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Yizhou Wu, Jesse Ward-Bond, Donglin Li, Jiafu Shi, Shaohua Zhang, and Zhongyi Jiang ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.8b00070 • Publication Date (Web): 15 May 2018 Downloaded from http://pubs.acs.org on May 15, 2018

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$g-C_3N_4@\alpha-Fe_2O_3/C$ Photocatalysts: Synergistically Intensified Charge Generation and Charge Transfer for NADH Regeneration

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ABSTRACT

Graphitic carbon nitride $(g-C_3N_4)$ is an emergent metal-free photocatalyst due to its band position, nature abundance and facile preparation. Synergetic intensification of charge generation and charge transfer of g-C₃N₄ to increase solar-to-chemical efficiency remains a hot yet challenging issue. Herein, a nano-shell with two moieties of α -Fe₂O₃ and carbon (C) is *in situ* formed on the surface of a g-C₃N₄ core through calcination of Fe³⁺/polyphenol-coated melamine, thus acquiring g-C₃N₄ $(\partial_{\alpha}$ -Fe₂O₃/C core@shell photocatalysts. The α -Fe₂O₃ moiety acts as an additional photosensitizer, offering more photo-generated electrons, whereas the C moiety bridges a "highway" to facilitate the electron transfer either from α-Fe₂O₃ moiety to g-C₃N₄ or from g-C₃N₄ to C moiety. By tuning the proportion of these two moieties in the nano-shell, a photocurrent density of 3.26 times higher than pristine $g-C_3N_4$ is obtained. When utilized for photocatalytic regeneration of reduced nicotinamide adenine dinucleotide (NADH, a dominant cofactor in biohydrogenation reaction), $g-C_3N_4(\partial_{\alpha}\alpha-Fe_2O_3/C)$ exhibits an equilibrium NADH yield of 76.3% with an initial reaction rate (r) of 7.7 mmol h^{-1} g⁻¹, among the highest r for photocatalytic NADH regeneration ever reported. Manipulating the coupling between charge generation and charge transfer may offer a facile, generic strategy to improve the catalytic efficiency of a broad range of photocatalysts other than g-C₃N₄.

KEYWORDS: Charge Generation; Charge Transfer; Graphitic Carbon Nitride; Photocatalysis; NADH Regeneration

1. INTRODUCTION

Photocatalysis, as a green and sustainable process for the conversion of solar energy into chemicals, has gained tremendous interests.^{1,2} Efficient solar-to-chemical conversion requires rapid energy-to-mass transfer in photocatalysis. Two critical steps in photocatalytic process, *i.e.*, charge generation and charge transfer, determine the utilization efficiency of solar energy that is finally stored in the form of chemicals through surface redox reaction.^{3,4} Design and preparation of photocatalysts capable of synergistically intensified charge generation and charge transfer with well-matched behaviors is the prerequisite of a number of photocatalytic processes, including water splitting,⁵⁻⁷ carbon dioxide (CO₂) reduction,⁸⁻¹¹ biohydrogenation,¹²⁻¹⁴ and so on.

Among various photocatalysts, graphitic carbon nitride $(g-C_3N_4)$ is being boomingly explored in recent years due to its unique band position, nature abundant source and facile preparation.^{1,15} Nevertheless, lower charge generation efficiency and slower charge transfer rate remarkably inhibit the practical application of pristine g-C₃N₄. Therefore, tremendous efforts have been devoted to intensify either of the two steps^{16, 17} for elevating the solar-to-chemical efficiency of g-C₃N₄.

Owing to their excellent charge mobility and good compatibility with g-C₃N₄, carbon materials have been incorporated into g-C₃N₄ to accelerate the charge transfer. Photo-generated electrons could be easily extracted from g-C₃N₄ to carbon *via* π - π stacking electric field. Then, the charge transfer could be greatly reinforced and, thereby, the electron-hole recombination could be inhibited.¹⁸⁻²¹ However, the intrinsic light absorption of carbon materials limits the efficient utilization of incident light by

g-C₃N₄. The unmatched charge behaviors, *i.e.*, attenuated charge generation and reinforced charge transfer, often result in a limited increase of available charge carriers or even a negative effect in the presence of excessive amount of carbon.^{1,22,23} Alternatively, several methods have also been developed to intensify the charge generation of g-C₃N₄, *e.g.*, constructing hierarchically structured g-C₃N₄ to achieve superior light-harvesting ability, 16,24,25 doping heteroatoms into g-C₃N₄ to broaden the wavelength for visible-light absorption,²⁶⁻²⁸ attaching secondary photosensitizers onto g-C₃N₄ to offer additional photo-generated electrons,²⁹⁻³¹ etc. The charge generation efficiencies are enhanced by $2.4 \sim 3.7$ times compared to pristine g-C₃N₄, which benefit to improving the overall solar-to-chemical efficiency.^{16,25,27,29} Albeit some significant progress in the intensification of either charge generation step or charge transfer step, the synergistic manipulation of both steps is rarely reported.^{31,32} Particularly, it is still challenging but highly desirable to acquire well-matched charge transfer and charge generation in g-C₃N₄-based photocatalysts.

In this study, for the first time, g-C₃N₄@ α -Fe₂O₃/C core@shell photocatalysts with a g-C₃N₄ core and an α -Fe₂O₃/C nano-shell are prepared to achieve highly efficient regeneration of reduced nicotinamide adenine dinucleotide (NADH). Redox reactions afford the essential driving force for all varieties of life. NADH is utilized as a hydride donor in majority of redox reactions performed by oxidoreductases, and in many energy-relevant catalytic hydrogenation reactions spanning from alcohol deracemization, oxygen reduction to hydrogen production.^{33,34} The expensive but indispensable features of NADH requires facile and effective regeneration methods.

