Non-Stacked γ-Fe2O3/C@TiO2 Double-Layer Hollow Nanoparticles for Enhanced Photocatalytic Applications under Visible Light

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Abstract: Herein, a non-stacked γ-Fe2O3/C@TiO2 double-layer hollow nano photocatalyst has been developed with ultrathin nanosheets-assembled double shells for photodegradation phenol. High catalytic performance was found that the phenol could be completely degraded in 135 min under visible light, due to the moderate band edge position (VB at 0.59 eV and CB at −0.66 eV) of the non-stacked γ-Fe2O3/C@TiO2, which can expand the excitation wavelength range into the visible light region and produce a high concentration of free radicals (such as -OH, O2·−, holes). Furthermore, the interior of the hollow composite γ-Fe2O3 is responsible for charge generation, and the carbon matrix facilitates charge transfer to the external TiO2 shell. This overlap improved the selection/utilization efficiency, while the unique non-stacked double-layered structure inhibited initial charge recombination over the photocatalysts. This work provides new approaches for photocatalytic applications with γ-Fe2O3/C-based materials.

Keywords: double-layer hollow nanoparticles; non-stacked structure; synergistic effect; phenol; photodegradation

1. Introduction

Phenol containing wastewater is produced in many industries, such as pharmaceuticals, polymer, dye, etc. [1]. Once phenol is released into the environment, it cannot be degraded inherently under the natural environment, and it causes harm to human health [2,3]. The phenol degradation is complex due to the high conjugated molecular system [4] and lower phenol concentration is also toxic [2]. Therefore, designing an environmentally friendly, cost-effective and highly efficient approach for phenol treatment is urgent. Photocatalysis is a simple technology among water treatment technologies [5–7], owing to its high mineralization and sturdy treatment efficiency [8,9].

Titanium dioxide (TiO2) is the most-used semiconductor material in the photocatalytic field, due to its chemical/physical excellent profound mineralization capability and stability under ultraviolet light [10]. However, two significant problems need to be solved: The low specific surface area of TiO2 (50 m2/g for P25, TiO2 with a mixed rutile phase, and anatase phase with an average particle size of 25 nm) confines its adsorption capacity for pollutant molecules. Additionally, it has a wide energy gap and is challenging to utilize visible light. Therefore, the preparation of a TiO2 catalyst with an extensive specific surface area and response to visible light is the bottleneck problem in applying TiO2.
To enhance the visible light absorption capacity, the commonly used means [11] are constructing heterojunction, defect engineering, and element doping. The construction of heterojunction catalysts can enhance the absorption of visible light and enhance the separation efficiency of photogenerated carriers because photogenerated electrons and holes can migrate from one phase to another through the two-phase interface, which can effectively inhibit the recombination of the photogenerated carriers [12–14]. More recently, double-layer hollow microsphere semiconductor catalysts have been applied as photocatalysts [15]. By virtue of the advantages of the double-layer structure, the heterogeneous junction catalyst based on the double layer structure is explored.

The construction of a core-shell heterojunction, $\gamma$-Fe$_2$O$_3$, maybe an ideal inner material that can improve solar energy utilization efficiency, which can also simplify the separation process with magnetic properties [16]. Most of the related work has concentrated on the design of functional cores or shells, but the effect of space accumulation between the two layers has been neglected. Based on the photocatalysis mechanism [17–19], the specific energy barrier formed at the interface between the core and the shell can be changed by adjusting the overlap mode between the two layers, promoting the separation of photogenerated carriers. Hence, the structure of the outer TiO$_2$ needs a directional design. It is an urgent problem to build a non-simple stacked TiO$_2$ shell and increase its specific surface area.

Recently, Zhao’s group [20] developed a TiO$_2$ shell material composed of ultrathin nanosheets. This shell material composed of ultrathin TiO$_2$ nanosheets increases the specific surface area of the catalyst. It constructs a non-simple stacked core-shell structure, making the catalyst appear in a porous state, which improves the light utilization rate and the adsorption capacity of pollutant molecules. Because the structure permits light scattering and refraction, the diffusion distance of photogenerated electron-hole pairs is reduced, and the light utilization is maximized [4].

