary condensation of N₂ in pores (Figure S2). The dominant pore size of CeO₂, TiO₂/CeO₂-A, TiO₂/CeO₂-B, TiO₂/CeO₂-C is 3.8, 1.5, 1.5, 1.3 nm, respectively (Figure S2, Table 1). Their corresponding total pore volume is 0.0545, 0.0589, 0.0575, 0.0612 cm³ g⁻¹, respectively. The BET surface area of CeO₂, TiO₂/CeO₂-A, TiO₂/CeO₂-

The XRD analysis reveals that CeO₂ in all the TiO₂/CeO₂ samples has a cubic fluorite structure (JCPDS 89-8436) as shown in Figure 3A. There is a weak peak observed at 25.3° for TiO₂/CeO₂-C with higher Ti/Ce molar ratio of 0.216 (Table 1), which belongs to {101} planes of anatase (JCPDS 89-4921). This is in agreement to the observation by HRTEM. But no XRD peaks of anatase are observed for TiO₂/CeO₂-A and TiO₂/CeO₂-B with lower Ti/Ce molar ratio (Table 1). This is attributed to the lower fraction of anatase in the TiO₂/CeO₂ nanocomposites than the detection limit by XRD. Figure 3B shows the Raman spectra of the samples. For TiO₂/CeO₂-A, there is a weak Raman peak observed around ~143 cm⁻¹, which is attributed to Eg mode of anatase.^{11, 45} Increasing the Ti/Ce molar ratio from 0.043 to 0.108 and 0.216 leads to a gradual enhancement of the intensity for the Eg mode of anatase.



Figure 3. XRD pattern (A) and Raman spectra (B) of CeO₂ (a), TiO₂/CeO₂-A (b), TiO₂/CeO₂-B (c), and TiO₂/CeO₂-C (d).

Figure 4A shows diffuse reflectance UV-Vis spectra of the samples. The microsized mesoporous CeO₂ and TiO₂/CeO₂ nanocomposites have absorption up to ~500 nm. The visible absorption is attributed to the presence of Ce³⁺ in the microsized mesoporous CeO₂ and TiO₂/CeO₂ samples ^{40,46} as the band gap of CeO₂, which is due to the indirect O2*p*—Ce4*f* transition along the *L* high-symmetry lines of the Brillouin zone, is correlated with the Ce³⁺ concentration.⁴⁶ The existence of Ce³⁺ in the samples is confirmed by analyzing their Ce3d XPS spectra (Figure 4B). Six peaks labeled as v, v'', v''' (3d_{5/2}), u, u'', u''' (3d_{3/2}) referring to three pairs of spin-orbit doublets are characteristic of Ce⁴⁺3d. Four peaks labeled as v₀, v'(3d_{5/2}), u₀, u' (3d_{3/2}) correspond to Ce³⁺3d.^{27,47} The molar ratio of

 $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ in CeO₂, TiO₂/CeO₂-A, TiO₂/CeO₂-B, and TiO₂/CeO₂-C is estimated by the deconvolution of their Ce3d XPS spectra to be 0.30, 0.31, 0.33, 0.35 (Table 1), respectively.



Figure 4. Diffuse reflectance UV-Vis absorption (A) and Ce3d XPS spectra (B) of CeO₂ (a), TiO_2/CeO_2 -A (b), TiO_2/CeO_2 -B (c), and TiO_2/CeO_2 -C (d).

3.2. Photothermocatalytic activity. The photocatalytic activity of the samples was measured by evaluating the rate of CO_2 formation from the gas-phase oxidation of benzene under the irradiation of a Xe lamp. The catalytic oxidation of benzene is chosen as benzene is carcinogenic and recalcitrant, and one of main VOC pollutants. As shown in Figure 5A, the microsized mesoporous CeO₂ exhibits efficient catalytic activity for benzene oxidation. After the irradiation for 60 min, the concentration of CO₂ produced is 3587.4 mg m⁻³. Loading a small amount of TiO₂ nanoparticles on the microsized mesoporous CeO₂ (TiO₂/CeO₂-A) leads to a significant enhancement of its photocatalytic activity.