The g-C₃N₄(∂_{α} -Fe₂O₃/C is formed through calcination of Fe³⁺/polyphenol-coated melamine, which exhibits a core@shell structure. The optical and photoelectric properties of g-C₃N₄($\alpha\alpha$ -Fe₂O₃/C confirm the simultaneous intensification of charge generation and charge transfer. Excitation of the α -Fe₂O₃ moiety endows the nano-shell with charge generation ability, minimizing the inefficient light absorption from the C moiety. Meanwhile, the C moiety facilitates the electron transfer either from α -Fe₂O₃ moiety to g-C₃N₄ or from g-C₃N₄ to the surface of C moiety, thus suppressing the initial charge recombination in g-C₃N₄. By altering the ratios of α -Fe₂O₃ moiety to C moiety in the nano-shell, the two steps of charge generation and charge transfer could be well-matched and synergistically intensified, leading to significantly enhanced efficiency for NADH regeneration. Notably, the preparation process integrates the dual functions of polyphenols,³⁵⁻³⁹ *i.e.*, substrate-independent surface adhesion and transition metal coordination, which offers a facile and generic method to form α -Fe₂O₃/C nano-shell onto a broad range of substrates. The strategy of synergistically intensifying charge generation and charge transfer based on α -Fe₂O₃/C nano-shell in this study is applicable to other photocatalysts other than $g-C_3N_4$.

2. MATERIALS AND METHODS

2.1. Materials. Melamine (99%), sodium chloride (NaCl, 99.8% GR), bis-tris hydrochloride (99%), ferric trichloride hexahydrate (99% AR), triethanolamine (TEOA, \geq 99% GC), disodium hydrogen phosphate (99 AR), sodium dihydrogen phosphate (AR), pentamethylcyclopentadienylrhodium (III) chloride dimer (99%), 2,2'-dipyridyl (99% AR) were purchased from Aladdin Industrial Corporation (Shanghai, China). Tannic acid (95%) was obtained from J&K Chemical (Beijing,

China). β -nicotinamide adenine dinucleotide hydrate (\geq 98%), amorphous silicon dioxide (powder, an average size of 0.2-0.3 µm) and methylviologen dichloride (98%) were received from Sigma-Aldrich (St. Louis, USA). Hydrochloric acid (HCl, 36.0-38.0 *wt*%) was obtained from Rionion (Tianjin, China). Oolong tea and red wine were commercial products and purchased from convenience store. All other chemicals or reagents were used without further purification.

2.2. Preparation of g-C₃N₄@ α -Fe₂O₃/C Core@Shell Photocatalysts. 1 g melamine was dispersed in 15 mL 0.133 M bis-tris, 0.8 M NaCl solution. 5 mL tannic acid (10 mg mL⁻¹) was added into the solution. The solution was kept stirring at 25 °C in water bath for 24 hours. The powder was collected by centrifugation and washed with deionized (DI) water. To prepare g-C₃N₄@C, the freeze-dried powder was sealed in a crucible and calcined with the following process: 300 °C for 1 h, 400 °C for 1 h, then 550 °C for 4 h with the heating rate of 5 °C min⁻¹. For g-C₃N₄@ α -Fe₂O₃/C, the powder was re-dispersed in 15 mL DI water. 0.1 mmol FeCl₃·6H₂O (dissolved in 5 mL DI water) was instantly added into the suspension. The solution was kept stirring for 5 minutes and centrifuged to obtain the precipitate. The as-obtained precipitate was washed with DI water, freeze-dried overnight, and then calcined with the same procedure. After calcination, the samples were ground for further experiments.

To prepare C·M, 1.68 mmol melamine and 1.68 mmol cyanuric acid were dissolved in 70 mL DI water at 42 °C in water bath, respectively. The solution of cyanuric acid was slowly added into the solution of melamine. White precipitate was formed immediately and the suspension was kept stirring at 42 °C for 20 minutes. The precipitate was collected by centrifugation and freeze-dried. C·M-g-C₃N₄@ α -Fe₂O₃/C and C·M-g-C₃N₄@C were prepared by replacing melamine with C·M.

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To prepare samples with different ratio of α -Fe₂O₃ moiety and C moiety, FeCl₃·6H₂O were altered from 0.01 mmol to 0.2 mmol before adding into the suspension. The acquired samples were denoted as g-C₃N₄@ α -Fe₂O₃/C-X (X was the millimole of FeCl₃·6H₂O initially added). Samples prepared by tea and red wine followed the same procedure. In detail, 1 g oolong tea was dispersed in 60 mL hot water for 5 minutes to obtain tea water. 5 mL tea or red wine was used as polyphenols to replace tannic acid.

For the samples corroded by hydrochloric acid (HCl), 50 mg samples was dispersed in 10 mL concentrated HCl. The suspension was kept stirring at 80 °C in water bath for 6 hours. After the first 3-hour reaction, another 10 mL concentrated HCl was added in the suspension. The powder was collected by centrifuged and washed by DI water until the pH of supernatant turned into neutral.

2.3. Synthesis of $[Cp*Rh(bpy)H_2O]^{2^+}$. Pentamethylcyclopentadienylrhodium (III) chloride dimer (61.8 mg) was dispersed in 5 mL methanol to form a red suspension. 31.2 mg 2,2'-dipyridyl was added into the suspension. The suspension was kept stirring until it turned into bright orange solution. The solution was evaporated to 1mL at ambient condition. 10 mL diethyl ether was added into the solution to acquire orange precipitate. The precipitate was collected by centrifugation and dry at 50 °C overnight to obtain [Cp*Rh(bpy)Cl]Cl. [Cp*Rh(bpy)H_2O]^{2+} was formed after dissolved in DI water. The stock solution (20 mM) was prepared and kept at 4 °C avoiding direct light irradiation.

2.4. Photocatalytic Regeneration of NADH. Typically, the reaction solution was composed of 1 mM NAD⁺, 0.2 mM Rh complex, 400 mM TEOA, 1 mg photocatalyst and 100 mM phosphate buffer (pH 8). The total volume of the solution was 2 mL. The solution was placed in a quartz cuvette and kept stirring. A blue LED (405 nm, 100W)

was used as the light source and the distance was kept at 5 cm. Before turning on the light, the reaction system was kept stirring in dark for 5 minutes to reach adsorption/desorption equilibrium, the rationality of which was confirmed and shown in **Figure S15** and **S16**. The concentration of NADH was determined by measuring the absorbance of the solution at 340 nm by a UV-vis spectrophotometer (U-3010, Hitachi). The initial reaction rate was calculated based on the first 6-min reaction with [Eq.1]:

$$r = \frac{V}{m_{nc}t}(c_t - c_0) \tag{1}$$

where *r* was the initial reaction rate, *V* was the volume of reaction solution, *c* was the concentration of NADH, m_{pc} was the mass of photocatalyst and *t* was the reaction time.

