Electronic Supplementary Information (ESI†)

Porous carbon nitride photocatalysts prepared by calcination of hydroxyl-substituted melamine derivatives

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CONTENTS

Methods

Synthesis of catalysts

The CN powders were prepared by calcination of the respective precursors: 1 g of each of the respective precursors (MM, AN, AD, or cyanuric acid) was put in an aluminum oxide crucible. The crucible was left in a muffle furnace and heated to 550 °C under N_2 flow (0.2 L min^{-1}), with a heating rate of 2 °C min^{-1} and a holding time of 3 h.

Photocatalytic H_2 generation

Photocatalytic H_2 generation was performed in a quartz reaction vessel connected to a closed gas-circulation system.[1,2] Catalyst (50 mg) was added to 10 vol% triethanolamine (TEOA) solution (100 mL) and ultrasonicated for 15 min. The mixture and a $H_2PtCl_6 \cdot 6H_2O$ solution (1.33 mg in 136 µL water) were put into the reaction vessel. The vessel was connected to the gas-circulation system and evacuated to 2 kPa. The Ar gas purging and evacuation cycles were repeated three times, and Ar gas (50 kPa) was finally filled. The solution was magnetically stirred and photoirradiated with visible light ($\lambda > 420$ nm, solar simulator with a cut-off filter) at room temperature (298 K). The amounts of H_2 were quantified using a GC-8A gas chromatograph equipped with TCD (Shimadzu). The apparent quantum yield (Φ_{AQY}) for H_2 generation was determined by the irradiation of monochromated light using the following equation.

$$\Phi_{\mathrm{AQY}}[\%] = \frac{[\mathrm{H_2\ evolved\ (\mu mol)}] \times 2}{[\text{photon number entered into the reaction system}]} \times 100$$

Electrochemical measurements

The electrochemical measurements were performed at room temperature in 0.1 M Na_2SO_4 (pH 6, 70 mL). The Pt coil and Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. The working electrodes were prepared as follows: the catalyst ink was made by ultrasonication of a mixture of pure water (2 mL), catalyst (20 mg), 5 wt% Nafion dispersion (200 µL), and 2-propanol (1 mL). The ink (10 µL) was put onto a FTO glass (catalyst area: 0.5 cm × 0.5 cm square) and dried at room temperature. The obtained FTO glasses were left in a muffle furnace at 200 °C for 30 min under N_2 atmosphere. The exposed FTO surface was covered with an epoxy resin, affording the catalyst-loaded FTO working electrode. Prior to measurements, cyclic voltammetry (CV) cycles (–0.2 ~ 0.6 V (vs. Ag/AgCl)) were performed for 5 cycles for cleaning the catalyst surface. EIS measurements were performed on a HZ-Pro S2A system (Meiden Hokuto). The Mott-Schottky plots and photocurrent response measurements were performed on a HZ-7000 system (Meiden Hokuto). All potential values were referred to the reversible hydrogen electrode (RHE) using the following equation.[3]

$$E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.1976 + 0.0591 \times \text{pH}$$
$$(E(\text{Ag/AgCl (ref.)}) = 0.1976\ \text{V vs. NHE at 25 °C})$$

Analysis

The powder XRD patterns were recorded on a PANalytical XPert PRO with a Cu-Kα radiation. DR UV-vis spectra were measured on a UV-vis spectrophotometer (JASCO Corp.; V-750). FT-IR spectra were measured on a JASCO FT/IR-6100 by transmission method. The TEM and STEM images and EELS spectra were obtained using a JEOL ARM200F at an accelerating voltage of 200 kV. ICP-AES analysis was performed on a SPS7800 plasma spectrometer (SII). SEM observations were performed using S-5000H microscope (HITACHI). The N_2 adsorption/desorption measurements were performed at 77 K using BELSORP MINI X (Microtrac BEL). The specific surface area was determined on the basis of the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were determined based on the Barrett–Joyner–Halenda (BJH) methods. XPS spectra were obtained on JPS-9010MX (JEOL) spectrometer with Mg Kα radiation as the energy source. Solid-state ^{13}C-NMR spectra were measured using Bruker AVANCE400WB at 13 kHz.[4] ESR spectra were measured using JEOL RESONANCE JES X320 at room temperature under dark conditions. CN powders were preheated at 80 °C for 2 h under vacuum before the measurements. The TG-DTA curves were obtained on a DTG-60H system (Shimadzu) using the coverable aluminum oxide sample cell. The cell was heated to 550 °C with a heating rate of 10 °C min^{-1} under Ar flow (50 mL min^{-1}). FD-MS analysis was performed using JEOL JMS-700.

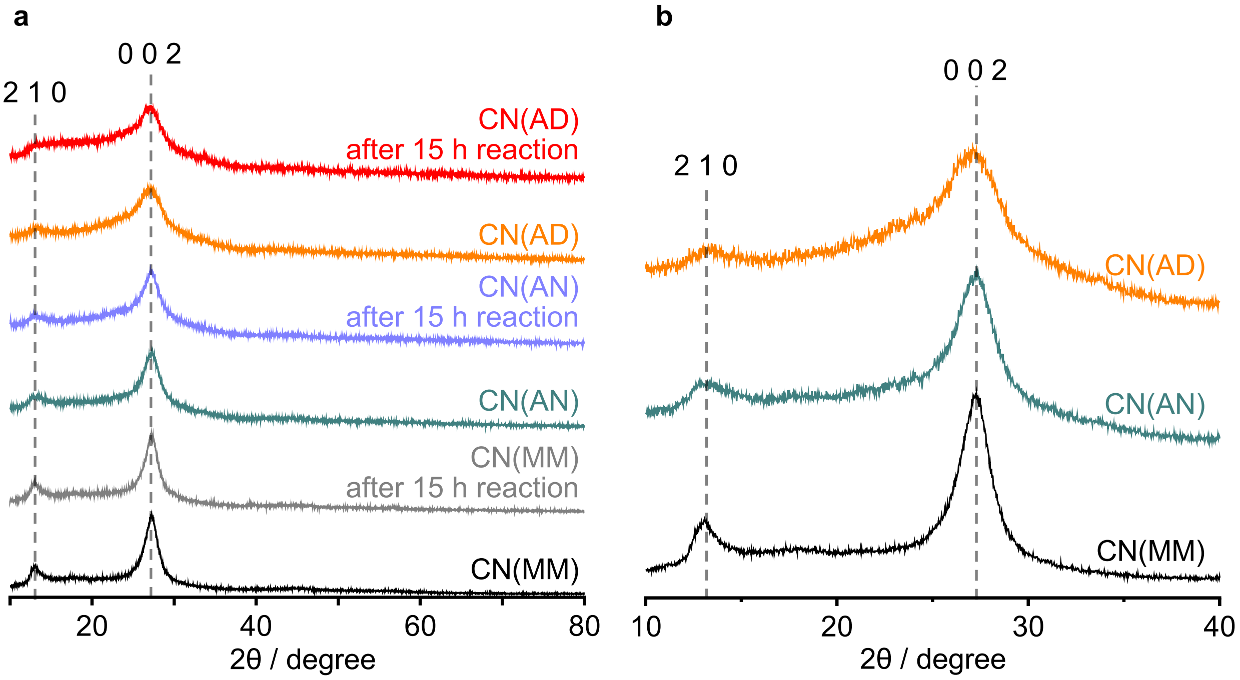


Fig. S1 (a) XRD patterns of CN powders and (b) their enlarged views.

