Dissolution and Performing Homogeneous Photocatalysis of Polymeric Carbon Nitride

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As a metal-free conjugated polymer, carbon nitride (CN) has attracted tremendous attention as heterogeneous (photo)catalysts. By following prototype of enzymes, making all catalytic sites of accessible via homogeneous reactions is a promising approach toward maximizing CN activity, but hindered due to the poor insolubility of CN. Herein, we report the dissolution of CN in environment-friendly methane sulfonic acid and the homogeneous photocatalysis driven by CN for the first time with the activity boosted up to 10-times, comparing to the heterogeneous counterparts. Moreover, facile recycling and reusability, the hallmark of heterogeneous catalysts, were kept for the homogeneous CN photocatalyst via reversible precipitation using poor solvents. It opens new vista of CN in homogeneous catalysis and offers a successful example of polymeric catalysts in bridging gaps of homo/heterogeneous catalysis.

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Dissolution and Performing Homogeneous Photocatalysis of Polymeric Carbon Nitride

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ABSTRACT: As a metal-free conjugated polymer, carbon nitride (CN) has attracted tremendous attention as heterogeneous (photo)catalysts. By following prototype of enzymes, making all catalytic sites of accessible via homogeneous reactions is a promising approach toward maximizing CN activity, but hindered due to the poor insolubility of CN. Herein, we report the dissolution of CN in environment-friendly methane sulfonic acid and the homogeneous photocatalysis driven by CN for the first time with the activity boosted up to 10-times, comparing to the heterogeneous counterparts. Moreover, facile recycling and reusability, the hallmark of heterogeneous catalysts, were kept for the homogeneous CN photocatalyst via reversible precipitation using poor solvents. It opens new vista of CN in homogeneous catalysis and offers a successful example of polymeric catalysts in bridging gaps of homo/heterogeneous catalysis.
Awareness of a sustainable society calls for the development of highly efficient catalysts: heterogeneous and homogeneous. Each of them demonstrate characteristic sets of advantages and limitations with regards to accessible catalytic sites, separation, and recycling, thus it is highly anticipated to combine all merits in a single catalyst.¹ As a promising metal-free heterogeneous catalyst, polymeric carbon nitride (CN) has stimulated substantial interest in conversion of organic molecules and solar-to-chemical energy conversion and beyond, e.g. optoelectronic biosensing, due to its unique electronic structure and surface properties.² By following prototype of enzymes, making all the catalytic sites accessible via homogeneous reactions is a promising approach toward maximizing CN activity. However, the poor solubility of CN, ascribing to the interlayer van der Waals forces,³ makes CN for homogeneous catalysis difficult. Concentrated H₂SO₄ was reported as the first solvent for CN, but the harsh condition hinders further applications. Polar aprotic solvents, such as dimethyl sulfoxide (DMSO), were disclosed to dissolve bulk poly(triazine imide) (PTI-LiBr)-based CN with controllable luminescent properties.⁴ As an innovative alternative, exfoliating bulk CN into nanosheets, greatly boosted photocatalytic activates.⁵ Similarly, in the early days of graphene and carbon nanotubes research, the insolubility in any solvents also remained as one of the biggest impediments to the realization of their potential applications.⁶ Therefore, seeking more general solvents to solubilize CN and perform homogeneous catalysis would be fascinating to pave the subsequent research of CN.
Herein, we report the dissolution of CN in CH₃SO₂OH (MSA), an environment-friendly solvent. As controls, other sulfonic acid group-containing solvents, including ClSO₂OH (ClSA), HOSO₂OH (H₂SO₄), and C₂H₅OSO₂CH₃ (EMS) were also investigated. Taking two photocatalytic oxidations as examples, up to 10-fold faster catalytic kinetics of homogenous CN were achieved relative to those of the heterogeneous one. Moreover, due to the capability for reversible dissolution and
recovery using good and poor solvents, CN could be facilely separated from the homogeneous system and reused, thus combining the advantages of both homogeneous and heterogeneous catalysts.

The starting CN with interlinked heptazine-based units (Fig. S1-S3) and stacked lamellar texture (Fig. S4) was prepared by a conventional thermal polymerization of dicyandiamide at 550 °C in air. The dissolution ability of CN in MSA and control solvents at room temperature is demonstrated in Fig. 1a. CN was completely dissolved in MSA, exhibiting a clear and yellow solution, and the stirring would accelerate the dissolution speed (Fig. S5). Different to CN nanosheets by liquid-exfoliation,5c no evident Tyndall effect was observed for CN in MSA (Fig. S6a), indicating CN macromolecules of minimal lateral dimensions rather than nanosheets in MSA. As controls, CN only partially dissolved in concentrated H_{2}SO_{4}, ClSA, and EMS at the same condition. Therefore, the dissolution ability of CN in the solvents followed the order MSA, H_{2}SO_{4}, ClSA and EMS.