2.5. Enzymatic Reduction of Formaldehyde with in situ NADH Regeneration. The reaction solution (4 mL) was composed of 1 mM NAD⁺, 0.2 mM Rh complex, 400 mM TEOA, 2 mg photocatalyst, 100 mM phosphate buffer (pH 8), 0.62 mg ADH (200 U) and 40 mM formaldehyde (from 37 % formaldehyde solution with 10~15 % methanol as stabilizer). The produced methanol was detected by gas chromatography (GC-2010 plus, Shimadzu). The total turnover number of NADH during the methanol production was calculated with [Eq.2]:

$$TON_{NADH} = \frac{c_{MeOH} \cdot V}{m_{pc}}$$
(2)

where TON_{NADH} was the turnover number of NADH, c_{MeOH} was the concentration of methanol, V was the volume of reaction solution and m_{pc} was the mass of photocatalyst. According to the enzymatic reaction,

HCHO + NADH $\xrightarrow{\text{YADH}}$ CH₃OH+NAD⁺

NADH was stoichiometric consumed during the reaction of methanol production. The mole of regenerated NADH was equal to the methanol obtained during the reaction.

The times of individual NADH used in methanol production was calculated with [Eq.3]:

$$N_{NADH} = \frac{c_{MeOH}}{c_{NADH}}$$
(3)

where N_{NADH} was the times of individual NADH utilized for methanol production, c_{MeOH} was the concentration of methanol and c_{NADH} was the concentration of NADH. The equilibrium yield of NADH was 76.3% in 16 minutes. The overall reaction rate was 0.0477 mM min⁻¹. For 40-min reaction, the theoretical regeneration of NADH could be obtained was 1.91 mM, which was close to the experimental data, 1.87 mM. Therefore, we chose the equilibrium yield of NADH as c_{NADH} for calculation.

2.6. Photoelectrochemical Evaluation. The sample was fabricated into electrode on a FTO glass. In general, 10 mg of sample was dispersed in 1 mL water solution containing 0.1 mL Nafion and sonicated for 10 minutes. Then, the solution was dropped on the 2×1.5 cm² FTO glass and dried at 50 °C overnight. The film was cut into 1×1.5 cm² for evaluation. All the photoelectrochemical measurements were performed in a three-electrode cell with a saturate-potassium-chloride sliver electrode (Ag/AgCl) as a reference electrode, a platinum foil (0.5×0.5 cm²) as a counter

electrode, and the sample of interest as a working electrode. The electrolyte was 0.1 M Na₂SO₄. A 300 W xenon lamp couple with an AM 1.5G global filter (100mW cm⁻²) were used as radiation source. Linear sweeps, transient photocurrent and electrochemical impedance spectroscope (EIS) Nyquist plot were measured by a CHI 660D electrochemical workstation. The initial voltage of transient photocurrent and EIS was kept at -0.1 V.

2.7. Characterizations. Scanning electron microscope (SEM) was carried out on an FEI Nova XL430 and Hitachi Limited instrument. Transmission electron microscope (TEM) images were taken on FEI Tecnai G2 F20 equipment. Powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/max 2500V/PC X-ray diffractometer with the graphite filtered Cu K α radiation ($\lambda = 1.54056$ Å), and the data was acquired in the range of $10-60^{\circ}$ (20) at a rate of 6° min⁻¹. Fourier transform infrared spectroscope (FT-IR) was measured on a Nicolet-560 spectrometer, where 64 scans were accumulated with a resolution of 4 cm^{-1} for each spectrum. The ⁵⁷Fe Mössbauer spectrum was carried out on a MFD-500AV-02 Mössbauer spectrometer made by Topologic Systems, Inc. with a ⁵⁷Co radioactive source. The X-ray photoelectron spectroscope (XPS) was performed on a Perkin-Elmer PHI 1600 ESCA X-ray photoelectron spectroscope with monochromatic Mg K α radiation (1253.6 eV). The UV-vis absorption spectra were recorded by a UV-vis spectrophotometer (U-3010, Hitachi) equipped with an integrating sphere for the diffuse-reflectance spectroscope (DRS), using BaSO₄ reference. as Photoluminescence spectra were recorded on Horiba Jobin Yvon Fluorolog3

fluorescence spectrometer at room temperature with excitation at 350 nm.

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterizations of $g-C_3N_4@\alpha-Fe_2O_3/C$ Core@Shell Photocatalysts. The preparation of $g-C_3N_4@\alpha-Fe_2O_3/C$ core@shell photocatalysts are presented in **Scheme 1**. Briefly, the solutions of polyphenols (tannic acid, tea or red wine) were mixed with well-dispersed melamine suspension in bis-tris/NaCl buffer. The solution were kept stirring at 25 °C in water bath for 24 hours to form a polyphenol coating on melamine. Then, Fe³⁺ were added to the suspended solution of melamine@polyphenol mixtures, the color of melamine@polyphenol changed instantly due to the rapid coordination of phenolic hydroxyl groups with Fe³⁺,³⁵ which also indicated the formation of Fe³⁺/polyphenol coating on melamine. The as-formed melamine@Fe³⁺/polyphenol was sealed in crucible and then calcined in muffle furnace. Finally, the core@shell photocatalysts with a g-C₃N₄ core and an α -Fe₂O₃/C nano-shell, denoted as g-C₃N₄@ α -Fe₂O₃/C, were acquired. For control, g-C₃N₄@C were also prepared though calcination of melamine@polyphenol.

Scheme 1. Preparation of g-C₃N₄(α -Fe₂O₃/C core@shell photocatalysts.