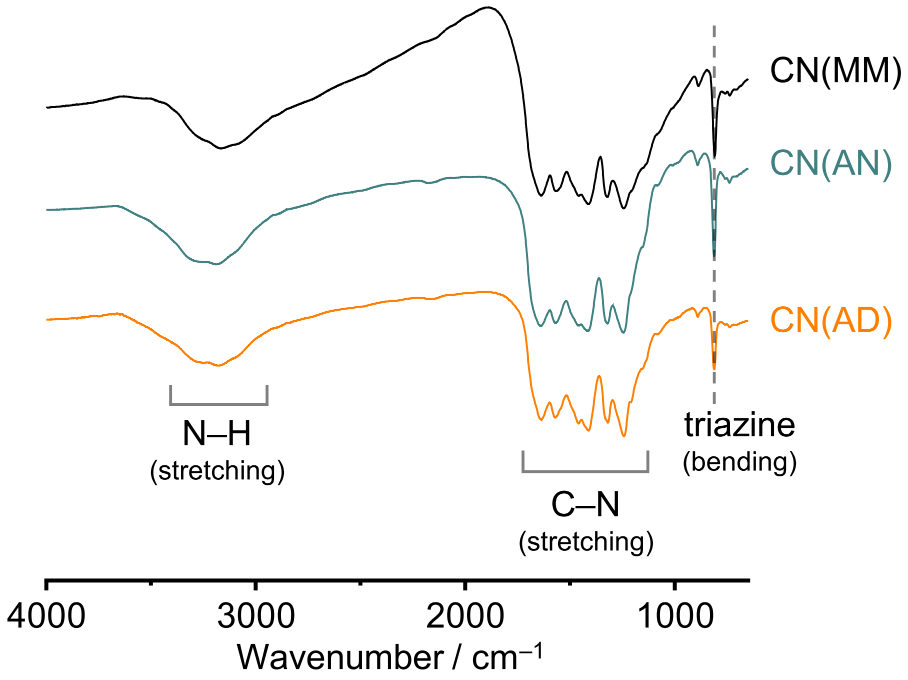


Fig. S2 FT-IR spectra of CN powders.

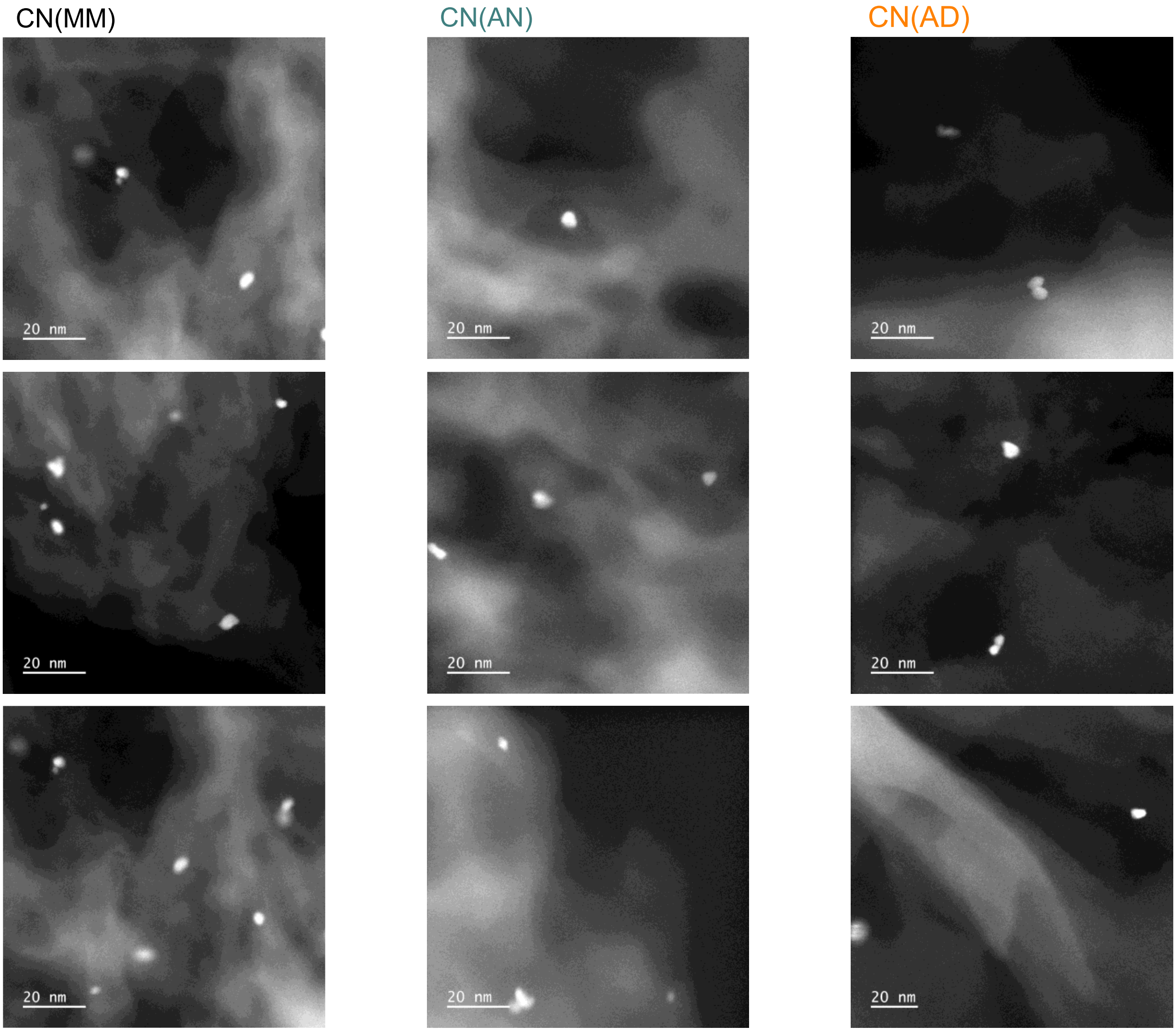
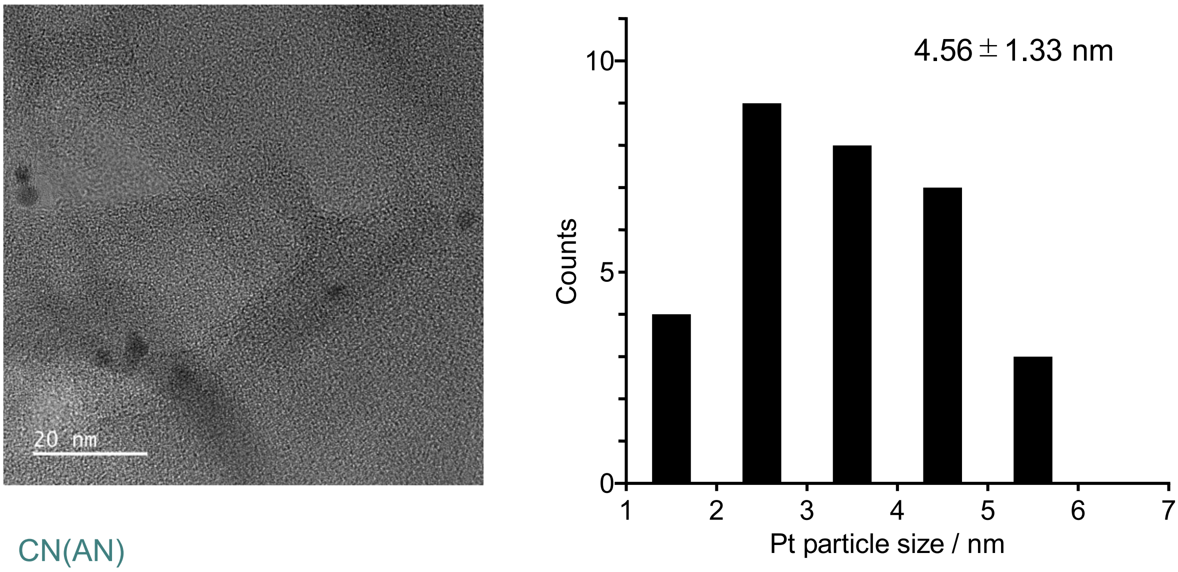
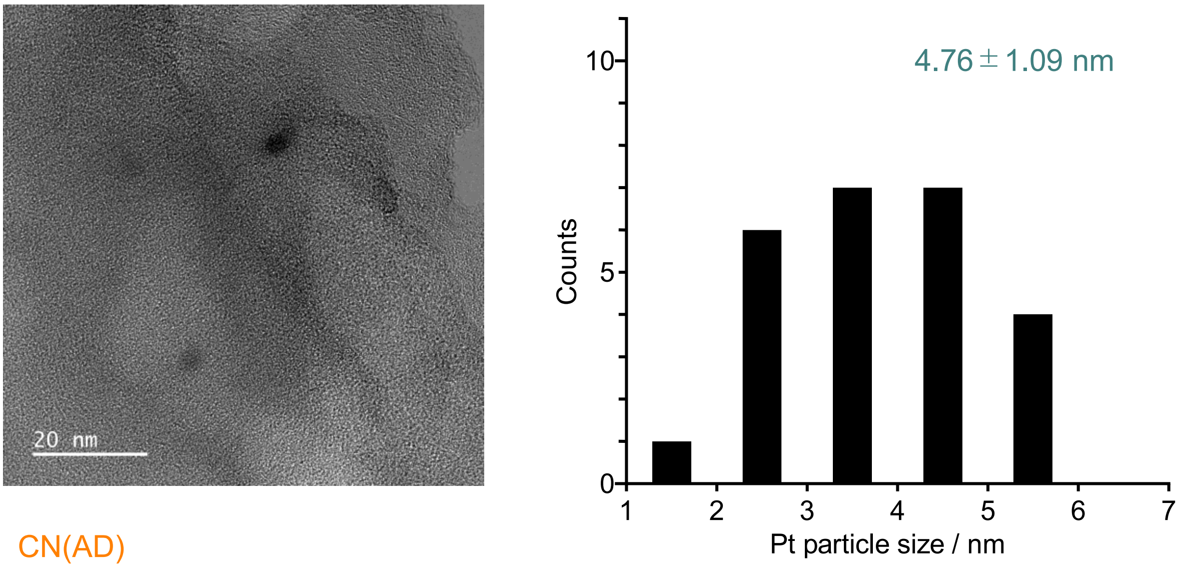