After the irradiation for 60 min, the concentration of CO₂ produced increases from 3587.4 to 5303.8 mg m⁻³. Increasing the Ti/Ce molar ratio from 0.043 to 0.108 results in a further improvement in the photocatalytic activity. After the irradiation for 60 min, the concentration of CO₂ produced increases to 5954.8 mg m⁻³ (TiO₂/CeO₂-B). However, further enhancing the Ti/Ce molar ratio to 0.216 does not increase the photocatalytic activity. TiO₂/CeO₂-C has the almost same photocatalytic activity as TiO_2/CeO_2 -B. This means that the optimum Ti/Ce molar ratio is 0.108 for the TiO_2/CeO_2 nanocomposites. It is well known that TiO₂ (P25), a mixture of anatase (80%) with band gap of 3.2 eV and rutile (20%) with band gap of 3.0 $eV_{,3}^{3}$ exhibits very good photocatalytic activity under UV irradiation, thus is widely used as benchmark photocatalyst. For comparison, we measured the photocatalytic activity of $TiO_2(P25)$ for benzene oxidation under the irradiation of the Xe lamp. After the irradiation for 60 min, the concentration of CO_2 produced is 2706.4 mg m⁻³. Its photocatalytic activity is much lower than the microsized mesoporous CeO_2 and the TiO_2/CeO_2 nanocomposites. We also measured the photocatalytic activity of pure nano TiO_2 for benzene oxidation under the irradiation of the Xe lamp. The pure nano TiO_2 has anatase crystalline structure with band gap of 3.2 eV and its BET surface area is 46.9 m² g⁻¹. After the irradiation for 60 min, the concentration of CO_2 produced is 3362.9 mg m⁻³. Its photocatalytic activity is much lower than the TiO₂/CeO₂ nanocomposites. Figure 5B shows the CO₂ formation rate per unit mass of catalyst (r_{CO2}). r_{CO2} of TiO₂/CeO₂-B (10.1 µmol g⁻¹) min⁻¹) is 1.7, 2.2, 1.8 times higher than CeO₂, TiO₂(P25), nano TiO₂, respectively. As the catalyst has different surface area (Table 1), we calculate the rate of CO₂ formation rate per unit surface area of catalyst (r_{SCO2}). r_{SCO2} of TiO₂/CeO₂-B (0.14 µmol m⁻² min⁻¹) is 2.0, 1.8 times higher than CeO₂ and $TiO_2(P25)$, respectively. This result reveals that the formation of the TiO_2/CeO_2 nanocomposites considerably enhances its photocatalytic activity. The photocatalytic durability of TiO₂/CeO₂-B for benzene oxidation under the irradiation of the Xe lamp was tested. As shown in Figure 5C, its photocatalytic activity keeps unchanged when the catalyst was recycled for 30 times, suggesting that TiO₂/CeO₂-B exhibits a good photocatalytic durability.

As the TiO₂/CeO₂ nanocomposites have absorption up to ~500 nm (Figure 4), in order to confirm whether they exhibit visible photocatalytic activity, we measured the photocatalytic activity of TiO₂/CeO₂-B for benzene oxidation under the visible-infrared irradiation above 420 nm or 480 nm from the Xe lamp. As shown in Figure 5D, TiO₂/CeO₂-B exhibits photocatalytic activity under the visible-infrared irradiation above 420 nm or 480 nm. After the visible-infrared irradiation above 420

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nm or 480 nm for 60 min, the concentration of CO₂ produced is 1398.3, 401.1 mg m⁻³, respectively. The r_{CO2} of TiO₂/CeO₂-B under the visible-infrared irradiation above 420 nm or 480 nm is 2.37, 0.68 μ mol g⁻¹ min⁻¹, respectively. The considerable decrease of the photocatalytic activity is attributed to the decreased absorption above 420 nm or 480 nm for TiO₂/CeO₂-B (Figure 4A).



Figure 5. Time course of CO₂ produced from benzene oxidation (A), r_{CO2} for benzene oxidation on the catalysts (B), the durability of TiO₂/CeO₂-B for the benzene oxidation (the reaction time of every cycle, 60 min) under the Xe lamp irradiation (C), and time course of CO₂ produced from benzene oxidation on TiO₂/CeO₂-B under the irradiation above 420 nm or 480 nm (D): CeO₂(a), TiO₂/CeO₂-A (b),TiO₂/CeO₂-B (c), TiO₂/CeO₂-C (d), TiO₂(P25) (e), and TiO₂(f).