The X-ray diffraction (XRD) patterns of g-C₃N₄@ α -Fe₂O₃/C and g-C₃N₄@C (**Figure 1a**) demonstrated that both α -Fe₂O₃/C and C nano-shells had negligible influence on the structure of g-C₃N₄. The peaks at around 12.8° (100) corresponded to the in-plane structure of tri-*s*-triazine. The small shift from 13.1° (PDF No. 87-1526, JCPDS) to 12.8° was caused by the partial oxidation of tri-*s*-triazine during the calcination process in air.⁴⁰ The peak at around 27.2° was ascribed to the interlayer periodic stacking.³² Fourier transform infrared (FT-IR) spectra (**Figure S1**) also confirmed the formation of g-C₃N₄. The bands at 810 cm⁻¹, 1200-1600 cm⁻¹ and 3100 cm⁻¹ corresponded to triazine units, aromatic C-N heterocycles and primary/secondary amines, respectively.⁴¹ Interestingly, no signals of α -Fe₂O₃ and C were found in either g-C₃N₄@ α -Fe₂O₃/C or g-C₃N₄@C as shown in both XRD patterns and FT-IR spectra.

Integrating C species with g-C₃N₄ caused little changes in XRD patterns and FT-IR spectra due to the similar structure between carbon ring and $g-C_3N_4$ (Figure 1a and **S2f**).^{19,42} As for g-C₃N₄@ α -Fe₂O₃/C, considering the trace amount of tannic acid and Fe^{3+} used in the experiment and the much thinner coating of Fe^{3+} /polyphenol compared with melamine, the signals emitted from α -Fe₂O₃/C nano-shells may be shielded by the strong signal of g-C₃N₄. To identify the phase of α -Fe₂O₃/C (particularly the phase of α -Fe₂O₃), a supramolecular assembly formed by melamine and cyanuric acid (C·M) was applied as a downsized precursor to prepare $g-C_3N_4(\partial_t\alpha-Fe_2O_3/C)$ (denoted as C·M-g-C₃N₄ $(\partial_t\alpha-Fe_2O_3/C)$, and the details can be seen in 2.2. Preparation of g- $C_3N_4(a)a$ -Fe₂O₃/C Core(a)Shell Photocatalysts and Figure S2). As shown in **Figure 1b**, the XRD pattern of $C \cdot M$ -g-C₃N₄($\partial_{1}\alpha$ -Fe₂O₃/C exhibited both signals of g-C₃N₄ and α -Fe₂O₃. The signals of α -Fe₂O₃ was consistent with cubic $Fe_{21.34}O_{32}$ (PDF No. 83-0112, JCPDS), which could be considered as α -Fe₂O₃. Moreover, Mössbauer spectrum was carried out to probe the chemical environment of Fe in the g-C₃N₄(α - Fe₂O₃/C sample. As shown in **Figure S3**, the main signal with an isomer shift of 0.364 mm s⁻¹ was corresponded to α -Fe₂O₃.⁴³ TEM images (Figure 1c and 1d) revealed the sheet-like structure of $g-C_3N_4(a)\alpha$ -Fe₂O₃/C. In the red area (Figure 1c, inset), the lattices of α -Fe₂O₃ were observed with the (110) plane. XRD, Mössbauer spectrum and HRTEM results confirmed the formation of α -Fe₂O₃ in the nano-shell.

To explore the microstructure of the nano-shell, electron energy loss spectroscope (EELS) was carried out in the edge area to explore the element distribution on the surface of the photocatalyst (**Figure S4**). C and N elements were uniformly distributed in g-C₃N₄@ α -Fe₂O₃/C and g-C₃N₄@/C. As shown in **Figure 1d** (inset) and **S4**, the boundary of C EELS (red color) extended further than the boundary of N EELS (green color) in g-C₃N₄@ α -Fe₂O₃/C, indicating the formation of the nano-shell on g-C₃N₄. The average thickness of the boundary was ~8 nm. The elemental mapping of Fe (**Figure S5e**) confirmed the uniform distribution of Fe on the surface of g-C₃N₄@ α -Fe₂O₃/C. Moreover, the structure of melamine@Fe³⁺/polyphenol was also investigated by TEM. As shown in **Figure S6**, a continuous coating shell was formed on the core of melamine. The EELS, elemental mapping and TEM results verified the formation of α -Fe₂O₃/C nano-shell and core@shell structure of g-C₃N₄@ α -Fe₂O₃/C.



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Figure 1. (a) XRD patterns of g-C₃N₄, g-C₃N₄@C and g-C₃N₄@ α -Fe₂O₃/C. (b) XRD pattern of C·M-g-C₃N₄@ α -Fe₂O₃/C. (c) TEM and (inset) HRTEM images of g-C₃N₄@ α -Fe₂O₃/C. (d) TEM and (inset) overlapped EELS images of g-C₃N₄@ α -Fe₂O₃/C. N EELS in green color was covered by C EELS in red color and the extra boundary of C of ~8 nm was marked.

The chemical environment for C, N and Fe were further probed by X-ray (XPS). photoelectron spectroscope The existence of Fe element in $g-C_3N_4(\partial_a\alpha-Fe_2O_3/C)$ was also verified by full scan XPS spectra with a ratio of 4.5 wt% (Figure 2a), which was consistent with the result of TEM energy dispersive spectrometer (EDS, 4.25 wt%, Figure S5f). Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was also carried out to determine the amount of Fe in bulk g-C₃N₄ $(a)\alpha$ -Fe₂O₃/C. The content of Fe element was 3.5 wt%. By contrast with the XPS/TEM results, the slight lower content of Fe measured by ICP-MS further confirmed the enrichment of α -Fe₂O₃ moiety on the surface of g-C₃N₄. In the high-resolution C1s spectra (Figure 2b), two main peaks at 284.7 eV and 288.1 eV were observed, which were assigned to sp² C-C bonds and sp² N-C=N bonds, respectively. The sp² N-C=N bonds corresponded to the tri-s-triazine unit, whereas the sp² C-C bonds mainly belonged to the C moiety/nano-shell on the surface.²⁵ Two small peaks at 285.9 eV and 288.9 eV corresponded to the residual C=O and C-O species in the nano-shell after calcination.⁴⁴ The N 1s spectra in Figure S7 again evidenced that the nano-shell had negligible influence on the primary structure of