Fig. S3 Annular dark field STEM images of Pt particles loaded on CN powders.

CN(MM)



CN(AN)



CN(AD)

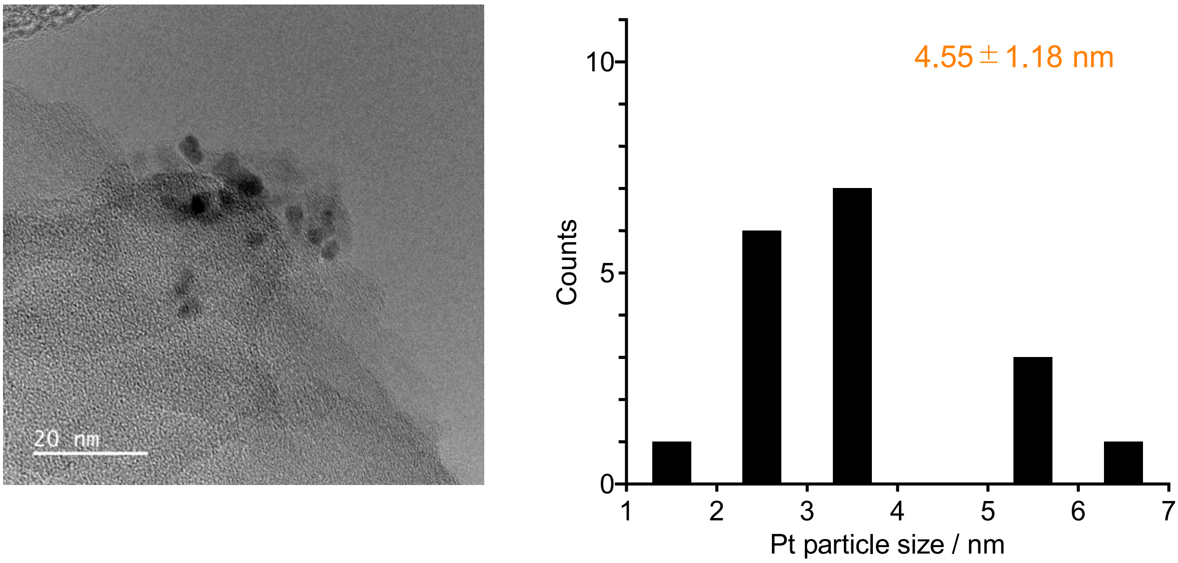


Fig. S4 TEM images and size distributions of Pt particles loaded on CN powders.

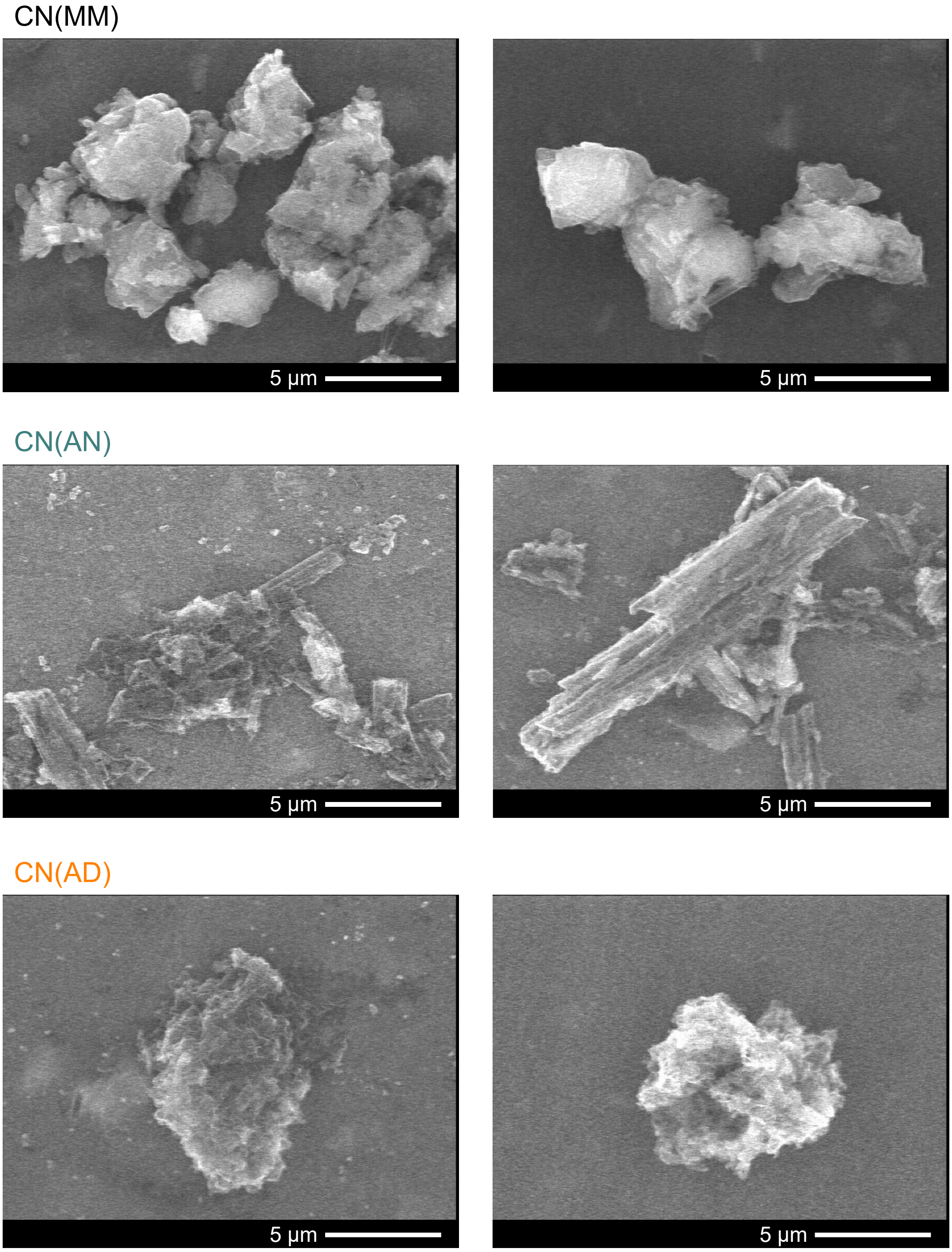


Fig. S5 SEM images of CN powders.