3.3. Mechanism. Nano TiO_2 has been regarded as one of the most effective UV photocatalysts.³ Some researchers reported that nano CeO₂ shows photocatalytic activity under UV or visible irradiation.²¹⁻²⁴ The photodegradation of organic pollutants on TiO₂ follows the well-known photocatalytic mechanism.³ To confirm whether the TiO₂/CeO₂ nanocomposites follow the conventional photocatalytic mechanism, the photocatalytic activity of CeO₂ and TiO₂/CeO₂-B for benzene oxidation

under the Xe lamp irradiation at near ambient temperature was measured. As can be seen from Figure 6, TiO₂/CeO₂-B shows photocatalytic activity while CeO₂ has almost no photocatalytic activity for benzene oxidation at ~40 °C. But, r_{CO2} of TiO₂/CeO₂-B under photothermocatalytic condition is 36.4 times higher than that of TiO₂/CeO₂-B under the photocatalytic condition at ~40 °C (Figure 6). This result clearly indicates the presence of a solar light driven thermocatalysis (schematically illustrated in Scheme 2) except for the photocatalysis for benzene oxidation on TiO₂/CeO₂-B under the irradiation of the Xe lamp: The irradiation of the Xe lamp on the TiO₂/CeO₂ nanocomposites results in a considerable increase of their temperature due to the photothermal conversion and the infrared heating effect (*See* **3.3.1. Photothermal conversion**). When the temperature increases to the thermocatalytic light-off temperature ($T_{\text{light-off}}$) of the TiO₂/CeO₂ nanocomposites, the thermocatalytic oxidation of benzene starts (*See* **3.3.2.Thermocatalysis**).



Scheme 2. Schematic illustration of solar light driven thermocatalysis and the synergetic effect between the photocatalysis on TiO_2 and thermocatalysis on CeO_2 for the TiO_2/CeO_2 nanocomposites.



Figure 6. Time course of CO₂ produced from benzene oxidation (A) and r_{CO2} for benzene oxidation on the catalysts (B) under the different cases: TiO₂/CeO₂-B under the Xe lamp irradiation (*photothermocatalytic*, a), TiO₂/CeO₂-B (b) and CeO₂ (c) under the Xe lamp irradiation at near room temperature (*photocatalytic*), TiO₂/CeO₂-B under the irradiation above 420 nm with higher light intensity (d), a mixture of TiO₂ and CeO₂ with the same Ti/Ce molar ratio as TiO₂/CeO₂-B under the Xe lamp irradiation (e).

3.3.1. Photothermal conversion. To prove the solar light driven thermocatalysis, first, we measured the temperature evolution of the samples with the irradiation of the Xe lamp. Under the Xe lamp irradiation, the temperature of all the samples quickly increases to a plateau (Figure 7A). The temperature increase is attributed to the photothermal conversion due to the absorption of the UV-visible irradiation by the samples (Figure 4A) as well as the heating effect of the infrared irradiation from the Xe lamp. When the photothermal conversion and the heating effect establish equilibrium with the energy dissipation from the sample to the surroundings, a plateau temperature is

observed. The plateau temperature of CeO₂, TiO₂/CeO₂-A, TiO₂/CeO₂-B, TiO₂/CeO₂-C is 212, 213, 205, 193 °C, respectively (Figure 7B). This result indicates a slight decrease of the plateau temperature with increasing the Ti/Ce molar ratio, which is due to the reflectance of the infrared light by TiO₂ as white pigment. The temperature evolution of TiO₂/CeO₂-B under the irradiation above 420 and 480 nm was also measured. In this case, the plateau temperature under the irradiation above 420 and 480 nm is 188, 174 °C, respectively.



Figure 7. Temporal evolution of the temperature on TiO_2/CeO_2 -B (A) and the plateau temperature of the samples (B) under the Xe lamp irradiation: CeO_2 (a), TiO_2/CeO_2 -A (b), TiO_2/CeO_2 -B (c), and TiO_2/CeO_2 -C (d).