This study demonstrates a facile route to synthesize non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ double-layer hollow nanoparticles. The C moiety constructs a channel for photo-generated electrons between iron oxide and TiO$_2$, facilitating the electron transfer from the $\gamma$-Fe$_2$O$_3$ moiety to TiO$_2$ moiety. The double-layer structure formed by stacking nanosheets has large pores, which alleviates the transmission of reactants in the catalyst. These constructs also inhibit the separation of electron-hole pairs and achieve a high treatment effect. In this study, phenol was selected as an indicator to study the catalyst’s efficiency for photocatalytic oxidation. We found that two-step charge generation and charge transfer were matched and synergistically enhanced in the non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ double-layer hollow nanoparticles, which significantly improved the photodegradation of phenol.

2. Materials and Methods

2.1. Catalyst Preparation

2.1.1. Materials

Ferrocene, hydrogen peroxide (H$_2$O$_2$), acetone, phenol, BaSO$_4$ and ethanol anhydrous were guarantee-grade reagents from Beijing Chemicals Co. Ltd. (Beijing, China). Concentrated ammonia solution (28 wt%), ethylene glycol, sodium acetate, tetra-butyl titanate (TBOT), tetraethyl orthosilicate (TEOS), HCl, NaOH and trisodium citrate were purchased from Tianjin Chemical Corp (Tianjin, China) and were analytical grade. All the water used for all experiments was deionized.

2.1.2. Synthesis of Non-Stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ Double-Layer Hollow Nanoparticles

Figure 1 shows the synthesis approaches for the non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ double-layer hollow nanoparticles. In this fraction, the nanoparticles were prepared by the following steps.

1. Synthesis of SiO$_2$@$\gamma$-Fe$_2$O$_3$/C nanoparticles
Monodispersed SiO$_2$ nanoparticles were first synthesized through the Stöber method. A modified hydrothermal approach prepared the core-shell SiO$_2$/$\gamma$-Fe$_2$O$_3$/$\gamma$-Fe$_2$O$_3$/C nanoparticles. Silica nanoparticles (100 mg) and ferrocene (200 mg) were suspended in ethanol (65 mL) using ultrasonic for 30 min. Then, 2 mL H$_2$O$_2$ was dropwise counted into the mixture and stirred for 10 h at room temperature before the products separated. Then the final product was washed 3 times, using ethanol and deionized water, and dried under vacuum.

2.2. Catalyst Characterization

X-ray powder diffraction (XRD) patterns with 2$^\theta$ ranging from 10 to 80$^\circ$ (40 kV and 30 mA, D/MAX-2500, Rigaku, Japan), as well as transmission electron microscopy (TEM, JEM-2100 FElectron microscope operating at 200 kV, Tokyo, Japan) were used to obtain the crystal and morphological structure. The samples’ specific surface areas were characterized.
by the Brunauer–Emmett–Teller (BET) model. Quadrasorb SI analyzer was used to obtain the N\textsubscript{2} adsorption-desorption isotherms at 77 K. The Barrett–Joyner–Halenda (BJH) model was used to analyze the pore size and volume. X-ray photoelectron spectroscopy (XPS) was performed using a 5300 ESCA equipment (PerkinElmer PHI Co., Hopkinton, Massachusetts, USA) with an Al K\textsubscript{α} X-ray source (250 W) to investigate the chemical compositions of samples. A UV–vis spectrophotometer (UV-2600, Shimadzu, Tokyo, Japan) with BaSO\textsubscript{4} was used to acquire the UV–vis diffuse reflection spectra (UV–vis DRS).

2.3. Catalytic Activity Measurement

The photocatalytic activity was evaluated using a photochemical reactor (TG-10B, Beijing, China) under xenon lamp (300 W). In each experiment, 0.1 g catalyst was weighed in a quartz glass tube, and 30 mL phenol (20 mg L\textsuperscript{-1}) was added into it. Before photocatalytic reaction, a dark reaction was carried out for 30 min to achieve the equilibrium of adsorption and desorption of phenol. The absorbency of phenol was determined by a UV-VIS spectrophotometer.

According to absorbance conversion of phenol, the formula of photocatalytic reaction removal rate was shown in (1).

\[
D\% = \frac{A_0 - A_t}{A_0} \times 100\%
\]

\(A_0\)—the initial absorbance of phenol.
\(A_t\)—Absorption of phenol at t min.