g-C₃N₄. The O 1s spectra (**Figure 2c**) exhibited two peaks at 533.2 eV and 531.8 eV for both g-C₃N₄@C and g-C₃N₄@ α -Fe₂O₃/C, which corresponded to C=O and C-O.⁴⁴ Two extra peaks in O 1s spectrum of g-C₃N₄@ α -Fe₂O₃/C were observed at 529.8 eV and 530.8 eV, which were originated from α -Fe₂O₃ and Fe-O-C, respectively.⁴⁴ The existence of Fe-O-C indicated the strong interaction between α -Fe₂O₃ moiety and C moiety, which may serve as an electron pathway to facilitate the electron transfer *via* Fe-O-C.⁴⁵ In Fe 2p spectrum (**Figure 2d**), the binding energy of 711.3 eV and 724.8 eV belonged to 2p_{3/2} and 2p_{1/2} of α -Fe₂O₃, respectively. The peak at 718.6 eV was the satellite peak of 2p_{3/2} for α -Fe₂O₃.⁴⁶ Both O 1s and Fe 2p spectra confirmed the formation of α -Fe₂O₃ in the g-C₃N₄@ α -Fe₂O₃/C sample.



Figure 2. (a) Full scan XPS spectra and high-resolution (b) C 1s and (c) O 1s spectra of $g-C_3N_4@C$ and $g-C_3N_4@\alpha$ -Fe₂O₃/C. (d) High-resolution Fe 2p spectrum of 16

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3.2. Optical and Photoelectric Properties of $g-C_3N_4(a)\alpha$ -Fe₂O₃/C Core(a)Shell Photocatalysts. The charge generation and charge transfer behaviors were characterized by a series of optical and photoelectric methods. UV-vis diffuse reflectance spectroscope (DRS) results revealed that g-C₃N₄ had an absorption edge at 464.6 nm (Figure 3a). After the introduction of α -Fe₂O₃/C or C nano-shell onto $g-C_3N_4$, the visible light absorption was expanded to 800 nm. It was worth noting that the expanded visible light absorption was primarily attributed to the C moiety or the C nano-shell, which had no function in generating available charge carriers. The C moiety would even weaken the incident light absorbed by $g-C_3N_4$, leading to a decrease of effective light absorption. The corresponding bandgap energies of g-C₃N₄@C and g-C₃N₄@ α -Fe₂O₃/C were 2.48 eV and 2.51 eV (Figure 3b), which was smaller than g-C₃N₄ (2.60 eV). The band position was calculated using XPS valence spectra (Figure 3c) and bandgap energies. $g-C_3N_4$ exhibited a band position of valence band (VB) at 1.78 eV and conduction band (CB) at -0.82 eV. As for $g-C_3N_4$ (a)C, VB stayed in almost the same positon (1.77 eV) while CB became less negative (-0.712 eV). According to previous literature,¹⁵ CB of g-C₃N₄ could be connected to the LUMO levels of tri-s-triazine, which predominantly consisted of carbon p_z orbitals. Accordingly, VB of g-C₃N₄ was a combination of the HOMO levels of tri-s-triazine, which was derived from the nitrogen p_z orbitals. More carbon pz orbitals introduced by C nano-shell in g-C₃N₄@C may stabilize the excited

electrons at lower energy. Another explanation was that the work function of C was less negative than CB of $g-C_3N_4$, leading to a band bending of CB towards less negative after the formation of g-C₃N₄@C.⁷ Considering the preparation process of *in* situ formation of C nano-shell on $g-C_3N_4$, the interaction between $g-C_3N_4$ and C nano-shell would turn into covalent bonds during calcination. The energy level hybridization were likely to happen at molecular level, where the orbitals played a circuital role in the formation of energy band. Notably, the detected VB of $g-C_3N_4(\hat{\alpha}\alpha-Fe_2O_3/C)$ became less positive (1.48 eV) than $g-C_3N_4$ and $g-C_3N_4(\hat{\alpha})C_3$ which may be arisen from the rearrangement of energy levels among CB of α -Fe₂O₃, the work function of C and/or VB of g-C₃N₄. Since the signal of α-Fe₂O₃ moiety in DRS was covered by the strong absorption of C moiety, the calculated CB of g-C₃N₄(α) α -Fe₂O₃/C (-1.032 eV) from XPS valence spectra and DRS results cannot reflect the real position of CB. We deduced that the CB of $g-C_3N_4(a)\alpha$ -Fe₂O₃/C was located at the same position with that of $g-C_3N_4@C$, considering the little impact of relative low CB of α -Fe₂O₃ to that of g-C₃N₄.

The charge recombination was measured through photoluminescence (PL) spectra (**Figure 3d**). Commonly, carbon materials could afford outstanding electron mobility to semiconductors. Electrons and holes were separated at the interface, which then decreased the charge recombination and prolonged the life time of excited charge carriers.¹⁹ As shown in **Figure 3d**, g-C₃N₄@ α -Fe₂O₃/C and g-C₃N₄@C showed much weaker peak intensity compared with g-C₃N₄, indicating the positive role of C moiety/nano-shell in suppressing charge recombination. Moreover,

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mainly a result of the enhanced charge generation from α -Fe₂O₃ moiety. (a) (b) g-C₃N₄ g-C₂N 1.0 g-C₃N₄@C g-C₃N₄@C Absorbance (a.u.) 900 0.4 002 0.5 g-C₃N₄@α–Fe₂O₃/C g-C₃N₄@a-Fe₂O₃/C Intensity (a.u.) 537.8nm 464.6nm 2.600 eV 0.0 ∟ 300 2.482 eV 700 400 500 600 800 2.5 3.0 3.5 2.0 4.0 4.5 Wavelength (nm) Band gap (eV) (d) (C) g-C₃N₄ g-C₃N₄ g-C₃N₄@C g-C₃N₄@C Intensity (a.u.) g-C₃N₄@α-Fe₂O₃/C g-C₃N₄@a-Fe₂O₃/C Intensity (a.u.) .78eV 1.48eV 12 10 8 6 4 2 0 -2 -4 400 450 500 550 600 650 14 **Binding energy (eV)** Wavelength (nm)

g-C₃N₄ $(a)\alpha$ -Fe₂O₃/C showed a little higher luminescence intensity than g-C₃N₄(a)C,

Figure 3. (a) UV-vis diffuse reflectance spectra. (b) Calculated band gap patterns based on UV-vis diffuse reflectance spectra. (c) Valance band XPS spectra and (d) PL spectra of g-C₃N₄, g-C₃N₄(a)C and g-C₃N₄ $(a)\alpha$ -Fe₂O₃/C.

