



# A new strategy for utilization of NIR from solar energy—Promotion effect generated from photothermal effect of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> for photocatalytic oxidation of NO



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## ABSTRACT

Photothermal effect was for the first time utilized to capture the energy from infrared light and to promote the photocatalytic oxidation activity of NO by a simply mechanical mixing of traditional photocatalysts and core-shell structured Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> absorbed the infrared light, transferred it into thermal energy based on photothermal effect, which then accelerated the NO photocatalytic activity of traditional photocatalysts. This promotion effect led by the addition of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> was confirmed by several classical photocatalysts such as TiO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, BiOI and CeO<sub>2</sub>. To quantitatively characterize the photothermal effect, thermo images were taken with a thermo imager to obtain the average temperature rise of samples under the illumination of simulated solar light. Specially, P25/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> was studied in depth for illustration of the promotion mechanism. Experimental results showed that with the contribution of SiO<sub>2</sub> shell, the photocorrosion of Fe<sub>3</sub>O<sub>4</sub> didn't occur during photocatalytic oxidation process and the photothermal effect of Fe<sub>3</sub>O<sub>4</sub> was maintained. The quantity of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> was a vital factor for promotion of photocatalytic activity and the optimum mass ratio of P25 and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> was 3–1. After 120 min of illumination, the temperature of optimum P25/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> rose to 57.4 °C from 25 °C and its NO conversion capability showed an enhancement of 38.9% with the comparison to pure P25. The experimental results confirmed that the rise of temperature was attributed to the photothermal effect and its contribution was the same as the directly heating of photocatalysts. Furthermore, the enhancement of NO conversion capability around 30–40% was observed for the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> mixed anatase TiO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, ZnO, BiOI and CeO<sub>2</sub>. In sum, we developed a new strategy for utilization of NIR light of solar energy to facilitate the photocatalytic reactions.

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## 1. Introduction

Efficient harvesting of solar energy is always a big challenge and a worldwide target for human being. For this challenge, heterogeneous photocatalysis using nano-scale semiconductor materials

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has attracted enormous interests. TiO<sub>2</sub> was a famous nanomaterial among these semiconductors and has been widely used as photocatalyst. However, TiO<sub>2</sub> has a large bandgap of ~3.2 eV [1,2] (for anatase phase) and requires UV light (<380 nm) to be activated, while the percentage of UV light in solar energy was only ~5% and more than 90% of overall solar spectrum consisted of visible light (about ~49%) and near infrared (NIR) light (about ~46%). In the past ten years, researchers paid lots of attentions to the utilization of visible light energy and they gained remarkable progress. Photocatalysts with narrow bandgap and broad absorption spectrum were developed or discovered. Besides the metal or non-metal modified TiO<sub>2</sub> [3], a lot of new photocatalysts such as g-C<sub>3</sub>N<sub>4</sub> [4], (BiO)<sub>2</sub>CO<sub>3</sub>

[5], BiOX [6], etc. appeared. However, the utilization of NIR light which accounts for about 44% in the solar spectrum [7] is seldom reported [8].

The photothermal effect of nanoparticles on tumor photothermal ablation therapy (PTA) has been a research focus currently [9,10]. With the irradiation of NIR, the tumor cells containing proper photothermal agents were killed due to high temperature resulted from photothermal effect. Photothermal agents such as organic compounds (indocyanine green [11], polyaniline nanoparticles [12], etc.), noble metal nanomaterials (Au [13], Ag [14] and Pd [15], etc.), carbon-based materials (carbon nanotubes [16], graphene [9,17,18], etc.) and transition metal nanoparticles ( $\text{Fe}_3\text{O}_4$  [19–21],  $\text{Cu}_3\text{BiS}_3$  [22],  $\text{Cu}_9\text{S}_5$  [23] and  $\text{Ti}_8\text{O}_{15}$  [1], etc.) have been studied. Noble metal nanoparticles (NPs) of Au, Ag, and Pd that support LSPR in the visible spectrum were the most studied plasmonic NPs, but they were expensive for application. Compared to noble metal NPs, transition metal NPs- $\text{Fe}_3\text{O}_4$  showed a list of desirable properties for efficient and stable photothermal reactions: (i) a substantial photon absorption cross-section, (ii) strong intraparticle bonds, (iii) strong bonds to any surfactants, and (iv) environmental friendly and economical [24]; that's why it attracted researchers' attention in photothermal applications.