3. Results and Discussion

3.1. Textural Properties of Catalysts

The wide-angle XRD pattern of non-stacked \(γ\text{-Fe}_2\text{O}_3/C@\text{TiO}_2\) is shown in Figure 2a. The characteristic peaks of the catalyst were indexed to anatase TiO\textsubscript{2} (JCPDS-ICDD21-1272) [21–23]. Other phases such as \(γ\text{-Fe}_2\text{O}_3\) were not observed because the thick TiO\textsubscript{2} shell passivated the X-ray diffraction. To better analyse the phase composition of the catalyst inner layer, the precursor (hollow \(γ\text{-Fe}_2\text{O}_3/C\)) of \(γ\text{-Fe}_2\text{O}_3/C@\text{TiO}_2\) was characterized by XRD also. As shown in Figure 2b, the diffraction peaks of \(γ\text{-Fe}_2\text{O}_3\) (JCPDS-ICDD 25-1402) were observed in hollow \(γ\text{-Fe}_2\text{O}_3/C\) [24,25]. Figure 2c shows the Raman spectra of hollow \(γ\text{-Fe}_2\text{O}_3/C\), stacked \(γ\text{-Fe}_2\text{O}_3/C@\text{TiO}_2\), and non-stacked \(γ\text{-Fe}_2\text{O}_3/C@\text{TiO}_2\). The five vibrational modes, located at 640, 545, 395, 193, and 142 cm\textsuperscript{-1}, represent \(E_g\) Raman active, \(A_{1g} + B_{1g}\), \(B_{1g}\), etc., and \(E_g\) modes, indicating that the anatase is the dominant phase of the TiO\textsubscript{2} hollow spheres.

Figure 2. XRD patterns of non-stacked \(γ\text{-Fe}_2\text{O}_3/C@\text{TiO}_2\) (a) and hollow \(γ\text{-Fe}_2\text{O}_3/C\) (b); Raman spectra (c) of non-stacked \(γ\text{-Fe}_2\text{O}_3/C@\text{TiO}_2\), stacked \(γ\text{-Fe}_2\text{O}_3/C@\text{TiO}_2\), and hollow \(γ\text{-Fe}_2\text{O}_3/C\).

The N\textsubscript{2} adsorption-desorption was used to measure the specific surface area of the catalyst. Type IV isothermal curves and N\textsubscript{2} hysteresis loops were observed in Figure 3a, which indicated that the non-stacked \(γ\text{-Fe}_2\text{O}_3/C@\text{TiO}_2\) was a mesoporous material. The pore volume and pore size distributions were also characterized. As shown in Figure 3b, the
pore size was mainly distributed from 5–30 nm, which indicated the catalysts’ mesoporous nature. The hollow structure expected to endow the material with a larger specific surface area (145.328 m²/g), which has a strong ability to absorb pollution molecules so that the active species produced on its surface can directly react with pollutants and enhance the catalytic performance.

![Figure 3. Pore size distribution (a) and N₂ hysteresis curve (b) of non-stacked γ-Fe₂O₃/C@TiO₂.](image)

As shown in Figure 4a’, the γ-Fe₂O₃/C layer was firmly attached to the outer surface of the SiO₂ sphere, and the wrapped SiO₂@γ-Fe₂O₃/C nanoparticles exhibited relatively uniform spherical structures. Then, the thin layers of SiO₂ and TiO₂ were successfully coated on the surface of the SiO₂@γ-Fe₂O₃/C core to form uniform SiO₂@γ-Fe₂O₃/C@SiO₂@TiO₂ nanoparticles (Figure 4b’). After treatment in a hot alkaline solution, the silicon component was removed, and the TiO₂ expanded both inside and outside to form non-stacked γ-Fe₂O₃/C@TiO₂ (Figure 4c’). ICP-AES results showed the nominal ratio of the components (Fe:Ti) was 3.9:1. Furthermore, from Figure 4a,b, almost all catalyst particles can maintain this particular structure. A clear lattice plane was exposed with interplanar spacings of 0.29 nm and 0.35 nm, which revealed the presence of anatase TiO₂ and γ-Fe₂O₃/C, respectively, which mainly expressed the (220) and (101) lattice planes (Figure 4d’).