To evaluate the possible changes of electronic structures of CN after dissolution, CN was recovered from the MSA solution by using poor solvents (e.g. acetonitrile). As shown in Fig. 1b inset, the recovered CN (r-CN) was still yellow, suggesting CN did not disintegrate after dissolution. The UV-Vis spectrum of r-CN (Fig. S7) showed a minor blue-shift relative to that of CN. Such blue-shift was also observed in the photoluminescence spectrum of r-CN (Fig. S8), presumably due to the protonation of CN by MSA.3a,7

The molecular structure of r-CN was further studied by Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). As
shown in Fig. 1b, for both CN and r-CN, the typical stretching mode of CN heterocycles (1200-1600 cm⁻¹) and the breathing mode (810 cm⁻¹) were mostly retained. The broad and intense bands at 2800-3500 cm⁻¹ and some peak-shifts were also observed, which might result from protonation by MSA.³⁻⁷ The C₁s XPS spectra of r-CN and CN showed two main peaks at 288.3 eV and 284.6 eV (Fig. 1c), which are attributed to N-C=N and random adventitious carbon contamination, respectively.⁵⁻³,⁸ Meanwhile, four N₁s XPS peaks ascribed to C=N-C (398.2 eV, tri-s-triazine rings), N-(C)₃ (399.4 eV, bridging N atoms), C-N-H (400.9 eV, bonded with H atoms) and the charge effect were observed for both CN and r-CN (Fig. 1d), further verifying that these two compounds had a similar C-N bonding characteristics.³⁴ Elemental analysis (Table S1) quantified the very similar molar C/N ratios of CN (0.68) and r-CN (0.67). The BET surface areas and pore volume of CN and r-CN (Fig. S9) were also not evidently changed. In addition, despite that the precipitation recovery led to a lowered crystalline, the X-ray diffraction (XRD) pattern of r-CN still demonstrated an exclusively similar predominant (002) diffraction peak as CN rather than its intermediate precursors (Fig. S2). All these facts jointly demonstrated the typical structure of CN was maintained after dissolution, rather than decomposed into smaller fragments.

To gain insight of MSA in dissolving CN, we carried out first-principles density functional theory (DFT) calculations to analyze the adsorption sites, and adsorption abilities using a polarizable continuum model. The hollow (H) position was found to be the most stable adsorption site relative to the top (T) and bridge (B) positions (Fig. 2a). Generally, a solvent molecule with the stronger absorption
ability could more competitively interact with CN and dissolve it. The calculated \( E_{\text{ads}} \) for MSA (-0.84 eV), \( \text{H}_2\text{SO}_4 \) (-0.73 eV), ClSA (-0.67 eV), and EMS (-0.14 eV) were all evidently higher than that for \( \text{H}_2\text{O} \) (-0.27 eV), supporting the facts that the sulfonic acid group-containing solvents were more effective than \( \text{H}_2\text{O} \) in dissolving CN, and MSA was the best one in this study (Fig. 2b-d). Besides, because of lack of protonation, the adsorption distance between the nearest H atom of EMS and CN plane was apparently larger than that of other three solvents, making EMS the poorest among them. Considering the contribution of entropy for the dissolution, the Gibbs energy was also calculated (see computational methods in SI), in agreement with the above results. It was also consistent with the recent computations for sulfonic acid group-containing surfactants in liquid-exfoliation of other layered materials.

**Fig. 2** (a) Structural model of single CN layer for calculating the adsorption energies in different solvents. The insets show the typical adsorption sites: top (T), hollow (H), and bridge (B). The most stable adsorption structures of MSA (b), \( \text{H}_2\text{SO}_4 \) (c), ClSA (d) and EMS (e) molecules on CN. \( E_{\text{ads}} \) and \( d_{\text{H-CN}} \) represent the adsorption energy and the distance between the nearest H atom and CN plane, respectively.
**Fig. 3** (a) Absorbance of TMB$_{\text{ox}}$ at 456 nm as a function of time during photocatalytic dehydrogenation using homogeneous CN catalyst (CN-homo, CN dissolved in MSA) and heterogeneous CN catalyst (CN-hetero, CN dispersed in H$_2$O). Catalyst loading: 0.5 mg/mL (see optimization in Fig. S12). (b) Ratio of the TOFs by different concentrations of CN-homo and CN-hetero catalysts. (c) C/C$_0$ of AB concentration as a function of time during photocatalytic N-demethylation using CN-homo and CN-hetero. (d) Re-use catalytic efficiency of the CN-homo catalyst in the photocatalytic N-demethylation of AB.