Photoelectronic properties of g-C₃N₄, g-C₃N₄@C and g-C₃N₄@α-Fe₂O₃/C were further investigated to elucidate the charge generation and charge transfer behaviors over g-C₃N₄@ α -Fe₂O₃/C. As shown in Figure 4a, g-C₃N₄@ α -Fe₂O₃/C exhibited the highest photocurrent density of 8.783 μ A/cm², which was 3.26 and 2.10 times that of $g-C_3N_4$ and $g-C_3N_4@C$, respectively. The photocurrent density reflected the available charge carriers migrating in the circuit, which was determined by charge generation

and charge transfer. Therefore, to interpret the prominent photocurrent density of $g-C_3N_4@\alpha-Fe_2O_3/C$, we favored to firstly investigate the charge generation ability. Methylviologen dichloride (MVCl₂) was adopted as a fast electron scavenger in electrolyte to measure the carrier density.⁴⁷ In the presence of MVCl₂, the electron transfer efficiency was considered to be 100%, in which case the charge recombination of photocatalysts would be minimized. The as-observed carrier density could be ascribed to the contribution of charge generation. Meanwhile, the photocurrent onset potential in a voltammogram was equal to the quasi Fermi level of majority carriers (electrons). The carrier density ratio between different samples could be calculated in the quasi Fermi level by Nernst equation [Eq.4]:⁴⁷

$$E_{f1} - E_{f2} = kT \ln(N_{f1} / N_{f2}) / e$$
(4)

where E_f was the quasi Fermi level, k was the Boltzmann's Constant, T was the temperature, N_f was the carrier density and e was the elementary charge.

As shown in **Figure 4b**, g-C₃N₄@C (0.220 V vs. RHE) had a less positive onset potential than g-C₃N₄ (0.239 V vs. RHE), whereas g-C₃N₄@ α -Fe₂O₃/C (0.250V vs. RHE) had a more positive onset potential than g-C₃N₄. The carrier density of g-C₃N₄@C was only a half as that of g-C₃N₄. However, g-C₃N₄@ α -Fe₂O₃/C exhibited higher carrier density than both g-C₃N₄ and g-C₃N₄@C, with the ratio of 1.53 and 3.21, respectively. The decreased carrier density of g-C₃N₄@/C was the result of the undesirable light absorption from C nano-shell that attenuated the charge generation ability. As shown in **Figure S8** and **Table S1**, the charge generation ability decreased sharply with the increased thickness of C nano-shell. As for g-C₃N₄@ α -Fe₂O₃/C,

despite the existence of C moiety, the co-excitation of the α -Fe₂O₃ moiety and g-C₃N₄ exhibited an even higher carrier density than that of g-C₃N₄. Therefore, α -Fe₂O₃ moiety in the nano-shell was not just eliminate the inefficient light absorption of C moiety but endowed g-C₃N₄(a) α -Fe₂O₃/C with extra charge generation ability compared to $g-C_3N_4$. As for the charge transfer behaviors, electrochemical impedance spectroscope (EIS) was carried out to study the resistance during interfacial charge transfer (Figure 4c). The arc radius of $g-C_3N_4(\partial \alpha - Fe_2O_3/C)$ and $g-C_3N_4(\partial C)$ on the EIS Nyquist plot was smaller than that of $g-C_3N_4$, indicating the smaller resistance of charge transfer of $g-C_3N_4(a)\alpha$ -Fe₂O₃/C and $g-C_3N_4(a)C$ than that of $g-C_3N_4$. The smallest resistance observed in g-C₃N₄ $(a)\alpha$ -Fe₂O₃/C indicated the interaction between α -Fe₂O₃ moiety and C moiety could further promote the charge transfer. Combined with the results of PL spectra, it can be derived that C nano-shell in g-C₃N₄@C or C moiety in g-C₃N₄(a) α -Fe₂O₃/C was responsible for the reinforced charge transfer. In consequence, for g-C₃N₄(∂ C, the enhanced charge transfer and partly light shielding by the C nano-shell led to the slightly altered photocurrent density. By contrast, the co-excitation of α -Fe₂O₃ and g-C₃N₄ as well as the C-reinforced electron transfer molety in g-C₃N₄@ α -Fe₂O₃/C eventually led to the significantly improved photocurrent density.



Figure 4. (a) Photocurrent responses under chopped simulated sunlight in 0.1 M Na₂SO₄. (b) Voltammogram under chopped simulated sunlight in 0.1 M Na₂SO₄ with 1 mM MVCl₂. (c) EIS Nyquist plots under dark in 0.1 M Na₂SO₄.

3.3. Photocatalytic Activities of $g-C_3N_4(@\alpha-Fe_2O_3/C$ Core@Shell Photocatalysts. Then, $g-C_3N_4(@\alpha-Fe_2O_3/C)$ photocatalysts were applied for NADH regeneration. As was well known, redox reactions afford the essential driving force for all varieties of life, where NADH was evolved as one essential hydride donor. Even in majority of redox reactions *in vitro* performed by oxidoreductases, NADH was frequently utilized for energy conversion and storage.^{13,48,49} The expensive but indispensable features of NADH required effective regeneration systems. In our regeneration system (**Figure 5a**), a rhodium complex, $[Cp*Rh(bpy)H_2O]^{2+}$, was utilized as a mediator to transfer

