A one-step deep eutectic solvents assisted synthesis of carbon nitride/metal oxide composites for photocatalytic nitrogen fixation

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1. Experiment Section

Photocatalytic Activity Test.

All photocatalytic activity experiments were conducted at ambient temperature using a 300 W xenon lamp. For the fixation of molecular nitrogen, 0.1 g of photocatalyst was added into 100 mL of distilled water in a reactor. The reactor was equipped with water circulation in the outer jacket in order to maintain at room temperature of 25 °C. The catalyst mixture is uniformly dispersed by ultrasound. Three milliliters of the solution was taken out each 30 min and after centrifuged to remove the photocatalyst, and the concentration was monitored by colorimetry with the PerkinElmer Lambda750 UV-vis spectrometer. Xenon light (PLS-SXE300D/DUV, PerfectLight Co. Ltd. China) with total light intensity of 200 mW/cm² was utilized as light source. Oxidation of water was carried out in a reaction cell under 300 W xenon lamp. At certain time intervals, liquid (NH₃) was determined by the Nessler’s reagent.

Photoelectrochemical measurements.

All the electrochemical and photoelectrochemical (PEC) measurements were carried out on a Princeton Applied Research Modulelab using a three-electrode system with a Pt sheet as the counter electrode, saturated calomel electrode (Ag/AgCl) as the reference electrode, and the as-prepared photoanodes as the working electrode. The Mott-Schottky (MS) plots were measured in a 0.5 M KPi buffer (pH 7) at a frequency of 800 Hz and amplitude of 10 mV under the dark condition. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 0.5 Hz-10⁵ Hz, with AC voltage amplitude of 10 mV in a 0.5 M Na₂SO₄ aqueous solution. For photocurrent density vs. potential (J-V) and photocurrent density vs. time (J-t) curves, the working electrode with an area of 1×1 cm² was immersed in 0.5 M Na₂SO₄ aqueous solution and illuminated using a 300 W Xe-lamp with a light density of 200 mW cm⁻².
Characterization.

Solution $^1$H NMR experiments were performed on a Bruker DMX 300 NMR spectrometer (300 MHz) with $D_6$-dimethyl sulfoxide as the standard. The chemical shift data were later processed by the MestReNova Program. Differential scanning calorimetry (DSC) was performed using a Q2000 DSC (TA Instruments-Waters LLC, USA) system at a heating rate of 10 °C·min$^{-1}$.

XRD patterns were collected using a Rigaku D/max-2500 diffractometer. Sample morphologies were characterized using a Hitachi SU8010 field emission scanning electron microscope (FESEM) and JEOL-2100F TEM. AFM was taken on a Bruker Multimode 8 instrument under the AC mode (tapping mode). X-ray photoelectron spectroscopic (XPS) analysis was performed by an ESCALAB MK X-ray photoelectron spectrometer. The spectra were calibrated using the C1s (284.8 eV). We fit peaks by means of XPS-peak-differenating analysis software called “XPSPEAK4.0”. FT-IR spectra were recorded on Bruker Tensor 27 IR spectrometer and the sample was prepared by the KBr pellet method. Specific surface areas and pore size distribution were analyzed on Micromeritics ASAP 2020 N$_2$ adsorption analyzer using the BET (Brunauer-Emmet-Teller) and BJH (Barrett-Joyner-Halenda) methods, respectively. UV-vis diffuse reflectance spectra (DRS) were obtained on a Model c spectrophotometer equipped with an integrating sphere using BaSO$_4$ as the reflectance standard. The photoluminescence spectra (PL) were recorded with a Perkin Elme LS-55 spectrophotometer excited with a 325 nm wavelength. Time-resolved diffuse reflectance (TDR) spectroscopy were recorded on an Edinburgh Instruments FLS980 spectrometer.
Density functional theory (DFT) calculation.

In this work, the Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation functional and the mixed basis set of 6-311++G(d,p) and LANL2DZ were used to optimize the geometry of the monomer and complex (Figure S3). The most stable configuration is obtained by comparing the energy of various structures in the calculation process. All calculations were carried out with the Gaussian 09 package.\cite{S1}

By calculation, $\Delta E$ of FeCl$_3$/urea and FeCl$_3$/urea/melamine is worked out as -203.1 kJ/mol and -250.1 kJ/mol, respectively. It is concluded that the interaction energy of the ternary system is stronger than the binary system, indicating that the addition of melamine is favorable for the entire system. Moreover, it further rationalizes that the ternary system is more dispersed, which contributes to the later sintering process. Moreover, as can be observed, the binding of FeCl$_3$/urea/melamine is completed by means of hydrogen bond, suggesting the solution is a mixture of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA). Therefore, we assume that a deep eutectic solvent based on FeCl$_3$/urea/melamine is formed.
2. Supplementary Figures and Discussion

Figure S1. Differential Scanning Calorimeter (DSC) spectra of FeCl$_3$/urea/melamine, VCl$_5$/urea/melamine, ZrCl$_4$/urea/melamine, InCl$_3$/urea/melamine, and CrCl$_3$/urea/melamine.
Figure S2. $^1$H NMR spectra of urea, melamine and urea/melamine/FeCl$_3$. The solvent is D$_6$-DMSO.
Figure S2b. $^1$H NMR spectrum of urea/melamine/FeCl$_3$.