CN catalyst has been widely explored in heterogeneous converting organic molecules and harnessing solar energy to form chemical fuels, however, the activities were limited by low exposure of potential active sites. For this, many attempts
have been made, e.g. to prepare nanostructured CN with as higher density of exposed active sites.\textsuperscript{5,11} Driving homogeneous catalytic reaction by CN at a molecular level would be an ultimate goal. Taking advantage of the excellent dissolution of CN in MSA,\textsuperscript{12} the photocatalytic dehydrogenation of 3, 3', 5, 5'-tetramethylbenzidine (TMB), a typical substrate for studies in enzymatic or biomimetic dehydrogenation oxidation (Fig. S10),\textsuperscript{13} was firstly investigated. TMB was originally colorless in MSA and turned reddish brown after photocatalytic reaction; thus, the reaction rate could be quantitatively determined by UV-Vis spectroscopy and the Beer–Lambert law when the concentration of oxidized TMB (TMB$_{\text{ox}}$) was low.

The UV-Vis absorbance of the TMB$_{\text{ox}}$ in MSA increased dramatically with time when CN was used as a homogeneous catalyst (CN-homo, CN dissolved in MSA) under irradiation (Fig. 3a circle scatters and Fig. S11). In contrast, only negligible color changes were observed without CN or without light irradiation (Fig. 3a triangle scatters). Control experiments also showed MSA itself did not promote the catalytic activity (Fig. S12). These facts jointly indicated that the oxidation of TMB was exclusively driven by CN-homo via a photocatalytic pathway. As a control, the same amount of CN was dispersed in an aqueous solution as a heterogeneous catalyst (CN-hetero) to drive the same reaction, but only very moderate activity was observed (Fig. 3a quadrangle scatters). Although the blue-shift of CN-homo was not favor of improving the photocatalytic activity due to the eliminated absorbance of light, Fig. 3b and Fig. S13 still show that the turnover of frequency (TOF)\textsuperscript{14} ratio of the CN-homo system to the CN-hetero system increased up to 10-fold when the concentration of CN increased up to 0.5 mg/mL, demonstrating
the inherent advantage of the CN-homo in exposing active sites, especially at a high concentration in driving a practical catalytic reaction. Notably, no activity in the first several minutes for CN-homo system, which may be attributed as an induction stage.\textsuperscript{15}

Recycling and reusability are challenging for homogeneous catalysts.\textsuperscript{16} Interestingly, this limitation did not happen for CN-homo, because of the unique dissolution/recovery ability of CN in MSA. The collection yield of CN in MSA using diethyl ether as poor solvent was up to ca. 95\%. To verify this assumption, in the second set of experiments, the CN-homo photocatalyst was exampled in the N-demethylation of Azure B (AB), which is an important chemical transformation in the pharmaceutical industry (Fig. S14).\textsuperscript{17} In contrast to the darken of TMB, the color of AB lightened after oxidation; thus, the Beer–Lambert law was valid for kinetic studies, especially when a high concentration of CN photocatalyst was used to eliminate the systematic loss of the catalyst during recycling.

Fig. 3c and Fig. S15 show the variation in the AB concentration with reaction time. When CN-homo was used, AB was almost completely oxidized (remnant \(<5\%\), see Fig. S16 and more discussion in SI) upon irradiation for 90 min, while for CN-hetero, more than 48\% of unreacted AB remained, suggesting that the CN-homo photocatalyst had a much faster oxidation rate. Control experiments without CN and without light irradiation (Fig. 3c, triangle scatters) resulted in negligible activity within the prescribed time, confirming the oxidation of AB was exclusively driven by CN via a photocatalytic pathway. The first-order rate constant (Fig. S17) of the reaction by CN-homo (0.041/min) was nearly six times that of the
reaction driven by CN-hetero (0.007/min). CN-homo was further explored in recycling experiments, in which the catalyst was separated by using diethyl ether as poor solvent after the reaction and recycled in the next experiment. As shown in Fig. 3d, CN-homo maintained most of the original high photocatalytic activity for at least three recycles. The stability of catalysts was also reflected by the similar XRD patterns of the CN after the photocatalytic reaction (Fig. S18). A minor deterioration in the catalytic activity was observed, presumably due to mechanical loss of the catalyst during the recycling process. Therefore, the recycling experiment demonstrated the unique features of the proposed CN photocatalytic system that combined the advantages of both homogeneous catalyst that often exhibited superior activity, and heterogeneous catalysts that can be easily recycled and reused without evident activity loss. The catalytic activities of dehydrogenation of TMB and the N-demethylation of AB were also compared using other (photo)catalysts (Table S2 and Table S3), and showed very competitive activities.