3.3.2. Thermocatalysis. To confirm whether the plateau temperature of the catalysts can reach to the light-off temperature ($T_{\text{light-off}}$) for benzene oxidation, we studied the effect of reaction temperature on the thermocatalytic activity of the catalysts for the oxidation of benzene in a flow fixed-bed reactor.

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As shown in Figure 8, compared to the thermocatalytic activity of the microsized mesoporous CeO₂, loading a small amount of TiO₂ nanoparticles on the microsized mesoporous CeO₂ (TiO₂/CeO₂-A, TiO₂/CeO₂-B) does not obviously alter its thermocatalytic activity. Further increasing the Ti/Ce molar to 0.216 (TiO₂/CeO₂-C) leads to a decrease of thermocatalytic activity above ~200 °C due to the much lower thermocatalytic activity of the nano TiO₂ (Figure 8, curve e) than CeO₂. For the microsized mesoporous CeO₂ and all the TiO₂/CeO₂ nanocomposites, benzene starts to be oxidized around ~ 160 °C. All the plateau temperatures of the microsized mesoporous CeO₂ and the TiO₂/CeO₂ nanocomposites under the Xe lamp irradiation (Figure 7B) are higher than their corresponding $T_{\text{light-off}}$ (~160 °C). Thus, the solar light driven thermocatalytic oxidation of benzene can take place. The plateau temperature of TiO₂/CeO₂-B under the irradiation above 420 nm or 480 nm is higher than its corresponding $T_{\text{light-off}}$. This is why TiO₂/CeO₂-B exhibits visible-infrared light driven thermocatalytic activity for benzene oxidation.



Figure 8. Benzene conversion versus reaction temperature over the catalysts for benzene oxidation under the condition of benzene concentration = 2.0 g m^{-3} , space velocity (SV) = $48000 \text{ mL g}^{-1}_{\text{catalyst}} \text{ h}^{-1}$, ambient pressure: CeO₂ (a), TiO₂/CeO₂-A (b), TiO₂/CeO₂-B (c), TiO₂/CeO₂-C (d), and nano TiO₂ (e).

3.4. Synergetic effect. We tested the photocatalytic activity of TiO_2/CeO_2 -B under the irradiation above 420 nm with higher irradiation intensity by reducing the distance between the Xe lamp and the reactor (Figure 6). By increasing the visible-infrared irradiation intensity, its plateau temperature is equal to that under the full solar spectrum irradiation of the Xe lamp (205 °C, Figure 7). In this case, only visible-infrared light driven thermocatalysis on CeO₂ occurs as anatase TiO₂ can not be photoactivated by the visible irradiation above 420 nm because of its large band gap (3.2 eV, 386 nm). Its thermocatalytic activity should be the same as under the full solar spectrum irradiation of the Xe lamp. Interestingly, r_{CO2} of TiO₂/CeO₂-B under the full solar spectrum irradiation is 1.9 times higher than the sum of its r_{CO2} under the irradiation above 420 nm with higher irradiation intensity (5.15 µmol g⁻¹ min⁻¹) and its r_{CO2} under the full solar spectrum irradiation at near ambient temperature. This result suggests the presence of a synergetic effect between the light driven thermocatalysis on CeO₂ and the photocatalysis on TiO₂ for TiO₂/CeO₂-B under the full solar spectrum irradiation

In order to further prove the synergetic effect, we tested the photocatalytic activity of a mixture of the nano TiO₂ and the microsized mesoporous CeO₂ with the same Ti/Ce molar ratio as TiO₂/CeO₂-B under the Xe lamp irradiation. In this case, r_{CO2} of the mixture of the nano TiO₂ and the microsized mesoporous CeO₂ (4.95 µmol g⁻¹ min⁻¹) is 2.0 times lower than that of TiO₂/CeO₂-B (Figure 6). These results undoubtedly indicate that there is a synergetic effect between the light driven thermocatalysis on CeO₂ and the photocatalysis on TiO₂ for TiO₂/CeO₂-B, and the synergetic effect takes place at the interface of the TiO₂/CeO₂ nanocomposites as schematically illustrated in Scheme 2:

Upon UV excitation, electrons on the valence band of TiO₂ are excited to the conduction band, leaving hole on the valence band. The photogenerated holes and electrons move to the surface of TiO₂. The electrons reduce the electron acceptor (e.g. O₂) adsorbed on the surface of TiO₂ to form active oxygen (e.g. O₂⁻) due to the lower oxidation potential of e (-0.18 V vs NHE at pH = 1) than that of O₂ (e.g. O₂/O₂⁻, -0.16 V vs NHE).^{48, 49, 50} The holes oxidize donors: adsorbed H₂O or hydroxyl group on TiO₂ to produce hydroxyl radical (•OH), and adsorbed organic molecule (e.g. benzene) to form active organic molecules (e.g. benzene⁺)^{3, 48-51} due to the higher oxidation potential of h (3.02 V vs NHE) than those of hydroxyl groups (e.g. OH·/OH⁻, 1.89 V vs NHE)⁵⁰ and organic molecules (e.g. benzene, 2.995 V vs NHE).⁵² Thus, the photocatalytic oxidation of organic molecule (e.g. benzene) proceeds.

Meanwhile, the light driven thermocatalysis proceeds on the microsized mesoporous CeO_2 . The widely accepted Mars–van Krevelen mechanism for the thermocatalytic oxidation on CeO_2 is as follows: organic molecule adsorbed on the surface of CeO_2 is oxidized by the lattice oxygen of CeO_2 , and the reduced ceria is subsequently re-oxidized by gas phase oxygen.^{14, 17, 18, 20}

The active benzene (e.g. benzene⁺) produced by the photocatalysis on TiO_2 is more active than benzene according to molecular orbital theory as the electron number in the bonding molecular orbital of benzene⁺ is less than that of benzene.⁵³ Thus the reduction of CeO₂ by the active benzene is thermodynamically favorable. The active benzene undoubtedly migrates to CeO₂ through the interface

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of the TiO₂/CeO₂ nanocomposite, promoting the reduction of CeO₂ (Scheme 2) because the active benzene, also existed on TiO₂ in the mixture of the nano TiO₂ and the microsized CeO₂, does not leads to an enhancement in the catalytic activity of CeO₂ (clumn a in Figure 5B and clumn e in Figure 6B). The active oxygen (e.g. O₂⁻) and hydroxyl radical (•OH) produced by the photocatalysis on TiO₂ are more active than gas phase oxygen (O₂) in the conventioanl thermocatalysis on CeO₂. Thus the oxidation of the reduced ceria by the active oxygen (e.g. O₂⁻) and hydroxyl radical (•OH) is thermodynamically favorable. The active species formed by the photocatalysis on TiO₂ migrate to CeO₂ via the interface of the TiO₂/CeO₂ nanocomposite, accelerating the oxidation of the reduced ceria formed by thermocatalyis (Scheme 2). Therefore, the synergetic effect between the photocatalysis on TiO₂ and the light driven thermocatalysis on CeO₂ considerably increases the catalytic activity of the TiO₂/CeO₂ nanocomposites under the Xe lamp irradiation.

3.5. Origin of synergetic effect. It is widely accepted that the reducibility of CeO₂ plays a decisive role in its thermocatalytic activity, because the reduction of CeO₂ is much slower than the re-oxidation of reduced ceria.^{14, 17, 18, 20} In order to put insight in the origin of the synergetic effect, the effect of the irradiation on the reduction of CeO₂ is investigated by CO temperature-programmed reduction under the irradiation of the Xe lamp and in dark (Experimental). Under the dark condition without the irradiation of the Xe lamp, no peak is observed for pure TiO2. A negative peak around 130 °C is observed for TiO₂/CeO₂-B due to the desorption of CO on CeO₂ (Figure 9A). There are observed two broad TPR peaks around ~276, ~394 °C, which are attributed to the oxidation of CO by two types of surface lattice oxygen on CeO2.^{14, 17} Interestingly, under the irradiation of the Xe lamp, the two broad TPR peaks shift to lower temperature of ~259, ~353 °C, respectively. This observation indicates that the irradiation of the Xe lamp reduces the oxidation temperature of CO by the lattice oxygen on CeO₂. Moreover, the intensity of the two TPR peaks is considerably enhanced. We quantitatively measure the amounts of CO consumed for TiO₂/CeO₂-B by calculating the area of their TPR profiles calibrated by the reduction of a known amount of CuO by CO. The total amounts of CO consumed for TiO₂/CeO₂-B in dark is 580.1 μ mol g⁻¹. Under the irradiation of the Xe lamp, the total amounts of CO consumed increases to 1033.1 μ mol g⁻¹. In striking contrast, for a mixture of the nano TiO₂ and the microsized mesoporous CeO₂ with the same Ti/Ce molar ratio as TiO₂/CeO₂-B, the irradiation of the Xe lamp does not lead to an obvious evolution of its CO-TPR profile as compared to that in dark (Figure 9B). This result reveals that the irradiation of the Xe lamp significantly accelerates the reduction of CeO_2 by CO