The DES was chosen to carry out nuclear magnetic resonance experiment (Figure S2b).

Since the formed DES is a mixture, we did the following calculations. Combined with the integration of the NMR spectrum, we determined that there is indeed a hydrogen bond in DES.

A urea molecule contains 4 hydrogens, so the $\text{H}_{\text{urea}}$ is $0.12 \times 4 = 0.48$ mol.

A melamine molecule contains 6 hydrogens, so the $\text{H}_{\text{melamine}}$ is $0.1092 \times 6 = 0.6552$ mol.

Therefore, $\text{H}_{\text{urea}}:\text{H}_{\text{melamine}} = 0.48:0.6552 = 4.4:1$.

Peak at 6.44 ppm belongs to melamine, it just shifted. However, the characteristic peak of urea not only shifted but split as well. The broad peak appearing at 7.18 ppm corresponds to the formation of a hydrogen bond. Besides, the integrated area ratio of the peaks is $\text{H}_{\text{urea}}:\text{H}_{\text{melamine}} = 4.38:1$, which coincides with the calculation above.
Figure S3. DFT optimized structures of the (a) FeCl$_3$/urea and (b) FeCl$_3$/urea/melamine.
**Figure S4.** SEM images of a, b) g-C₃N₄/40 wt. % VO₂, c, d) g-C₃N₄/40 wt. % In₂O₃, e, f) g-C₃N₄/40 wt. % ZrO₂, and g, h) g-C₃N₄/40 wt. % Cr₂O₃.
Figure S5. TEM images of a, b) g-C$_3$N$_4$/40 wt. % VO$_2$, d, e) g-C$_3$N$_4$/40 wt. % In$_2$O$_3$, g, h) g-C$_3$N$_4$/40 wt. % ZrO$_2$, and j, k) g-C$_3$N$_4$/40 wt. % Cr$_2$O$_3$; HRTEM images of c) g-C$_3$N$_4$/40 wt. % VO$_2$, f) g-C$_3$N$_4$/40 wt. % In$_2$O$_3$, i) g-C$_3$N$_4$/40 wt. % ZrO$_2$, and l) g-C$_3$N$_4$/40 wt. % Cr$_2$O$_3$. 
Figure S6. AFM image of the g-C₃N₄/40 wt. % Fe₂O₃.

Figure S7. Nitrogen adsorption-desorption isotherm and pore size distribution (inset) of the g-C₃N₄/40 wt. % Fe₂O₃.
Figure S8. FT-IR spectra of g-C$_3$N$_4$ and g-C$_3$N$_4$/40 wt. % Fe$_2$O$_3$.

Figure S9. FT-IR spectra of g-C$_3$N$_4$/40 wt. % VO$_2$, g-C$_3$N$_4$/40 wt. % ZrO$_2$, g-C$_3$N$_4$/40 wt. % In$_2$O$_3$, and g-C$_3$N$_4$/40 wt. % Cr$_2$O$_3$. 
Figure S10. XPS survey spectra of a) g-C₃N₄/40 wt. % VO₂, b) g-C₃N₄/40 wt. % ZrO₂, c) g-C₃N₄/40 wt. % In₂O₃, and d) g-C₃N₄/40 wt. % Cr₂O₃.
Figure S11. XRD patterns of a) g-C$_3$N$_4$/40 wt. % VO$_2$, b) g-C$_3$N$_4$/40 wt. % ZrO$_2$, c) g-C$_3$N$_4$/40 wt. % In$_2$O$_3$, and d) g-C$_3$N$_4$/40 wt. % Cr$_2$O$_3$. 
To demonstrate the electron transfer of Fe$_2$O$_3$ in the g-$C_3N_4$/Fe$_2$O$_3$ materials, photoelectrochemical measurements with photocurrent responses, current density-potential (J-V), and electrochemical impedance spectroscopy (EIS) of different Fe$_2$O$_3$ loading amount were investigated under visible light irradiation and shown in Figure S12. When the g-$C_3N_4$/Fe$_2$O$_3$ modified electrodes (Figure S12a) were illuminated, response photocurrents with repeatable on/off cycles were observed. The responsive photocurrents for g-$C_3N_4$/Fe$_2$O$_3$ (mass ratio varies from 30, 35, 40 to 50 wt. %) are ca. 11.3, 12.6, 44.0, 45.8, and 52.5 μA·cm$^{-2}$, respectively. And g-$C_3N_4$/40 wt. % Fe$_2$O$_3$ showed the highest current density (52.5 μA·cm$^{-2}$). The J-V curves in Figure S12b shows that the current density followed the same trend. It was attributed to the highest efficiency of interfacial charge transfers in moderate load g-$C_3N_4$/Fe$_2$O$_3$ heterostructures. Importantly, when the electrodes were upon light irradiation, the current densities improved greatly compared to current densities under dark condition, in which g-$C_3N_4$/40 wt. % Fe$_2$O$_3$ showed the highest current density and reached to 5.2 mA·cm$^{-2}$. This result suggests g-$C_3N_4$/Fe$_2$O$_3$ absorbed photons and generated electrons under light irradiation. As higher charger separation efficiency resulted in higher photocurrent densities, g-$C_3N_4$ with 40 wt. % Fe$_2$O$_3$ loading gives the highest charger separation efficiency.