In summary, CN was dissolved in environment-friendly MSA at room temperature. The DFT results verified the sulfonic acid group significantly reducing their absorption energies. Taking the dehydrogenation of TMB and the N-demethylation of AB as examples, homogeneous CN photocatalyst exhibited a dramatic enhancement in activity by a factor of up to 10 relative to the heterogeneous one due to the increase of potential accessible catalytic sites. Moreover, the reversible dissolution of CN using good/poor solvents allowed the homogeneous CN to be effectively recycled and reused, which united the advantages of both homo/hetero-
ogeneous catalysts. This work may extend the application of CN as a homogeneous (photo)catalyst and highlights the utility of polymeric catalysts with intrinsic catalytic properties in bridging the gap between homo/heterogeneous catalysis.

ACKNOWLEDGMENT

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Supporting Information

Dissolution and Performing Homogeneous Photocatalysis of Polymeric Carbon Nitride

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**Table S2** Comparison of the catalytic dehydrogenation activity of TMB using different catalysts

**Table S3** Comparison of the catalytic N-demethylation of AB using different catalysts

**Supporting references**
Experimental Procedures

Reagent
Dicyandiamide (DCDA, 99%, Sigma-Aldrich), concentrated sulfuric acid (H_2SO_4, 95-98%, Sinopharm chemical Reagent), methanesulfonic acid (MSA, 99.5%, Aladdin), Chlorosulfonic acid (ClSA, 99%, Energy Chemical), Ethyl methyl sulfonate (EMS, 99%, Aladdin), Azure B (AB, 90%, J&K), 3,3',5,5'-tetramethylbenzidine (TMB, Aladdin) were used without further purification. All other reagents were of analytical grade and used as received unless otherwise specified. Ultrapure water (18.2 MΩ·cm) was obtained from a Smart2 water purification system (Thermo Scientific, USA).

Preparation of CN
CN was prepared by heating dicyandiamide for 4 hours to 550 °C and kept at this temperature for 4 hours in air. The final product was ground into fine powder with sizes of several micrometers before use.

Preparation of different CN solution
The CN solution (50 mg/mL) was obtained by stirring the mixture of CN (500 mg) and 10 mL MSA, H_2SO_4, ClSA or EMS at room temperature for 10 hours.

Precipitated CN from CN solution
CN powder could be recovered from CN solution by adding some poor solvents (e.g., methanol, acetonitrile, or ether) to initiate the precipitation, washing with the same solvent and lastly H_2O, and freeze drying. The as-obtained CN powder was denoted as r-CN. Unless otherwise specified, all r-CN in this work was recovered using acetonitrile as the poor solvent with a collection yield of ca. 40%.

Photocatalytic dehydrogenation of TMB
TMB (4.5 mg) and CN-homo (CN dissolved in MSA, 0.5 mg/mL, 30 mL MSA) or CN-hetero (CN dispersed in H_2O, 0.5 mg/mL, 29 mL H_2O+1 mL MSA) were added in a quartz tank (5×5×5cm³), respectively. The reaction system was top-irradiated by using a 300 W Xe lamp (CEL-HXUV300E, China).

Photocatalytic N-demethylation of AB
Firstly, CN-homo (CN dissolved in MSA, 10 mg/mL) or CN-hetero (CN dispersed in

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H$_2$O, 10 mg/mL) was added in a quartz tank (5×5×5cm$^3$). Then, AB solution in MSA or water (0.1 mg/mL) was added, respectively. Afterwards, the quartz tank was filled with oxygen by balloon and sealed. Finally, the reaction system was top-irradiated by using a 300 W Xe lamp (CEL-HXUV300E, China).