![Figure 4. (a,b) the images of non-stacked γ-Fe₂O₃/C@TiO₂; (a’–c’) of the process of catalyst preparation, and (a’) the image of SiO₂@γ-Fe₂O₃/C; (b’) the image of SiO₂@γ-Fe₂O₃/C@SiO₂@TiO₂; (c’) the image of image of a single sphere of non-stacked γ-Fe₂O₃/C@TiO₂; (d’) HRTEM images.](image)

To further investigate the composition distribution of the inner shell, the Fe, C, and O species located in hollow γ-Fe₂O₃/C were characterized by XPS. The typical peaks of Fe₂p₃/2 and Fe₂p₁/2 were located at 711.0 and 724.5 eV, respectively (Figure 5a) [26–28]. The presence of the characteristic satellite peak at 719.0 eV confirmed the formation of γ-Fe₂O₃, which is the key characteristic distinguishing Fe₂O₃ from Fe₃O₄. In the O1s spectra (Figure 5b), the presence of Fe-O-C indicated strong interactions between γ-Fe₂O₃ and C, which may serve as an electron pathway to facilitate electron transfer via Fe-O-C.
Two small peaks at 285.9 and 288.7 eV correspond to the residual C = O and C-O species in the nano-shell after calcination (Figure 5c). The distribution of Ti and O species located in the shell of non-stacked γ-Fe₂O₃/C@TiO₂ is shown in Figure 5d,e. The peaks at binding energies of 464.9 and 458.9 eV were assigned to the Ti₂p₁/₂ and Ti₂p₃/₂ core levels of Ti⁴⁺, respectively. The two peaks located at 458.2 and 463.7 eV corresponded to the characteristic peaks of Ti₂p₁/₂ and Ti₂p₃/₂ of Ti³⁺. The O1s spectra displayed two major oxygen peaks at 530.1 and 531.7 eV, which were attributed to lattice oxygen (O_{lat}) and surface-absorbed oxygen (O_{surf}), respectively. The lattice oxygen species are nucleophilic reagents that are usually responsible for oxidation reactions.

**Figure 5.** XPS Fe 2p spectrum (a), O1s inner shell (b), C1s (c), Ti2p (d), and O1s outer shell (e) for non-stacked γ-Fe₂O₃/C@TiO₂.

### 3.2. UV-Vis Absorbance Spectra of Non-Stacked γ-Fe₂O₃/C@TiO₂

The optical absorption of TiO₂ was affected by impurities and changes in the bandgap. The impact of catalysts’ overlap modes on the absorption of visible light was analyzed using UV-vis-DRS. Figure 6a shows that the three catalysts generated the absorption band-edge around 550 nm, corresponding to the transition of electrons from the top of the valence band to the footing of the conduction band. The absorption band edge did not immediately decline to 0 from 550 to 800 nm; however, it entered an extended buffer period, corresponding to the energy of photon needed to transition electrons from the O₂p level to the impurity station. This extensive absorption range reflected the main characteristics of γ-Fe₂O₃/C.

**Figure 6.** UV-Vis diffuse reflectance spectra (a) and calculated band gap patterns based on UV-Vis diffuse reflectance spectra (b) of non-stacked γ-Fe₂O₃/C@TiO₂, stacked γ-Fe₂O₃/C@TiO₂, and hollow γ-Fe₂O₃/C.
From Figure 6b, the first maximum at 2.3 eV (540 nm) is associated with point lattice defects, namely oxygen vacancies, while the subsequent growth at energies above 2.3 eV corresponds to the fundamental bandgap [29,30]. The corresponding bandgap energies of non-stacked γ-Fe₂O₃/C@TiO₂ and stacked γ-Fe₂O₃/C@TiO₂ were 1.25 and 1.32 eV (Figure 6b), which were both higher than hollow γ-Fe₂O₃/C (1.11 eV). The band locations (Figure 7) were calculated using the XPS valence spectra and bandgap energies. The γ-Fe₂O₃/C exhibited a valence band (VB) at 0.08 eV and a conduction band (CB) at −1.03 eV. The CB and VB of stacked γ-Fe₂O₃/C@TiO₂ and non-stacked γ-Fe₂O₃/C@TiO₂ were notably different. According to previous literature, the shell affects the energy band depending on the material [31–34]. The TiO₂ layer had a more positive conduction band voltage than γ-Fe₂O₃. The surface dipole layer formed by the TiO₂ shell caused the conduction band voltage of the γ-Fe₂O₃ inner layer to migrate, and the migration direction and magnitude depended on the dipole parameters due to the usage of the two materials and the different stacking modes. Non-stacked γ-Fe₂O₃/C@TiO₂ had a moderate band edge position (VB at 0.59 eV and CB at −0.66 eV). During the photodegradation of organic pollutants, the suitable band edge position enabled three active substances (·OH, ·O₂⁻, holes) to function simultaneously.