Nowadays, the studies on graphene-based nanocomposites,  $\text{NaYF}_4:\text{Yb},\text{Tm}/\text{TiO}_2$  and  $\text{Ti}/\text{TiO}_2$  for photocatalysis inspired us and attract our interesting for the utilization of NIR light. Zhixing Gan et al. [25] reported that the photothermal effect of graphene-based nanocomposites could play an important role in enhancing photocatalytic performance. Yanna Tang et al. had synthesized a core-shell  $\text{NaYF}_4:\text{Yb},\text{Tm}/\text{TiO}_2$  by using a solvothermal method to response to NIR. It was found that the upconversion luminescence  $\text{NaYF}_4:\text{Yb},\text{Tm}$  core could absorb NIR light and give out UV light which could be absorbed by the anatase  $\text{TiO}_2$  shell [26]. Also, a stable core-shell  $\text{Ti}/\text{TiO}_2$  with NIR response was reported. The photocatalyst could response from UV to NIR light region and exhibited photothermal effect as a result of Ti core [27]. These works pointed out a new path for the utilization of NIR light energy, but currently there was very few studies focused on  $\text{Fe}_3\text{O}_4$  and gas-solid phase photocatalytic reaction.

As one of the major air pollutants, NO is difficult to be removed by the widely used wet scrubbing methods because NO is nearly insoluble in water [28]. At present, the most effective method of NO removal, selective catalytic reduction (SCR), is expensive and requires extreme conditions including high temperature and toxic ammonia. Therefore, photocatalytic oxidation of NO, in which NO is oxidized into soluble species at low temperature and without introduction of toxic ammonia, costs less and has good potential in industrial application [29]. Herein, for the first time, we selected  $\text{Fe}_3\text{O}_4$  NPs as photothermal agent to improve utilization of NIR light from solar energy for photocatalytic oxidation of NO. We intended to take advantage of this energy to enhance NO conversion of photocatalysts. But we also concerned that  $\text{Fe}_3\text{O}_4$  NPs would be oxidized while it exposed to photocatalyst due to the produced  $\text{HNO}_3$ . To prevent this oxidation,  $\text{Fe}_3\text{O}_4$  NPs were coated with a passive material, such as  $\text{SiO}_2$ , to form a core-shell structured  $\text{Fe}_3\text{O}_4/\text{SiO}_2$ . Series of composed photocatalysts were synthesized by simply mixing traditional photocatalysts and core-shell structured  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  together mechanically, such as  $\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/\text{SiO}_2$ ,  $\text{BiOI}/\text{Fe}_3\text{O}_4/\text{SiO}_2$ , and  $\text{CeO}_2/\text{Fe}_3\text{O}_4/\text{SiO}_2$ . The physicochemical properties of prepared photocatalysts were studied and a new characterization method-thermo image was used to obtain the average surface temperature rise on the photocatalysts by photothermal effect (i.e. analyzing the photothermal effect quantitatively). The promotion effect caused by photothermal effect from NIR light in photocatalytic oxidation of NO was discussed and its promotion mechanism was proposed.

## 2. Experimental

### 2.1. Sample preparation

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_3 \cdot \text{H}_2\text{O}$  solution (25%–28%) and PEG2000 were purchased from Sinopharm Chemical Reagent Co. Ltd., China.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was purchased from Quzhou JuHua reagent Co., Ltd., China. P25 was purchased from Evonik Degussa, AG. TEOS was obtained from Aladdin Industrial Co., Shanghai, China.