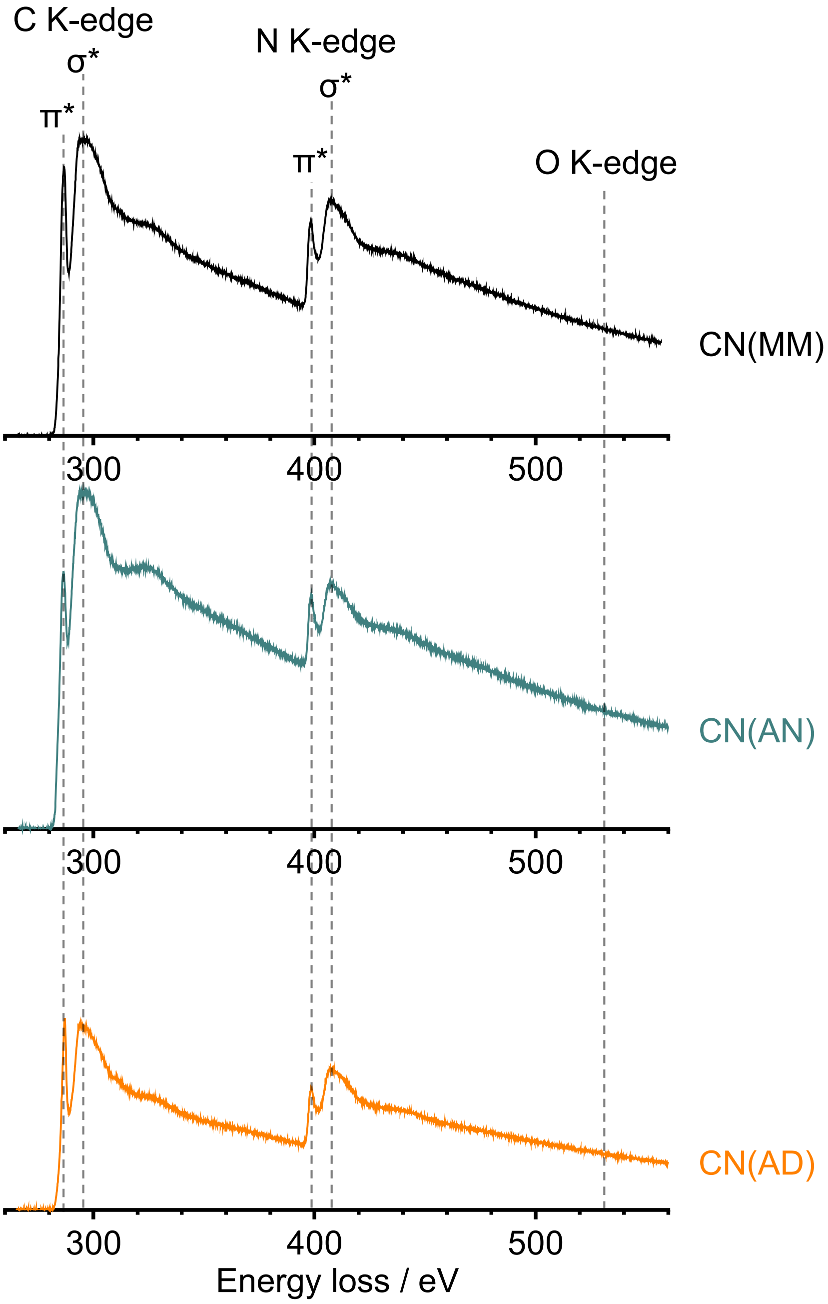


Fig. S6 C K-edge and N K-edge EELS spectra of CN powders.

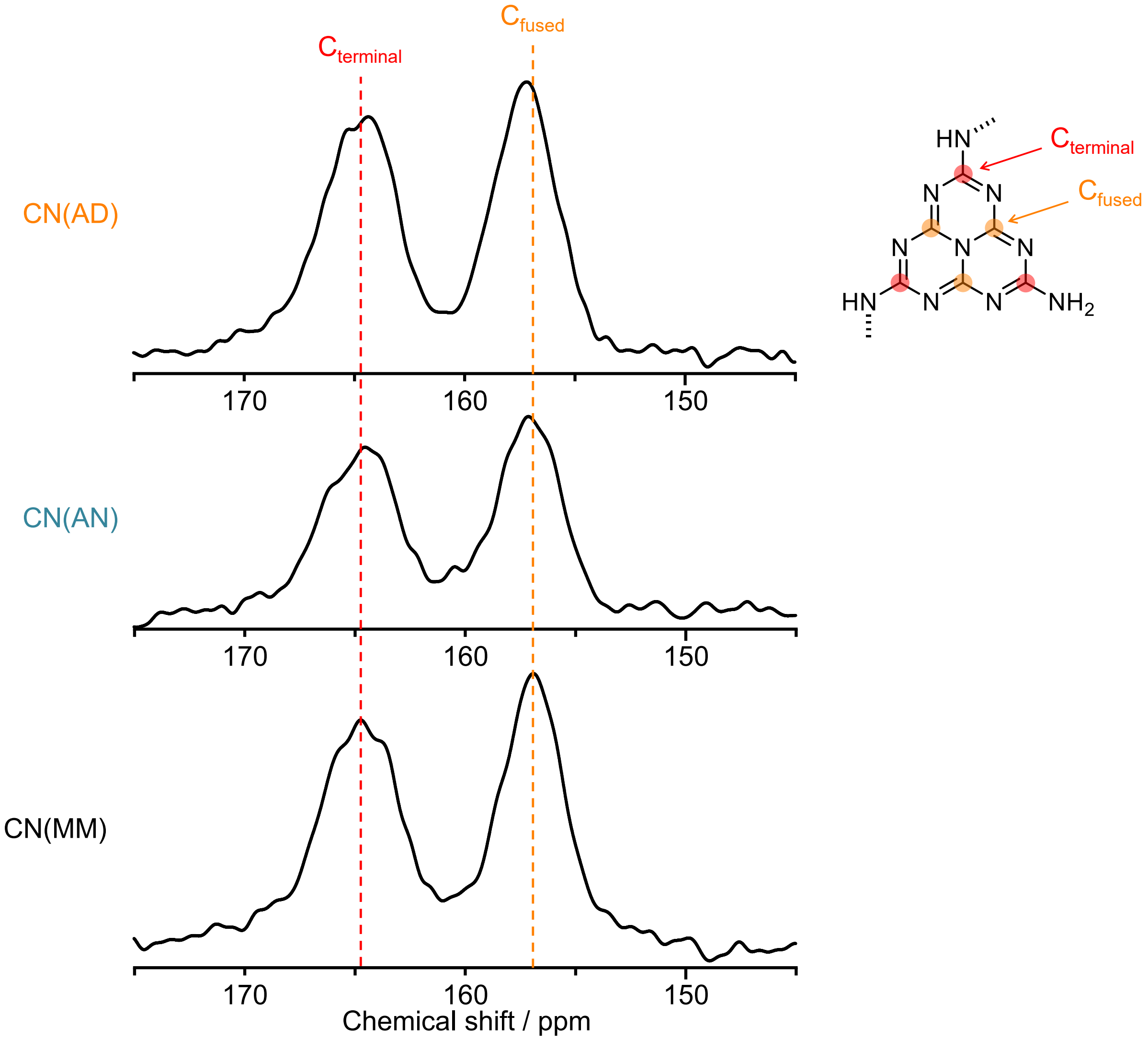


Fig. S7 Solid-state DDMAS/^{13}C-NMR spectra of CN powders.