The charge generation and charge transfer behaviors over non-stacked γ-Fe₂O₃/C@TiO₂ are proposed in Scheme 1. Incident light can induce the transition of γ-Fe₂O₃. Excited electrons generated in γ-Fe₂O₃ can be efficiently transmitted to the conduction band of TiO₂ through C species while holes remain in the valence band of γ-Fe₂O₃, resulting in effective electron-hole separation. Therefore, the bandgap will become smaller, and the excitation wavelength range of the TiO₂ composite was expanded into the visible light region. From Scheme 1, the ·OH, ·O₂⁻ and holes will contribute to the degradation of organic matter, and the hydroxyl radicals are not obtained from hole oxidation of water but from the interaction of electrons, hydrogen ions, and superoxide radicals. And the production process of hydroxyl radical is as follows [11]:

\[ e^- + O_2 = \cdot O_2^- \]
\[ O_2^- + \cdot O_2^- + 2H^+ = H_2O_2 \]
\[ H_2O_2 + e^- = \cdot OH + OH^- \]

Figure 7. Valance band XPS spectra of non-stacked γ-Fe₂O₃/C@TiO₂, stacked γ-Fe₂O₃/C@TiO₂, and hollow γ-Fe₂O₃/C.
3.3. Photocatalytic Degradation of Phenol

Hollow $\gamma$-Fe$_2$O$_3$/C, stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$, and non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ photocatalysts were used to degrade phenol under visible light irradiation. As shown in Figure 8a, non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ showed the highest performance and thoroughly degraded phenol after 135 min of irradiation under Xe lamp with 300 W power (Figure 8b). The catalytic performance was as follows: non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ > stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ > hollow $\gamma$-Fe$_2$O$_3$/C. Compared with stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$, the performance of non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ was significantly enhanced due to the unique designed morphology and structure, which can enhance the absorption capacity of visible light and improve the activity of adsorption sites. The hollow inner cavity also permitted the scattering and refraction of light; therefore, the diffusion distance of electron-hole pairs generated by light was reduced, maximizing light utilization. Simultaneously, the unique structure also expanded the specific surface area of the catalytic material. The carbon species can facilitate charge transfer from $\gamma$-Fe$_2$O$_3$ to the outer TiO$_2$, reducing the recombination probability of photogenerated carriers. The reusability of non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ was investigated (Figure S1), and the catalytic activity of the catalyst decreased by only about 5.0% after 5 catalytic cycles.

![Scheme 1. Schematic illustration of the non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$.](image)

![Figure 8. Conversion (a) degradation of phenol and (TOC) (b) total organic carbon over non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$, stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$, and hollow $\gamma$-Fe$_2$O$_3$/C catalysts.](image)

The degradation of phenol using the non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ was analysed by UV-Vis absorbance spectra (Figure 9a) and in situ DRIFTS (Figure 9b). Interestingly, Figure 9a shows that the absorption band (269 nm) of phenol over non-stacked $\gamma$-Fe$_2$O$_3$/C@TiO$_2$ substantially increased upon prolonging the irradiation time beyond 30 min, suggesting the formation of more intermediate products. When the irradiation time was
prolonged, the intermediate products formed during the degradation of phenol decomposed to form small molecules, consistent with the results of in situ DRIFTS (Figure 9b). The absorption bands centered at 1410 cm\(^{-1}\) represented the stretching vibration of -OH functional group of phenol. The characteristic peaks of phenol significantly decreased when exposed to light after 30 min. This shows that the phenolic -OH was first oxidized during phenol degradation.

![Figure 9](image_url)

**Figure 9.** UV-Vis absorbance spectra (a), in situ DRIFTS (b) of phenol degradation over non-stacked \(\gamma\)-Fe\(_2\)O\(_3\)/C@TiO\(_2\).