**The recyclability of CN in homogeneous catalysis**

Firstly, the CN was separated from the reaction mixture by precipitation and washing with ether for several times. Then, the separated CN solids (10 mg/mL) were dissolved in MSA again and later mixed with a fresh AB solution (0.1 mg/mL) in 20 mL MSA. After that, the absorbance spectra of the reaction mixture were measured after 3 h. Such procedures were repeated for 3 times.
Characterization

X-ray diffraction (XRD) measurements were undertaken by using SmartLab diffractometer (Rigaku, Japan). The Fourier transform infrared (FT-IR) spectra were carried out on a Nicolet iS10 FT-IR spectrometer (Thermo, USA), equipped with an attenuated total reflection (ATR) setup. The photoluminescence (PL) spectra were performed by fluorescence spectrometer (Fluoromax-4, Horiba Jobin Yvon, Japan). UV-vis absorption spectra were obtained from Cary 100 (Agilent, Singapore) with a diffuse reflectance accessory. Elemental analysis was performed on a Vario EL elemental analyzer (Germany). The size distribution was obtained at a NanoBrook Omni particle size and zeta potential analyzer (Brookhaven Instruments Corporation, USA). Brunauer-Emmett-Teller (BET) surface area and pore volume were calculated from 77 K N\textsubscript{2} adsorption-desorption isotherms by using a NovaWin 1000e instrument (Quantachrome, USA).
Computational methods and results

Adsorption models of single MSA, H₂SO₄, ClSA and EMS solvent molecules on CN were studied by quantum chemical calculations. CN nanosheet was modeled by a 5×5×5 trigonal 2-dimensional cluster to compromise the computational cost and accuracy. Firstly, the 5×5×5 trigonal 2-dimensional CN cluster and solvent molecules were optimized, separately. Then, the four adsorbed systems of solvent molecules on CN cluster were optimized. The adsorption energy ($E_{\text{ads-molecule}}$) is calculated by

$$E_{\text{ads-molecule}} = E_{\text{CN+molecule}} - E_{\text{CN}} - E_{\text{molecule}}$$

where $E_{\text{CN+molecule}}$ and $E_{\text{CN}}$ are the total energies of the CN cluster with and without adsorbed molecule, respectively. $E_{\text{molecule}}$ is the energy of the adsorbed molecule. All equilibrium geometries were optimized by the density functional theory (DFT) with double hybrid M06-2X exchange-correlation functional and 6-31G(d) basis set; meanwhile, the calculations were implemented with polarizable continuum model (PCM) for all systems. All the calculations were carried out by using the Gaussian 09 program.⁵¹

As a result, the adsorption energies were calculated by as-described methods and illustrated in this work with an ascending order (-0.84 eV (MSA@CN), -0.73 eV (H₂SO₄@CN), -0.67 eV (ClSA@CN), and -0.14 eV (EMS@CN)). Considering the solubility of CN in solvents is determined not only by adsorption energy but also by entropy, the Gibbs free energies have also been obtained by frequency analyses on the four optimized adsorption models, it turned out to be -0.22 eV (MSA@CN), -0.19 eV (H₂SO₄@CN), -0.14 eV (ClSA@CN), and 0.33 eV (EMS@CN), respectively. Therefore, the dissolution ability of the solvent molecules in this paper was in accordance with the relative strength of the interaction between solvent molecules and CN, which is the descending order of MSA, H₂SO₄, ClSA, and EMS.

Mülliken charge population analysis⁵² was further implemented to study the superiority of the sulfonic acid groups over H₂O and HNO₃, two common solvents for liquid-
exfoliation. The H-atom of the hydroxyl in sulfonic acid groups was found to be more extensively protonated (hole density: 0.55 e) than those in H2O and HNO3 (hole density: 0.33 e), which induced stronger Columbic attraction between the sulfonic acid groups and the electron-delocalized CN layer and accordingly led to an improved dissolution. The differences of dissolving in MSA, H2SO4, and ClSA that all had sulfonic acid group were ascribed to the electron pull-push effect of the other substituents in solvent molecules. The electron-donating methyl group in MSA and the electron-accepting Cl atom in ClSA give rise to different charge densities in the adsorbed hydroxyls of MSA, H2SO4, and ClSA, which are negatively charged with values of approximately -0.18 e, -0.13 e, and -0.09 e, respectively, and accordingly affected the Coulombic interactions with CN layer.
More discussion of the maintenances of the chemical structure of the bulk CN before and after the dissolution in MSA