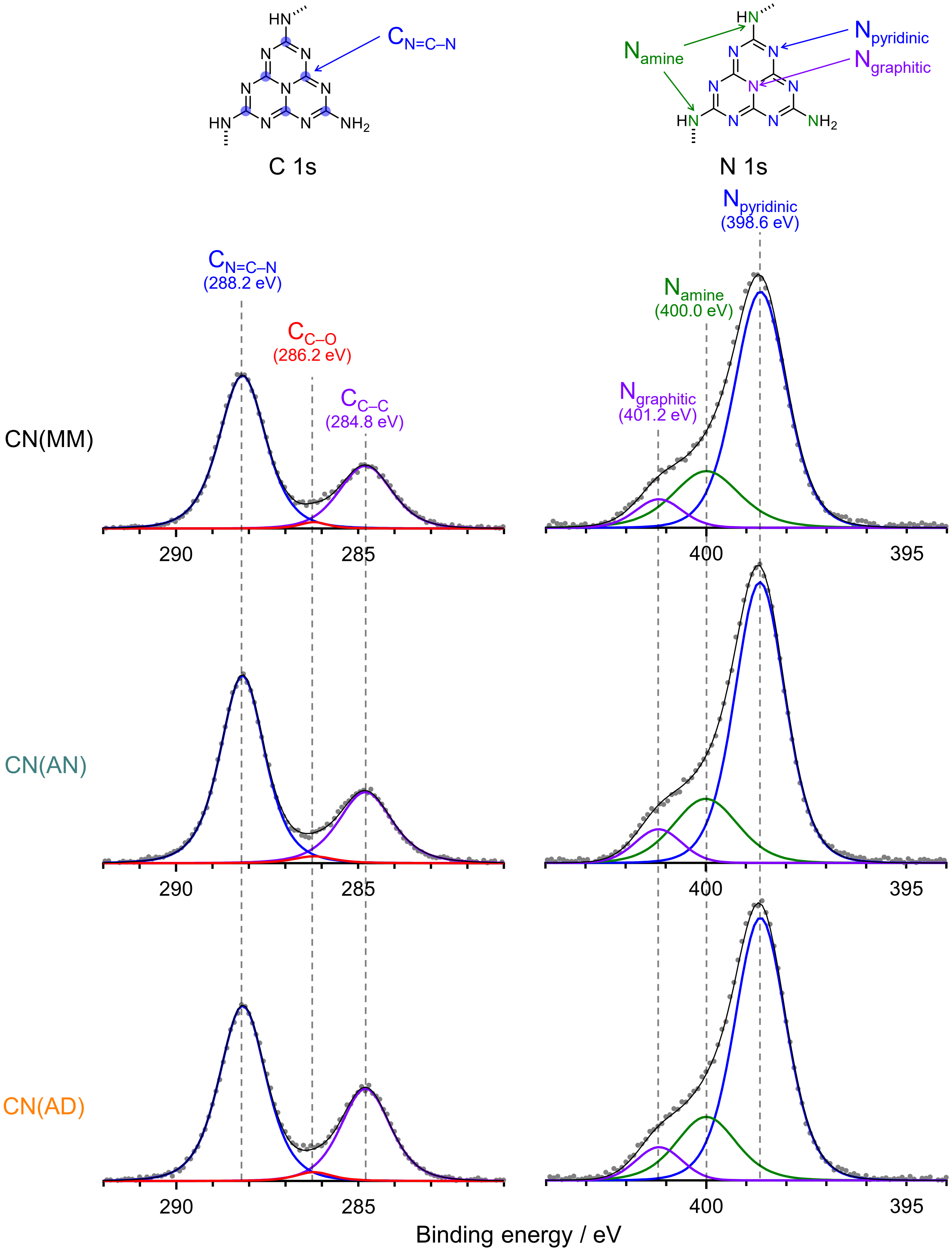


Fig. S8 C 1s and N 1s XPS spectra of respective CN powders.[5–7] The components in the C 1s spectra at 284.8 and 286.2 eV correspond to C–C and C–O, respectively, which originate from the background (carbon tapes).

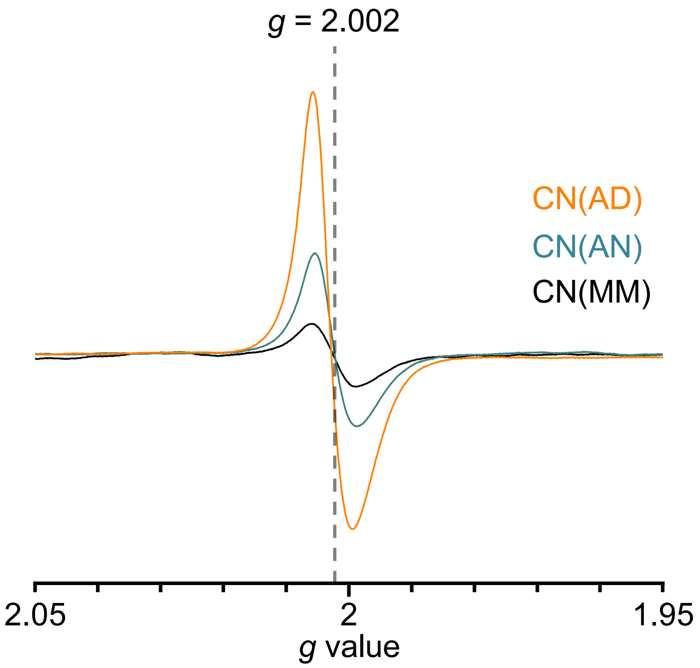


Fig. S9 ESR spectra of CN powders measured in the dark.

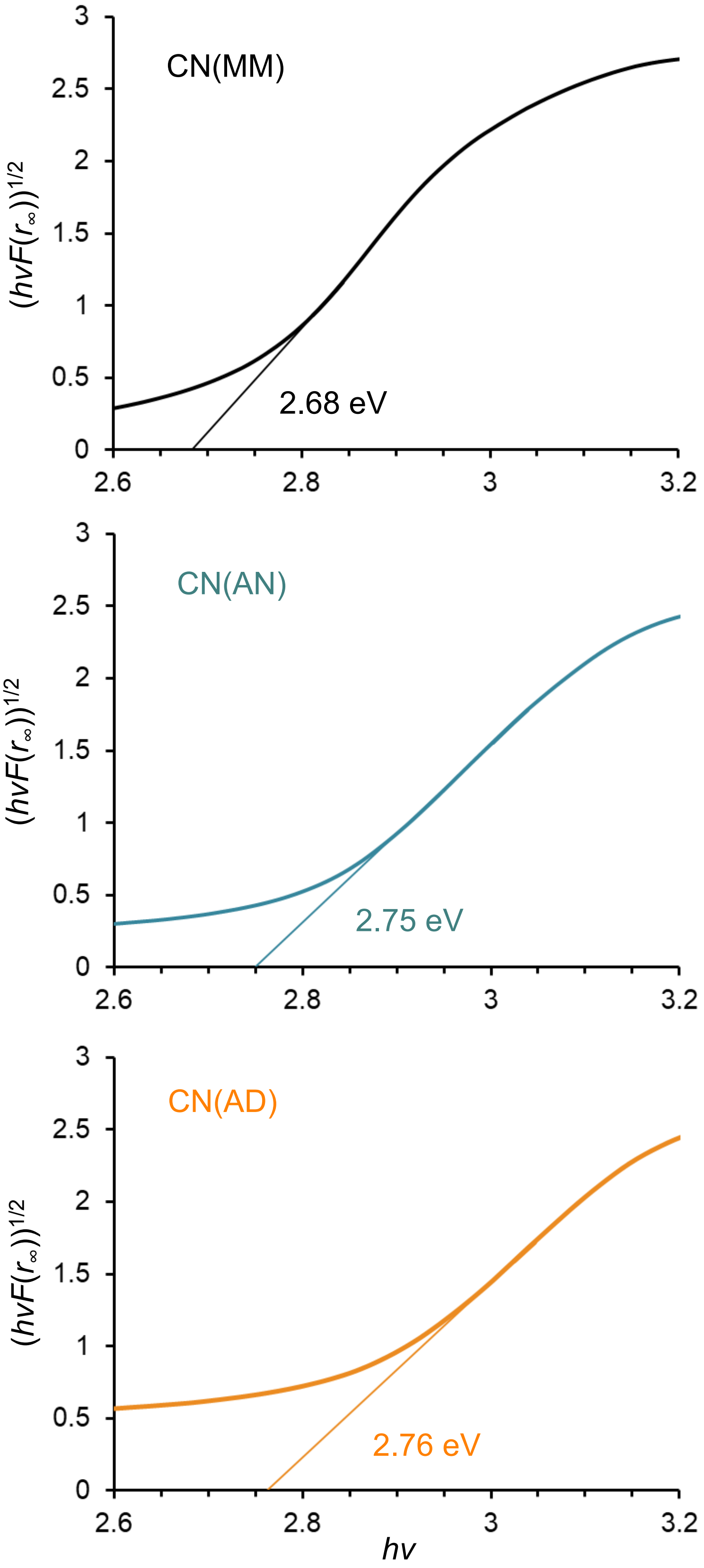


Fig. S10 Tauc plots of CN powders.