To further investigate the degradation of phenol over non-stacked \(\gamma\)-Fe\(_2\)O\(_3\)/C@TiO\(_2\), the intermediate products (\(p\)-dihydroxybenzene, \(o\)-dihydroxybenzene, \(p\)-benzoquinone, oxalic acid, acetic acid, and formic acid) were measured by high-performance liquid chromatography (Figure 10a,b). Under light irradiation, the holes formed by \(\gamma\)-Fe\(_2\)O\(_3\)/C@TiO\(_2\) reacted with phenol to generate unstable free radicals containing phenoxy groups. The \(o\) and \(p\)-phenolic hydroxyl groups tend to form stable \(o\)-dihydroxybenzene, \(p\)-dihydroxybenzene, which were further oxidized to \(p\)-benzoquinone. Small molecules, such as oxalic acid, acetic acid, and formic acid, were formed through ring-opening and were eventually mineralized into CO\(_2\) and H\(_2\)O. Non-stacked \(\gamma\)-Fe\(_2\)O\(_3\)/C@TiO\(_2\) had a moderate band edge position, allowing it to excite hydroxyl radicals, superoxide free radicals, and holes to oxidize organic compounds. This was ascribed to an appropriate overlap mode between the two layers. Moreover, Table 1 shows a comparison of the double-layer hollow nanoparticles with the other catalysts; it is found that the catalysts in this paper have better catalytic performance and can use fewer catalysts in a short time to achieve higher catalytic efficiency.

![Figure 10](image_url)

**Figure 10.** Intermediate products (a,b) for phenol degradation over non-stacked \(\gamma\)-Fe\(_2\)O\(_3\)/C@TiO\(_2\).
Table 1. Comparison of catalyst performance.

| Photo Catalyst | Phenol | Characteristics | % Degradation |
|----------------|--------|-----------------|---------------|
| Er\(^{3+}\): YAlO\(_3\)/TiO\(_2\): 0.39 g | 50 mgL\(^{-1}\) | Visible light | 58% (8 h) [35] |
| N-doped TiO\(_2\): 0.3 g | 50 mgL\(^{-1}\) | \(\lambda = 312\) nm UV | 99.6% (540 min) [36] |
| 2P-TiO\(_2\)-500: 50 mg | 10 mgL\(^{-1}\) | Xenon lamp (300 W) | 100% (180 min) [37] |
| TiO\(_2\)-CdS-gCNNSs: 50 mg | 10 mgL\(^{-1}\) | Visible light | 80% (300 min) [38] |
| TiO\(_2\)/MoS\(_2\) heterostructures | - | Visible light | 78% (150 min) [39] |
| This work: 0.1 g | 20 mgL\(^{-1}\) | Visible light | Almost 100% (135 min) |

4. Conclusions

A facile route was used to synthesize non-stacked \(\gamma\)-Fe\(_2\)O\(_3\)/C@TiO\(_2\) double-layer hollow nanoparticles with appropriate overlap mode between the two layers. This unique material structure reduces the catalyst’s energy band, which can broaden the light response range to the visible light absorption range, and reduces the recombination rate of photo-generated carriers owing to the C moiety facilitated electron transfer from the \(\gamma\)-Fe\(_2\)O\(_3\) moiety to TiO\(_2\). The non-stacked \(\gamma\)-Fe\(_2\)O\(_3\)/C@TiO\(_2\) displayed an excellent photocatalytic performance for phenol degradation under visible light irradiation, which is attributed to the cooperativity of the existence of ·OH, ·O\(_2^−\), holes. In situ DRIFTS further explored the degradation pathway of phenol; during phenol degradation, ·OH was first oxidized, and combined with the identification results of intermediate products, then the benzene rings were destroyed to form small molecule organic acid and eventually mineralized into CO\(_2\) and H\(_2\)O. This overlap mode enhanced both charge generation and charge transfer over photocatalysts. The \(\gamma\)-Fe\(_2\)O\(_3\) moiety endows the nano-shell with an ability of charge generation, while the C moiety facilitated electron transfer from the \(\gamma\)-Fe\(_2\)O\(_3\) moiety to TiO\(_2\). The unique non-stacked double-layer structure inhibited the initial charge recombination in TiO\(_2\). The non-stacked \(\gamma\)-Fe\(_2\)O\(_3\)/C@TiO\(_2\) double-layer hollow nanoparticles can make the two steps of charge generation and charge transfer well-matched and synergistically enhanced, which significantly improved the efficiency of the photodegradation of phenol. The preparation of non-stacked \(\gamma\)-Fe\(_2\)O\(_3\)/C@TiO\(_2\) catalysts also provides a novel approach for the future design of a higher-efficiency photocatalytic system.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12020201/s1, Figure S1: The lifetime of Non-stacked \(\gamma\)-Fe\(_2\)O\(_3\)/C@TiO\(_2\).

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