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excited electrons and hydrogen to NAD⁺, thereby accomplishing the process of NADH regeneration.⁵⁰ The photocurrent density measured in the rhodium complex solution suggested that the α -Fe₂O₃/C nano-shell may possess better affinity to the rhodium complex (Figure S9). The photocatalytic NADH regeneration was then conducted under the following conditions by using TEOA as a sacrificial agent, a blue LED (100W, 405nm) incident light with single wavelength as the light source, the rhodium complex as the electron mediator. In Figure 5b, $g-C_3N_4(\partial_1\alpha-Fe_2O_3/C)$ showed enhanced photocatalytic NADH regeneration yield compared to $g-C_3N_4$ and g-C₃N₄@C. The reaction enabled by g-C₃N₄@ α -Fe₂O₃/C reached equilibrium in approximately 16 minutes, acquiring a yield of 76.3% and an initial reaction rate (r)of 7.7 mmol h⁻¹ g⁻¹ (based on the first 6-min reaction, calculated with [Eq.1] in 2.5), which was, to the best of our knowledge, among the highest r for photocatalytic NADH regeneration.³³ Notably, the slow reaction rate of the first 2-min was due to the photo-activation of mediator.⁵⁰ The kinetic analysis was also performed in the first 6-min reaction. The $\ln(C/C_0)$ versus time showed linear curve, identifying the first-order kinetics of the reaction (Figure 5c). The reaction kinetics constants of $g-C_3N_4@C$ and $g-C_3N_4@\alpha-Fe_2O_3/C$ were calculated, which exhibited increasing factors of 1.49, 2.92 compared with $g-C_3N_4$, respectively. The recycling ability of g-C₃N₄@ α -Fe₂O₃/C was shown in Figure S10. The relative activity retained 66.8% after 8 cycles. We further incubated the photocatalyst in the reaction medium for 2 hours and explored the photocatalytic activity. As shown in **Figure S11**, the relative activity decreased about 20% after incubation. The activity loss was attributed to the

self-reduction of photocatalyst by accumulated excited electrons. The higher loss of activity during recycling was attributed to the operation, considering the few amount of photocatalyst (1 mg) we used in experiment.

The amount of Fe^{3+} was then altered to prepare g-C₃N₄(∂_{α} -Fe₂O₃/C with different contents of α-Fe₂O₃. All g-C₃N₄@α-Fe₂O₃/C samples exhibited better NADH regeneration yield compared to $g-C_3N_4 @C$ (Figure 5d). The highest yield achieved by $g-C_3N_4(\partial_a\alpha-Fe_2O_3/C-0.1)$ was contributed to the well-matched behaviors of charge generation and charge transfer. To verify the universality of our method, natural polyphenols, such as tea and red wine, were also applied to form α -Fe₂O₃/C nano-shell on g-C₃N₄. The NADH regeneration yields of g-C₃N₄@_α-Fe₂O₃/C derived from tea and wine were also investigated as a function of reaction time (Figure S12). Both g-C₃N₄@ α -Fe₂O₃/C samples showed yield enhancement when compared with g-C₃N₄ and g-C₃N₄@C (Figure 5e). After reaction equilibrium, the NADH regeneration yields of g-C₃N₄(α , G-Fe₂O₃/C prepared by tea and wine were 75.6% and 73.3%, respectively. The corresponding initial reaction rates were calculated as 8.9 mmol h⁻¹ g⁻¹ and 8.6 mmol h⁻¹ g⁻¹. Hydrochloric acid (HCl) was then applied to corrode g-C₃N₄@ α -Fe₂O₃/C and g-C₃N₄@C (as a reference) to study the chemical stability of α -Fe₂O₃ moiety in the nano-shell. In Figure S13, the NADH regeneration yield increased after the corrosion of HCl for both g-C₃N₄@\alpha-Fe₂O₃/C and g-C₃N₄@C. The non-decrease phenomenon indicated that α -Fe₂O₃ moiety was quite stable in the nano-shell, which was ascribed to the strong interaction of Fe-O-C between α-Fe₂O₃ moiety and C moiety. The increased yield was due to the exfoliation

of the samples after the corrosion. As shown in Figure S14, the SEM images of samples before and after corrosion indicated that the bulk $g-C_3N_4(\partial_t\alpha-Fe_2O_3/C)$ and $g-C_3N_4$ (a)C were exfoliated into flakes with increased BET surface area (Table S2), which shortened the distance of electrons transfer from the bulk to the surface and provided more active sites for surface reaction.^{51,52} Finally, the photocatalytic NADH regeneration driven by g-C₃N₄@ α -Fe₂O₃/C was coupled with enzymatic reduction of formaldehyde to examine the reactivity of photo-regenerated NADH towards a commercial enzyme, alcohol dehydrogenase (ADH, from Saccharomyces cerevisiae). In Figure 5f, 1.87 mM methanol was generated in 40 minutes in the presence of 1 mM NAD⁺, confirming the reactivity of photo-regenerated NADH. The total turnover number of NADH during 40 minutes was 3.74 mmol g⁻¹ and each single NADH molecule was utilized 2.45 times for methanol production (for details of calculation, see 2.5). Control experiments were also carried out, which indicated light, photocatalyst and ADH were all indispensable for the production of methanol in our system.

It should be noted that the sustainability of the photocatalytic NADH regeneration utilization noble was restricted by the of а metal-based mediator $([Cp*Rh(bpy)H_2O]^{2+})$. The mediator commonly used in the system not only promoted the electron transfer between photocatalyst and NAD⁺, but more importantly, exhibited 100% selectivity towards enzymatic active 1,4-NADH. Great efforts have been devoted to this field to explore a mediator-free system. Liu et al.¹² reported the possibility of direct electron transfer between $g-C_3N_4$ based photocatalyst and NAD⁺.

Without the assistant of mediator, the yield of NADH could reach 50% in alkaline media (pH = 10). The selectivity of 1,4-NADH was only about 34% according to the subsequent enzymatic reaction, which left us a research space to further improve the selectivity for acquiring a better and more sustainable system. Wang et al.⁵³ reported a heterogeneous catalytic NADH regeneration system using a commercial Pt/Al₂O₃ as catalyst and H₂ as reductant. The yield of NADH reached 50% with a selectivity of 100% towards 1,4-NADH. The mediator-independent system exhibited a superior selectivity and comparable activity by contrast with mediator-dependent system expect that the utilization of noble metal Pt and H₂ may lower the sustainability. If the mechanism of the superior selectivity is revealed and then applied to non-noble metals, such as nickel, iron or copper, in the future, it would be a promising strategy to explore noble metal-free mediator or even highly integrated heterogeneous photocatalysts for NADH regeneration and enzymatic reactions.