#### 2.1.1. $\text{Fe}_3\text{O}_4$ and $\text{Fe}_3\text{O}_4/\text{SiO}_2$

$\text{Fe}_3\text{O}_4$  was prepared using a coprecipitation method under an atmosphere of nitrogen as reported previously [20]. In a typical synthesis,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (9.41 g) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were dissolved in 50 mL DI water by ultrasonic in a three-necked round-bottom flask with nitrogen bubbling. Under vigorous mechanical stirring, 50 mL PEG2000 solution (400 g/L) was added to the solution. When the solution was homogeneous blended, 70 mL  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (8%) was introduced dropwise to the solution. After stirring for 1 h and left for another 1 h at 60 °C, the black precipitate was washed with ethanol and DI water for three times.

The as prepared  $\text{Fe}_3\text{O}_4$  was coated with silica by the Stöber method whereas 0.4 g of  $\text{Fe}_3\text{O}_4$  was thoroughly dispersed in 40 mL ethanol with sonication for 30 min, and then 2 mL of the ammonia solution was added into the solution. With mechanical stirring, 1.6 mL TEOS was added to the solution. After stirring for 3 h, the products were washed with ethanol and DI water for several times and finally dried at 60 °C in vacuum for 6 h.

#### 2.1.2. Composed photocatalyst/ $\text{Fe}_3\text{O}_4/\text{SiO}_2(x:1)$

Composed photocatalyst/ $\text{Fe}_3\text{O}_4/\text{SiO}_2(x:1)$  was prepared by solid-solid mixing method. Base photocatalyst represents sample with photocatalytic capability for NO oxidation, that is P25, anatase  $\text{TiO}_2$  (A- $\text{TiO}_2$ ),  $\text{g-C}_3\text{N}_4$ , ZnO, BiOI, or  $\text{CeO}_2$ . The x:1 stands for the mass ratio of base photocatalyst and  $\text{Fe}_3\text{O}_4/\text{SiO}_2$ . In particular, sample with optimum mass ratio is recorded as Base photocatalyst/ $\text{Fe}_3\text{O}_4/\text{SiO}_2$ .

A- $\text{TiO}_2$  [30],  $\text{g-C}_3\text{N}_4$  [31], ZnO [32], BiOI [33] and  $\text{CeO}_2$  [30] were prepared by the methods reported in References.

### 2.2. Characterization

X-ray diffraction (XRD, model D/max RA, Rigaku Co., Japan with  $\text{Cu K}\alpha$  radiation) was conducted to analyze the crystal phase and composition of the samples. X-ray photoelectron spectroscopy (XPS) measurements for analyzing the surface properties were performed using a Thermo ESCALAB 250 instrument equipped with Al  $\text{K}\alpha$  X-ray irradiation (1486.6 eV) at 150 W. The binding energy scale was corrected referenced to the  $\text{C}1s$  level at 285 eV. The morphology of the samples was obtained from scanning electron microscopy (SEM, FEI-quanta 200F, USA) and transmission electron microscope (TEM, H-600, Hitachi, Ltd., Japan). The specific surface areas were determined with a static adsorption instrument (JW-BK 132F, Beijing JWGB Sci & Tech Co., China) by the Brunauer–Emmett–Teller (BET) method. UV–vis-NIR spectra were obtained from a UV–vis-NIR spectrophotometer (SOLID3700, Shimadzu, Japan). Thermo images were taken with a thermo imager (Testo Co., Ltd., Testo 885) to perform quantitative analyses of photothermal effect of samples. A testo IR soft was used to obtain the average temperature distribution for every thermo image. Thermogravimetry (TG) was measured by a simultaneous thermal analyzer (STA 409 PC NETZSCH, Germany) at a heating rate of 10 °C/min in air flowing of 20 mL/min. Raman spectra were obtained from a SPEX-1403 laser Raman spectroscopy at room temperature. A 514.5 nm Ar-ion laser in a backscattering configuration was used to excite the crystals (Raman: Lab RAM-HR, SPEX-1403, France). In-

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