After dissolution, the original chemical structure of the bulk CN was supposed to be not broken down. Firstly, as the direct evidences, the FT-IR and XPS spectra in the main text demonstrated that the major bonding manner of the bulk CN was not significantly altered before and after dissolution, except for the protonation interaction. Moreover, if the decomposition happened, the electronic structure and crystalline of CN would also significantly altered. However, the UV-vis and PL spectra demonstrated that only a very moderate blue-shift was observed, which was also ascribed to the protonation interaction. Similarly, the XRD patterns of the precipitated CN was most like to that of pristine bulk CN, and quite different to its intermediate species, such as DCDA, melamine, and melem (Fig. S2). Besides, the high collection yield of the CN precipitation from MSA solution (ca. 95%) and the unchanged C/N ratio before and after dissolution by elemental analysis (Table S1) also supported the maintenances of the chemical structure of CN before and after the dissolution in MSA.
Characterization of the starting bulk CN

The proposed successive thermal condensation of dicyandiamide (DCDA) into the heptazine-based bulk CN that was used in this study has been widely recognized as a facile synthetic pathway to prepare heptazine-unit based polymeric carbon nitride.\textsuperscript{54} TGA measurement in previous report had disclosed that when the polymerization temperature successively increased up to 550 °C, the polymerization degree gradually improved,\textsuperscript{55} and at higher temperature the as-obtained CN would decompose.\textsuperscript{56}

\textbf{Fig. S1} The proposed successive thermal condensation of dicyandiamide (DCDA) into the heptazine-based bulk CN that was used in this study
Fig. S2 XRD patterns of DCDA, melamine, melem, melon, bulk CN and r-CN.

The conservation of the stacked framework was studied by X-ray diffraction (XRD). As shown, the representative peak at 27.4° (002) still existed for r-CN, most like that of pristine bulk CN, and quite different to its intermediate species, such as DCDA, melamine, and melem. It supported the fact that the major crystalline structure of CN was retained and the starting bulk CN did not disintegrate after the dissolution and recovered processes. Nevertheless, it became broader than that of the starting bulk CN powder, along with a much reduced intensity. The low crystallinity mainly resulted from the reduce length of interlayer periodicity due to the precipitation using acetonitrile from poor solvents and the protonation interaction by MSA (see the similar result in protonation of bulk CN using HCl). In addition, the peak between 10 to 20 degrees was a typical of more oriented CN. Based on the HRTEM result, this peak presumably relates to an in-plane structural packing motif of CN, such as the hole-to-hole distance of the nitride pores in the crystal. This peak weakens for r-CN showed that an interlayer contribution was contained, either within the distance (then being the distance to the next pore in the next layer) or via the pore regularity (stacked sheets were more flat). Other reasons include that the protonation would make the structure of nitride pores slightly distorted and then the hole to hole distance changed.
Fig. S3 FT-IR spectra of DCDA, melamine, melem, melon, bulk CN and r-CN.
Fig. S4 SEM image of the bulk CN.
More evidences of the dissolution of CN in MSA

Fig. S5 Photo of the bulk CN powders in the solvent MSA without stirring before and after 5 days.

Upon the careful addition of MSA to CN, the color of the solvent at the bottom of the vial changed after 5 days, as some bulk CN powers dissolved into MSA solvent. It could be persuasive to demonstrate spontaneous dissolution, suggesting the formation of a solution rather than suspension. Nevertheless, notably, the spontaneous dissolution speed was slower than that of high crystallinity PTI·LiBr-based CN by using DMSO\(^9\) which may be ascribed to different type of bulk CN and the subsequent different kinetics.
**Fig. S6** (a) Photograph of CN nanosheets dispersion in water (left, 0.1 mg/mL) and the CN solution in MSA (right, 50 mg/mL) at room temperature, and irradiated by using a red laser pointer. (b) Particle size distribution of CN in MSA (a preliminary failed measurement) evaluated by dynamic light scattering (DLS, $\lambda=640$ nm).

The Tyndall effect was not observed for CN dissolved in MSA, while that was evident for CN nanosheets dispersion that was obtained by liquid-state exfoliation from the bulk CN according to previous method.$^{510}$ As the Tyndall effect was negligible by naked eyes using a laser pointer (Fig. S6a), the scattering experiment was further undertaken on a commercial DLS facility which is often used for evaluation of colloids size distribution (Fig. S6b). Due to the potential small particle size of CN in MSA, the backscattering angle of 173° was used for best signal to noise and reproducibility of measurements (see the NanoBrook Omni brochure, URL: https://www.brookhaveninstruments.com/pdf/Zeta%20Potential/NanoBrook-Omni.pdf). Unfortunately, the DLS measurement did not give a reliable result, as the sizes were calculated to be smaller than the limit of detection of the instrument (0.3 nm-10μm) under the optimized conditions. It should be noted that because the complete solvent parameters of MSA was not available for the DLS measurement, the solvent parameters of water were used alternatively. Nevertheless, although it was failed to measure the size of CN in MSA, as an indirect evidence, it suggested that the sizes of CN in MSA was ultra-small, and was not a typical colloidal system. Therefore, complementary to FT-IR (Fig. S3), XPS (Fig. 1c and Fig. 1d), UV-vis (Fig. S7), PL (Fig. S8), elemental analysis (Table S1) and BET (Fig. S9) characterization, the bulk CN was most presumably dissolved in MSA and formed a true solution as macromolecules with minimal lateral dimensions.
Supplementary proofs for the recovery of CN by precipitation using poor solvents