for the TiO_2/CeO_2 nanocomposite, and the promotion of CeO_2 reduction by CO with the irradiation occurs at the interface of the TiO₂/CeO₂ nanocomposite. Munoz-Batista repoted that the reaction rate behavior in the TiO₂/CeO₂ composite system was dominated by the availability of holes at the surface of the material, and the photodegradation was a hole-triggered reaction.²⁷ For CO-TPR in dark, there is only the reduction of CeO₂ by CO. For CO-TPR under the irradiation of the Xe lamp, the photogenerated hole (h) on TiO2 reacts with CO to form active CO (e.g. CO⁺) due to the higher oxidation potential of h than that of CO (0.64 V vs RHE on Pt electrode).⁵⁴ The active CO (e.g. CO⁺) is more active than CO according to molecular orbital theory as the electron number in the bonding molecular orbital of CO^+ is less than that of CO^{53} . Thus the reduction of CeO_2 by the active CO (e.g. CO^+) is thermodynamically favorable. The active CO (e.g. CO^+) produced by photocatalysis on TiO₂ undoubtedly migrates to CeO_2 through the interface of the TiO_2/CeO_2 nanocomposites, promoting the reduction of CeO₂ (Figure 9A) because the active CO, also existed on TiO_2 in the mixture of the nano TiO_2 and the microsized CeO₂, does not leads to the promotion of CeO₂ reduction (Figure 9B). This accounts for the shift of the CO-TPR peaks to lower temperature as well as the enhancement of CO consumption with the irradiation of the Xe lamp for the TiO₂/CeO₂ nanocomposite (Figure 9A). It should be noted that in principle, photogenerated electrons and holes could be produced on the conduction band and valence band of CeO₂ upon UV or visible irradiation, respectively.^{27,31} However, the photogenerated holes on CeO_2 does not promote the reduction of CeO_2 (Figure 9B). The considerable promotion of CeO₂ reduction by the photocatalysis on TiO₂ rather than by the photocatalysis on CeO2 improves the solar light driven thermocatalytic activity of CeO2 for the TiO₂/CeO₂ nanocomposite as illustrated in Scheme 2.

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Figure 9. CO-TPR profile of TiO_2/CeO_2 -B (A), and a mixture of TiO_2 and CeO_2 with the same Ti/Ce molar ratio as TiO_2/CeO_2 -B (B) in dark and with the irradiation of the Xe lamp.

4. Conclusion

In summary, TiO_2/CeO_2 nanocomposites exhibit enhanced catalytic activity for benzene oxidation under the irradiation of the Xe lamp compared to pure CeO₂ and TiO₂. A solar light driven thermocatalysis on CeO₂ is found for the TiO₂/CeO₂ nanocomposites. There is a synergetic effect between the photocatalysis on TiO₂ and the thermocatalysis on CeO₂ for the TiO₂/CeO₂ nanocomposites, which significantly increases their catalytic activity. The synergetic effect, which occurs at the interface of the TiO₂/CeO₂ nanocomposites, is due to the considerable promotion of the CeO₂ reduction by the photocatalysis on TiO₂. The novel strategy using the synergetic effect between the photocatalysis on TiO₂ and the solar light driven thermocatalysis on CeO₂ is applicable for

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designing other nanocomposite catalysts for the environmental purification using renewable solar energy.

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Supporting Information

SEM and N_2 adsorption-desorption of the catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

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