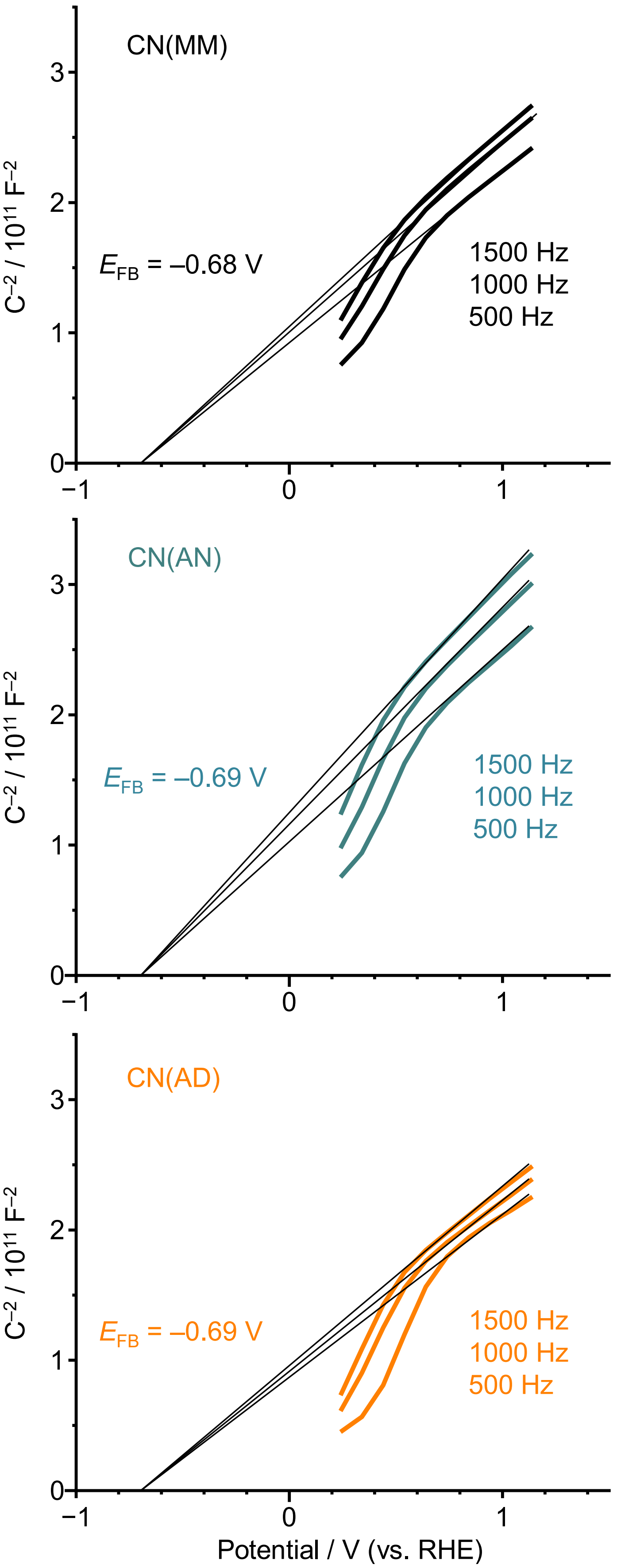


Fig. S11 Mott-Schottky plots of CN powders.

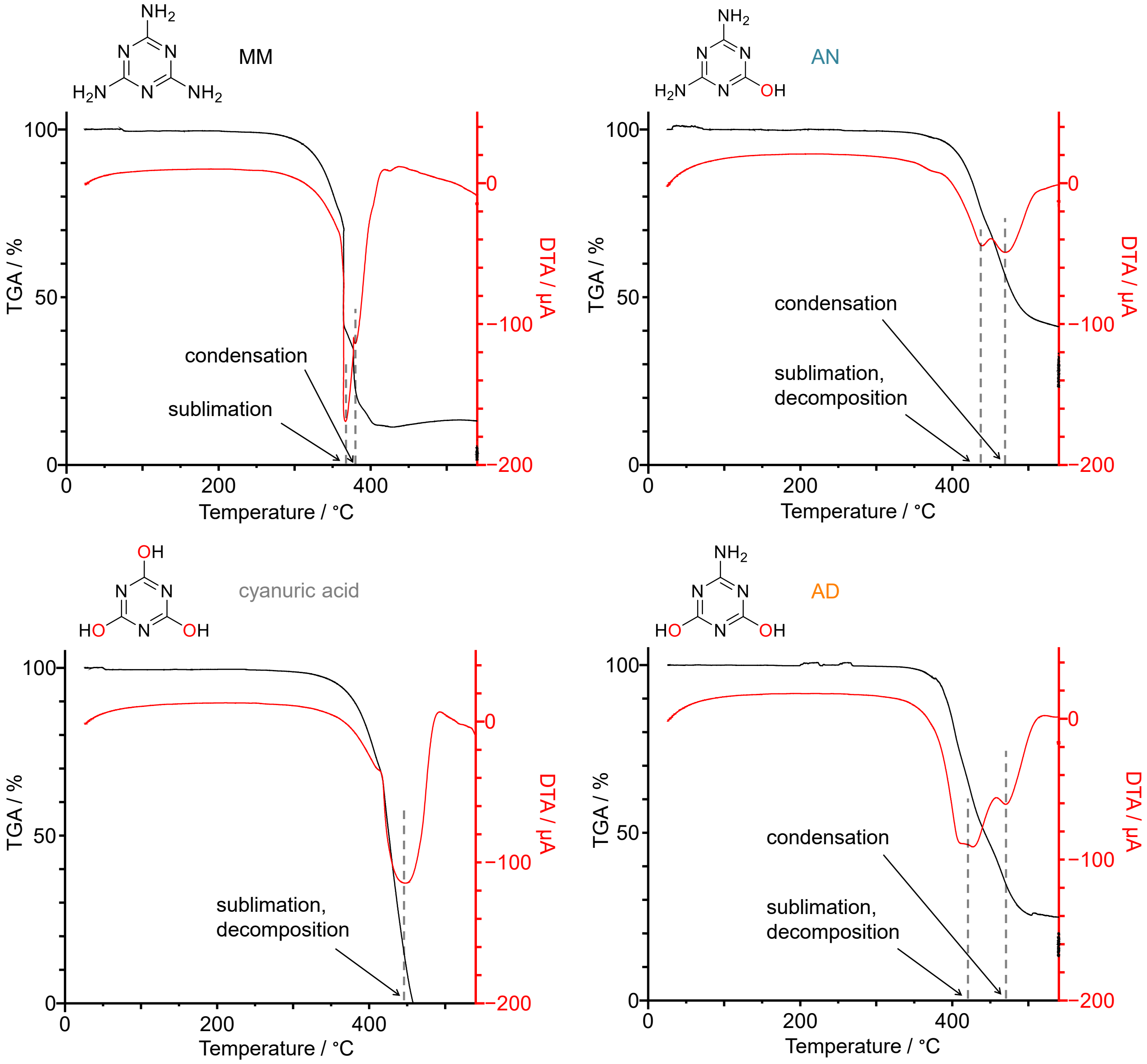


Fig. S12 TG-DTA curves of respective monomers.