In addition, EIS of above electrodes were measured to verify the internal resistances and interfacial electron transfers of the samples. Usually, the semicircle arc in the EIS spectra is used to evaluate the interfacial electron transfer, and smaller semicircle arc means faster interfacial electron transfer.$^{[52]}$ Under light irradiation, the smaller diameter of the semicircle arc for the g-$C_3N_4$/40 wt. % Fe$_2$O$_3$ heterostructure compared to the diameter of other samples indicated efficient interfacial charge mobility for g-$C_3N_4$/40 wt. % Fe$_2$O$_3$. These results suggest an effective interfacial charge transport upon light irradiation, and the heterostructure of g-$C_3N_4$/40 wt. % Fe$_2$O$_3$ gives the highest efficiency of interfacial charge transport (Figure S12c).
Figure S12. Photocurrent responses of g-C$_3$N$_4$/30 wt. % Fe$_2$O$_3$, g-C$_3$N$_4$/35 wt. % Fe$_2$O$_3$, g-C$_3$N$_4$/40 wt. % Fe$_2$O$_3$, and g-C$_3$N$_4$/50 wt. % Fe$_2$O$_3$ under light irradiation (a). J-V curves (b) and EIS spectra (c) of different samples in 0.5 M Na$_2$SO$_4$ solution under dark and visible light irradiation.

Figure S13. UV-vis DRS of a) g-C$_3$N$_4$ and b) α-Fe$_2$O$_3$ (insert image: the plot of (αhv)$^2$ versus hv).

The optical properties of g-C$_3$N$_4$ and α-Fe$_2$O$_3$ were analyzed by UV/Vis diffuse reflectance spectroscopy. As shown in Fig. S13, g-C$_3$N$_4$ nanosheets and α-Fe$_2$O$_3$ nanoparticles have major absorption at wavelengths smaller than 500 nm and 556 nm, respectively. According to the change of (αhv)$^2$ and hv, the energy band gap of g-C$_3$N$_4$ and α-Fe$_2$O$_3$ samples was 2.48 eV and 2.23 eV, respectively.
Figure S14. Mott-Schottky plots of a) g-C$_3$N$_4$ and b) α-Fe$_2$O$_3$.

Figure S15. The g-C$_3$N$_4$/40 wt. % Fe$_2$O$_3$ of PL intensity@425 nm in 2 mM NaOH solution with presence of 0.5 mM terephthalic acid.
Figure S16. The photocatalytic mechanism diagram of (a) traditional heterojunction and (b) Z-scheme construction in the sample of the g-C₃N₄/Fe₂O₃ composites.
### 3. Supplementary Tables

**Table S1.** Elemental analysis results of the g-C$_3$N$_4$/Fe$_2$O$_3$.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>C wt %</th>
<th>N wt %</th>
<th>H wt %</th>
<th>C/N atom ratio</th>
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<tr>
<td>g-C$_3$N$_4$/30 wt. % Fe$_2$O$_3$</td>
<td>26.85</td>
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<td>g-C$_3$N$_4$/35 wt. % Fe$_2$O$_3$</td>
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<td>g-C$_3$N$_4$/40 wt. % Fe$_2$O$_3$</td>
<td>22.83</td>
<td>37.6</td>
<td>1.18</td>
<td>0.708</td>
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<td>g-C$_3$N$_4$/50 wt. % Fe$_2$O$_3$</td>
<td>19.68</td>
<td>33.12</td>
<td>1.15</td>
<td>0.693</td>
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</tbody>
</table>

**Table S2.** Kinetic parameters of transient absorption decays of g-C$_3$N$_4$/Fe$_2$O$_3$, under 360 nm excitation with time profiles of absorption probed at 505 nm.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>Average lifetime (ps)</th>
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</thead>
<tbody>
<tr>
<td>g-C$_3$N$_4$/30 wt. % Fe$_2$O$_3$</td>
<td>40(79.13 %)</td>
<td>1040(20.87 %)</td>
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<td>g-C$_3$N$_4$/35 wt. % Fe$_2$O$_3$</td>
<td>50(77.68 %)</td>
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<td>g-C$_3$N$_4$/40 wt. % Fe$_2$O$_3$</td>
<td>100(78.60 %)</td>
<td>1100(21.40 %)</td>
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<td>g-C$_3$N$_4$/50 wt. % Fe$_2$O$_3$</td>
<td>70(78.23 %)</td>
<td>1060(21.77 %)</td>
<td>285.5</td>
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</table>
4. References