Figure 5. (a) Schematic illustration of the coupling system with photocatalytic NADH regeneration and enzymatic reduction of formaldehyde. (b) Time-resolved NADH regeneration yields and (c) kinetic analysis of g-C₃N₄, g-C₃N₄@C and g-C₃N₄@ α -Fe₂O₃/C. (d) Time-resolved NADH regeneration yields of g-C₃N₄@ α -Fe₂O₃/C. (d) Time-resolved NADH regeneration yields of g-C₃N₄@ α -Fe₂O₃/C as a function of Fe³⁺ amounts initially added for the preparation of g-C₃N₄@ α -Fe₂O₃/C. (e) NADH regeneration yields and initial reaction rates of g-C₃N₄, g-C₃N₄@ α -Fe₂O₃/C. (e) NADH regeneration yields and initial reaction rates of g-C₃N₄, g-C₃N₄@ α -Fe₂O₃/C. (f) Methanol production enabled by the coupling system with photocatalytic

NADH regeneration of $g-C_3N_4@\alpha-Fe_2O_3/C$ and enzymatic reduction of formaldehyde under different conditions.

3.4. Mechanism Analysis. The behaviors of charge generation and charge transfer in photocatalytic process are proposed in Scheme 2a. The charge transfer between α -Fe₂O₃ moiety and g-C₃N₄ follows the Z-scheme mechanism. Firstly, α -Fe₂O₃ moiety absorbs light and generates excited electron-hole pairs. The holes are quenched by TEOA whereas the electrons in CB of α -Fe₂O₃ transfer to VB of g-C₃N₄ through C moiety. Meanwhile, electrons in VB of $g-C_3N_4$ are excited by incident light and then transfer to CB of g-C₃N₄. The holes left in VB of g-C₃N₄ are occupied by the electrons from α -Fe₂O₃ moiety. The excited electrons in CB of g-C₃N₄ migrate to C moiety and participate in NADH regeneration. The complicated electron pathways are guaranteed by three factors: (1) outstanding electron mobility of C moiety; (2) strong interactions of Fe-O-C bond between α -Fe₂O₃ moiety and C moiety and (3) excellent interfacial compatibility between C moiety and $g-C_3N_4$. The energy levels of different species in our photocatalytic NADH regeneration system are shown in Scheme 2b. The redox potentials of rhodium complex (-4.01 eV) and NADH (-4.59 eV) are higher than CB of α -Fe₂O₃ (-4.78 eV), in which case only the electrons in CB of g-C₃N₄ have sufficient energy for NADH regeneration. This theoretically supports the existence of Z-scheme mechanism. The co-excitation of two photosensitizers and C-reinforced electron transfer increase the amount of available charge carriers for redox reaction. Briefly, the excitation of α -Fe₂O₃ moiety minimizes the inefficient light absorption by

C moiety and offers more photo-generated electrons, while the electron transfer "highway" constructed through C moiety maximizes the efficient utilization of photo-generated electrons. The synergistic effect of α -Fe₂O₃ moiety and C moiety in the α -Fe₂O₃/C nano-shell leads to a significantly enhanced photocatalytic efficiency.

Scheme 2. (a) Illustration of electron generation and transfer pathway in $g-C_3N_4@\alpha-Fe_2O_3/C$ and photocatalytic NADH regeneration coupled with enzymatic reduction of formaldehyde. (b) Normalized potential energy diagram of photocatalytic pathway. Red arrows represent the electron pathway in NADH regeneration process. The redox potentials are obtained from literature.^{15,19,54-57}



4. CONCLUSIONS

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In summary, g-C₃N₄@ α -Fe₂O₃/C core@shell photocatalysts are prepared through calcination of Fe³⁺/polyphenol-coated melamine for highly efficient photocatalytic NADH regeneration. The unique visible-light responsive feature of α -Fe₂O₃ moiety, superior electron mobility of C moiety, and excellent interfacial compatibility between the α -Fe₂O₃/C nano-shell and the g-C₃N₄ core lead to synergistically intensified charge generation and charge transfer based on Z-scheme mechanism. Accordingly, the available charge carriers for photocatalytic NADH regeneration are significantly increased, rendering an ultrahigh initial reaction rate of 7.7 mmol h⁻¹ g⁻¹. Our study opens a novel avenue to preparing the photocatalysts with rationally matched charge generation and charge transfer. Given the unique features of polyphenols, *e.g.*, substrate-independent surface adhesion, coordination towards virtually any kinds of transition metals, *etc.*, a variety of semiconductor@metal oxides/C photocatalysts could be designed to achieve highly efficient solar energy utilization.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

The additional experimental data including the preparation process of C·M-g-C₃N₄@ α -Fe₂O₃/C, the SEM images of C·M and C·M-g-C₃N₄@ α -Fe₂O₃/C, the EDS analysis of C·M-g-C₃N₄@ α -Fe₂O₃/C, the FT-IR spectra and XRD patterns of C·M-g-C₃N₄, C·M-g-C₃N₄@ α -Fe₂O₃/C, the FT-IR spectra and XRD patterns of g-C₃N₄@ α -Fe₂O₃/C, the EELS of g-C₃N₄@ α -Fe₂O₃/C, the element mapping of g-C₃N₄@ α -Fe₂O₃/C, the TEM images of melamine and melamine@Fe³⁺/polyphenol composite, the high-resolution N 1s XPS spectra of g-C₃N₄@ α -Fe₂O₃/C, the voltammogram of g-C₃N₄@ α with varying C and g-C₃N₄ ratio and corresponding carrier density, the photocurrent responses in solution with rhodium complex, the recycling ability and long term stability of g-C₃N₄@ α -Fe₂O₃/C and the time-resolved photocatalytic NADH regeneration yields.

ACKNOWLEDGMENT

The authors thank the financial support from National Natural Science Foundation of China (91534126, 21776213, 21621004), Tianjin Research Program of Application

Foundation and Advanced Technology (15JCQNJC10000), Open Funding Project of the National Key Laboratory of Biochemical Engineering (2015KF-03), Open funding supported by Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development (Y707s61001), and the Program of Introducing Talents of Discipline to Universities (B06006).

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