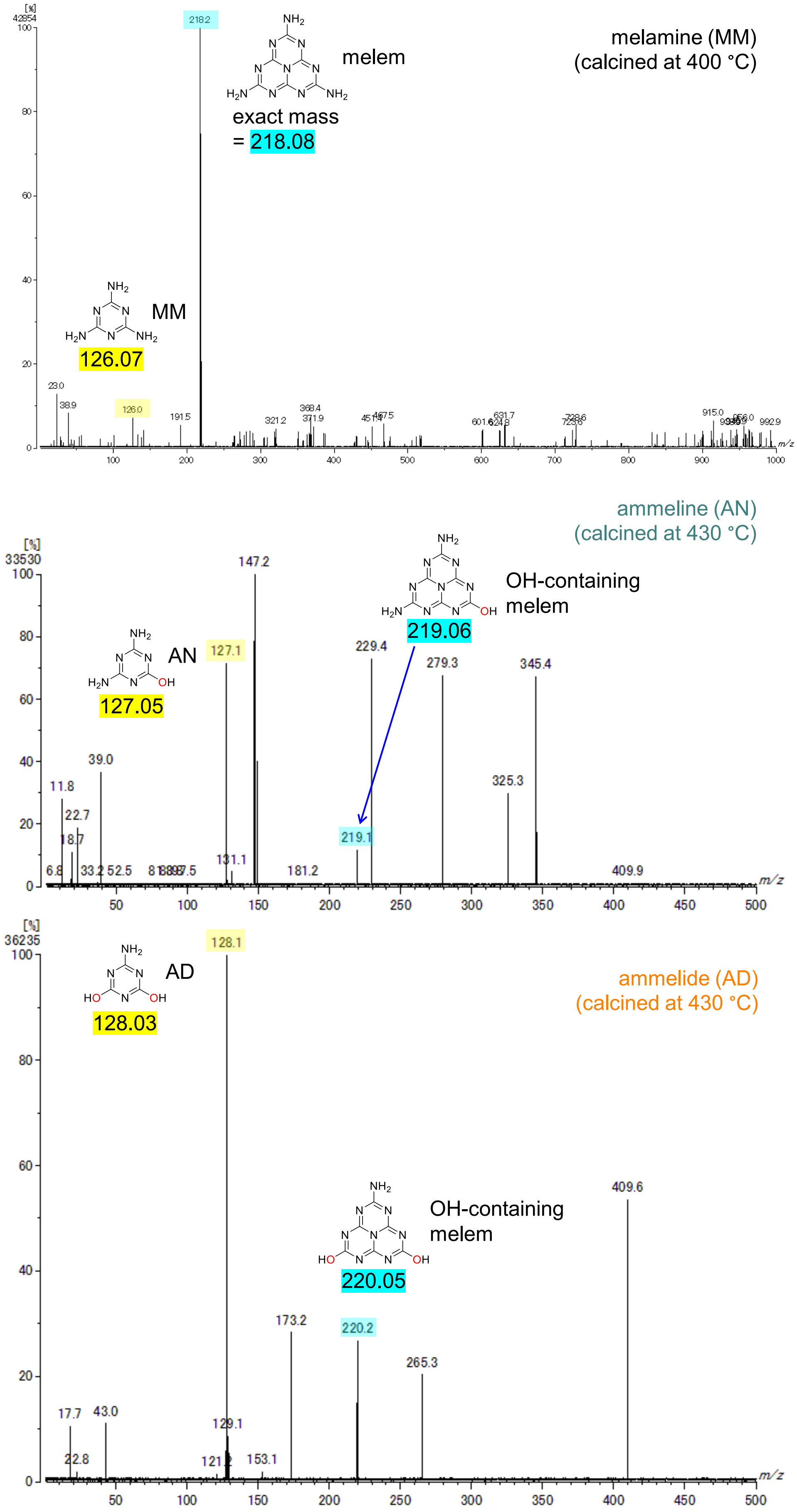


Fig. S13 FD-MS spectra of the powders obtained by calcination of MM, AN, and AD under N_2 flow (0.2 L min^{-1}) with a heating rate of 2 °C min^{-1} and a holding time of 3 h (430 °C).

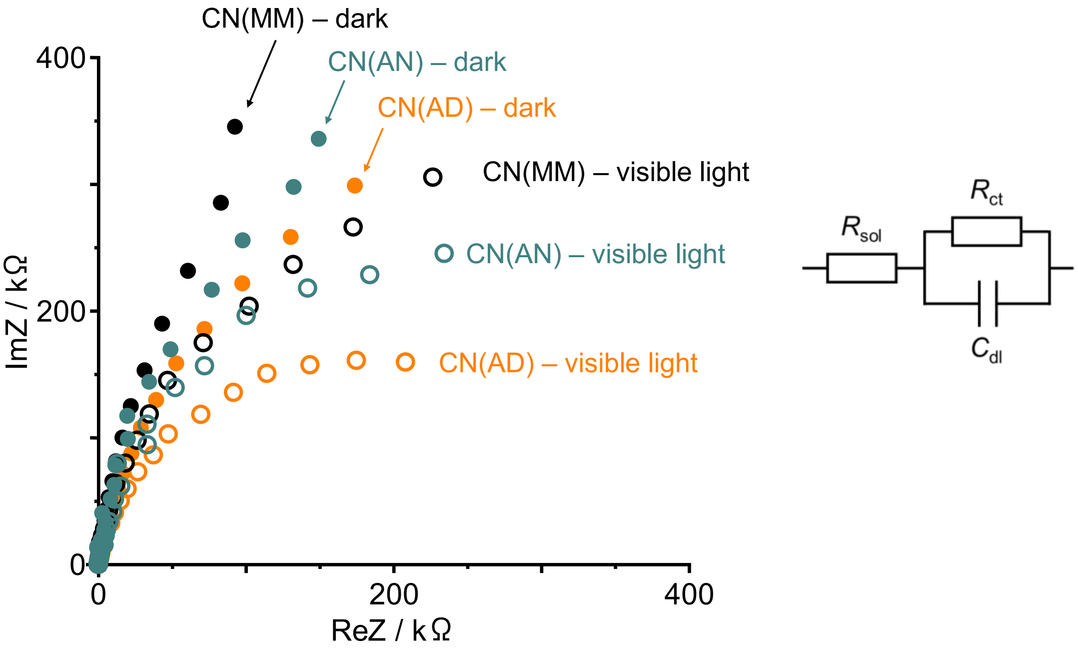


Fig. S14 EIS Nyquist plots measured on FTO electrodes loaded with respective CN powders.

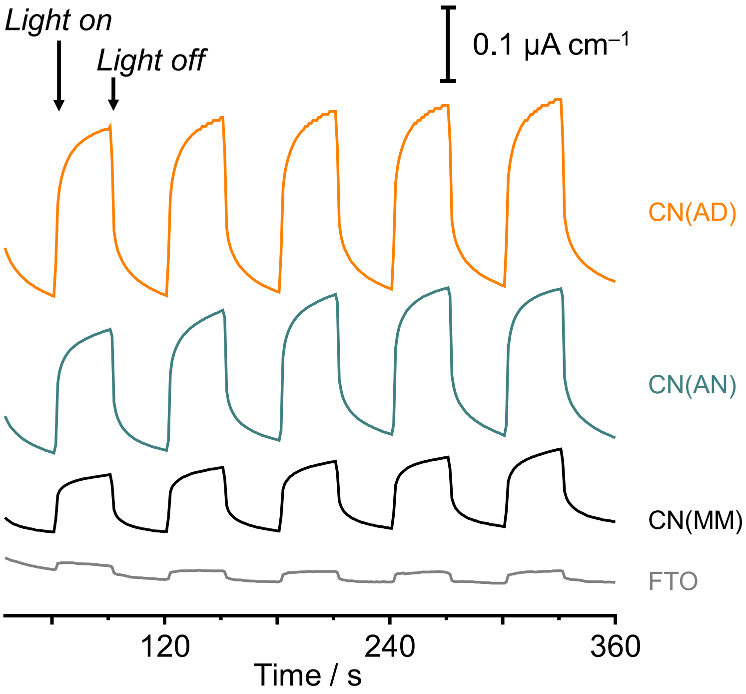


Fig. S15 Photocurrent response measured on FTO glass loaded with respective CN powders.