Fig. S7 UV-Vis spectra of the starting bulk CN powder and that recovered from the CN solution by precipitation using poor solvents (r-CN).
Fig. S8 PL spectra of the starting CN and r-CN (E<sub>x</sub> = 370 nm)

As shown, the starting bulk CN powder had a maximum PL emission peak at 465 nm, which was originated from the conjugated -C-N- network. Such emission was slightly blue-shifted to 443 nm for r-CN. The similar phenomenon in the protonation of CN with HCl was also observed. Thus, the blue-shift of PL spectra herein could be ascribed to the protonation of CN by MSA.
**Fig. S9** $N_2$ adsorption-desorption isotherm curves of the starting bulk CN powder and r-CN. Inset shows the pore volume and BET surface area.
Table S1 Elemental analysis of the starting bulk CN powder and r-CN

| Element (wt. %) | Molar ratio |
|----------------|-------------|
| CN             |             |
| C              | 34.93       | C/N=0.68   |
| N              | 59.52       |
| H              | 2.7         |
| r-CN           |             |
| C              | 29.27       | C/N=0.67   |
| N              | 50.96       |
| H              | 3.13        |

In order to confirm the molar ratio of C/N in the r-CN, the elemental analysis was performed. As shown, the molar ratio of C/N of bulk CN and r-CN were 0.68 and 0.67, respectively. The almost identical C/N ratio supported the facts that the dissolution in MSA did not disintegrate the structure of bulk CN. The amount of H increased for the precipitated CN from MSA solution, which could be explained by a protonation interaction.
Supplementary data for photocatalytic dehydrogenation of TMB and N-demethylation of AB

Fig. S10 Proposed mechanism of photocatalytic oxidation of TMB into TMB_{ox}^{S11}
Fig. S11 UV-vis absorption spectra of the reaction mixture for the dehydrogenation of TMB using heterogeneous (CN-hetero, CN dispersed in H$_2$O) and homogeneous (CN-homo, CN dissolved in MSA) CN photocatalysts at different reaction time.
Fig. S12 Absorbance of TMB$_{ox}$ at 456 nm as a function of time during photocatalytic dehydrogenation using MSA and CN-homo catalyst.

As TMB was only dissolvable in acidic aqueous solution, for CN-hetero system, 0.53 M MSA was also added. Moreover, as shown below, when only MSA or a low concentration of CN in MSA was used, the catalytic activity was negligible for CN-homo system. In contrast, when the concentration of CN in MSA increased, the activity increased and gradually reached a plateau. All these facts collaboratively verified that MSA did not significantly affect the catalytic activity. Besides, according to Fig. S12, for a balanced catalytic activity and economics of catalysts, a loading of 0.5 mg/mL was used as an optimal concentration.
Fig. S13 The turnover frequency (TOF) using CN-hetero (CN dispersed in H$_2$O) and CN-homo (CN dissolved in MSA) photocatalysts for dehydrogenation of TMB as function of different catalyst concentrations. The TOF was defined by n (TMB) per n (melem units) per hour.$^{12}$

In general, the TOF decreases as the loading amount of catalysts increases, and the TOF at sufficient low loading amount of catalysts is often used for theoretic investigation to exclude the concentration effect. Such situation is very similar to the concept of molar conductivity at infinite dilution in physical chemistry (https://en.wikipedia.org/wiki/Molar_conductivity).