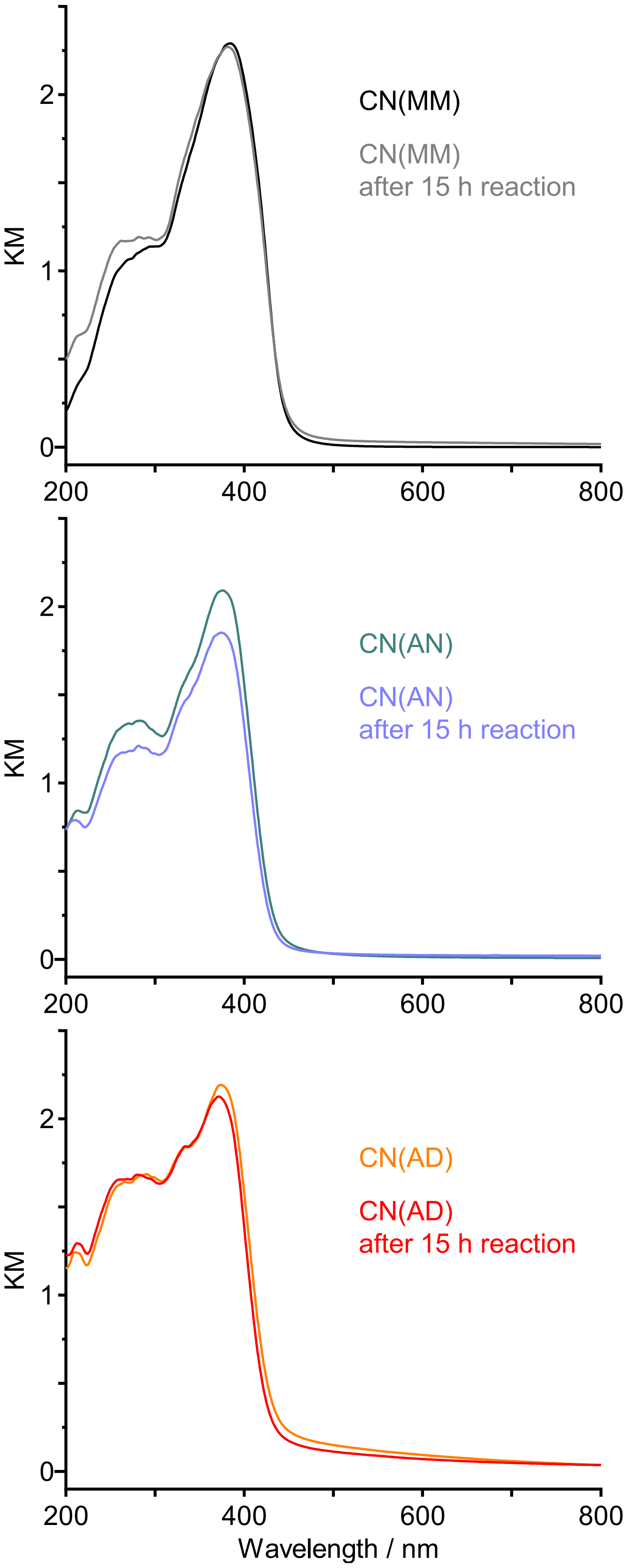


Fig. S16 DR UV-vis spectra of CN powders before and after 15 h of photoreaction.

Table S1 Comparison of Φ_{AQY} for photocatalytic H_2 generation on the reported CN-based catalysts.[a]

Catalyst	Procedure	Sacrificial reagent	S_{BET} / $m^2 g^{-1}$	Φ_{AQY} / % (@ λ / nm)	Ref.
CN(AD)	**One step** Calcination of AD at 550 °C (3 h) under N_2.	10 vol% TEOA	96.1	4.1 (420)	This work
mesoporous $g-C_3N_4$	**Two steps** (hard templating method) Calcination of a mixture of urea and mesoporous silica (SBA-15) at 500 °C (4 h) and removal of SBA-15 using 20 vol% HF.	10 vol% 2-PrOH	49.8	2.7 (420)	8
CCNNSs	**Two steps** (post treatment) Calcination of $g-C_3N_4$ in Al foil at 620 °C (2 h) under Ar.	10 vol% TEOA	34	9.0 (420)	9
$g-C_3N_4$ (550) seaweed	**Three steps** (pretreatment) Dicyandiamide was hydrothermally treated at 200 °C (4 h). The resultant was left in liquid N_2. The resultant was calcined at 550 °C under Ar.	10 vol% TEOA	130	7.8 (420)	10
$g-C_3N_4$ nanosheets	**Two steps** (post treatment) Ultrasonination of $g-C_3N_4$ in 2-PrOH (10 h).	10 vol% TEOA	384	3.8 (420)	11
2DPCM	**Two steps** (pretreatment) Melamine was hydrothemally treated in HCl at 180 °C (10 h). The resultant was calcined at 650 °C (2 h) under N_2.	10 vol% TEOA	50.2	1.3 (490)	12
TCN-1%CTAC	**Two steps** (soft templating method) Calcination of melamine with hexadecyl trimethyl ammonium chloride at 550 °C (4 h) and at 500 °C (2 h) under air.	10 vol% TEOA	43.8	3.4 (420)	13
worm-like porous $g-C_3N_4$	**Two steps** (soft templating method) Calcination of melamine with Pluronic P123 at 600 °C (4 h) under Ar and at 500 °C (2 h) under air.	10 vol% TEOA	90	1.8 (420)	14
ompg-CN-1	**Two steps** (hard templating method) Calcination of cyanamide with SBA-15 at 550 °C (4 h) and removal of SBA-15 using 4 M ammonium bifluoride (24 h).	10 vol% TEOA	234	3.0 (455)	15

ompg-CN-2	**Two steps** (hard templating method) Calcination of cyanamide with HCl-treated SBA-15 at 550 °C (4 h) followed by removal of SBA-15 using 4 M ammonium bifluoride (24 h).	10 vol% TEOA	517	6.8 (455)	15
CNHS	**Two steps** Calcination of melamine at 500 °C (2 h) and at 520 °C (2 h) under air. The resultant was calcined at 520 °C (6 h) under air.	10 vol% TEOA	278	4.0 (420)	16
FCN-5	**Two steps** (soft templating method) Dicyandiamide was mixed with polyurethane sponges in solution and concentrated. The resultant was calcined at 550 °C (1 h).	10 vol% TEOA	58.7	3.9 (420)	17
HCN	**Three steps** (pretreatment) Dicyandiamide was hydrothermally treated at 160 °C (20 h). The resultant was calcined at 380 °C (1 h) and 500 °C (2 h).	5 vol% MeOH	124	10.6 (420)	18
CN-AA	**Three steps** (pretreatment) Urea was hydrothermally treated at 200 °C (24 h). The resultant was calcined at 400 °C (4 h) under Ar and at 400 °C (2 h) under air.	4.8 wt% TEOA	270	20.9 (420)	19
DCN-550	**Two steps** (pretreatment) Dicyandiamide was hydrothemally treated at 180 °C (4 h). The resultant was calcined at 550 °C.	10 vol% TEOA	226	3.0 (420)	20
UCNs	**Two steps** (pretreatment) Melamine was hydrothermally treated at 180 °C (12 h) in sulfuric acid. The resultant was calcined at 550 °C (4 h).	10 vol% TEOA	180	8.4 (420)	21
MGCN-600	**Two steps** (pretreatment) Melamine and cyanuric acid were mixed in DMSO. The resultant was calcined at 600 °C (4 h) under air.	10 vol% TEOA	134	13.5 (400)	22
CNMS-600	**Two steps** (post treatment) CN powder was suspended in concentrated sulfuric acid. The reultant was calcined at 600 °C (2 h) under Ar.	10 vol% TEOA	132	6.3 (420)	23

[*a*] Determined using Pt cocatalyst.

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