When the concentration of CN was sufficient low, the CN-hetero photocatalyst would disperse in the reaction system just like a CN-homo photocatalyst, because all the active sites in both cases were similarly exposed. In this situation, the high TOF indicated the intrinsic activity of the catalyst. Nevertheless, at such low concentration of catalysts, the overall efficiency of the catalytic reaction was low, and virtually useless for practical applications. When the concentration of CN in the reaction system increased in realistic applications, the advantage of CN-homo photocatalyst in exposure of more active sites would gradually become evident. The Fig. S13 and the derived Fig. 3b aimed at the disclosure of these fundamentals and highlighting the evident increase of the catalytic activity due to the dissolution of CN.
Fig. S14 Proposed mechanism of photocatalytic oxidation of Azure B (AB) into Azure A (AA) \textsuperscript{S13}
**Fig. S15** UV-vis absorption spectra of the reaction mixture for the N-demethylation of AB using CN-hetero (CN dispersed in H₂O) and CN-homo (CN dissolved in MSA) photocatalysts at different reaction time.

The characteristic absorption peak at 594 nm and 660 nm were used to study the kinetics for CN-hetero and CN-homo photocatalytic reactions, respectively.
Considering the retention time of the standard O₂ and CO₂, Fig. S16 demonstrated that the gas product of photocatalytic N-demethylation of AB was CO₂ using gas chromatography. To examine the oxidation products quantitatively, the concentration changes of CO₂ was monitored during the AB oxidation. The yield of CO₂ was calculated using the equation of \( PV = nRT \) (P: Pa, V: m³, T: K, R: J/mol/K, and \( n \): mol). The results shown after the complete photocatalytic N-demethylation of AB by using CN-homo, the increase mole of CO₂ was ca. 0.8-fold of that of AB. Consisted with the previous reports, it indicated that one methyl group of AB was removed after the photocatalytic reaction.

**Fig. S16** Gas chromatography spectra of standard O₂, standard CO₂, and the gaseous products of photocatalytic N-demethylation of AB by using CN-homo.
**Fig. S17** Plot of $\ln(C_0/C)$ as a function of irradiation time for the N-demethylation of AB using CN-hetero and CN-homo photocatalysts.

For both CN-hetero and CN-homo photocatalysts, the first-order rate constant ($k$) for the N-demethylation of AB was calculated and shown in Fig. S17. The $k$ of CN-homo catalyst (0.04112/min) was about 6 times of that of CN-hetero catalyst (0.00703/min), indicating a higher activity.
Fig. S18 XRD pattern of r-CN that was recycled from CN-homo after photocatalytic oxidation of AB using ether as the poor solvent.

As shown, r-CN that was obtained from CN-homo after photocatalytic oxidation of AB by using ether as the poor solvent had a high collection yield (ca. 95%) and a similar crystallinity (Fig. S2) to that of the starting bulk CN powders. It suggested a high stability for the CN-homo catalyst in the recycling reaction tests. Moreover, it was noted that in contrast to r-CN of a lower crystallinity that was re-generated by using acetonitrile as the poor solvents (Fig. S2), the precipitation environments (e.g., type of solvents and the co-existence of other species) had a significant impact on the crystallinity of r-CN, which deserves a future study.
| Sample                | Catalyst (mg/mL) | TMB (mg/mL) | Catalytic rate (mg/min) | Reference |
|-----------------------|------------------|-------------|-------------------------|-----------|
| CN-homo \(^a\)       | 0.05             | 0.15        | 0.0129                  | this work |
| Cu(OH)$_2$ \(^b\)    | 0.06             | 0.192       | 0.0427                  | \(S_{11}\) |
| HRP \(^b\)           | 0.0006           | 0.192       | 0.0202                  | \(S_{11}\) |
| AuNPs/Cu-TCP \(^b\)  | 0.15             | 0.192       | 0.0064                  | \(S_{14}\) |
| GO-COOH \(^b\)       | 0.04             | 0.192       | 0.0028                  | \(S_{15}\) |

\(a\) Upon light irradiation; \(b\) Using H$_2$O$_2$ as the oxidation agent.
Table S3 Comparison of the catalytic activity of N-demethylation of AB using different catalysts

| Sample         | Concentration (mg/L) | catalytic time (min) | catalytic rate (mg/L/min) | Reference |
|----------------|----------------------|----------------------|---------------------------|-----------|
| CN-homo        | 100                  | 90                   | 1.11                      | this work |
| CS TiO₂        | 20                   | 20                   | 1.00                      | S16       |
| P25            | 20                   | 15                   | 1.33                      | S16       |
| Fe²⁺ a         | 9.17                 | 40                   | 0.23                      | S17       |
| ZnO-RGO        | 5.2                  | 20                   | 0.26                      | S18       |
| HRP (or LiP) a | 10                   | 120                  | 0.08                      | S19       |

a Using H₂O₂ as the oxidation agent instead of upon a light irradiation.
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