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Supplementary Information

Oxygen-mediated Formation of MoS_x-doped Hollow Carbon Dots for Visible Light-driven Photocatalysis

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1. Instruments

UV/Vis absorption and photoluminescence spectra of $_{\text{MoS}}$HCDs and NMP-CDs were measured using a UV/Vis spectrometer (Mega-2100, Scinco, Korea) and a spectrofluorometer (Nano Log®, Horiba Scientific, Japan), respectively. The structure and size of $_{\text{MoS}}$HCDs and NMP-CDs were characterized by atomic force microscope (AFM, XE-100, Park systems, Korea) and transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). Chemical composition of $_{\text{MoS}}$HCDs and NMP-CDs were identified by x-ray photoelectron spectroscopy (XPS, AXIS-His, KRATOS, UK). The amount of Mo doped in $_{\text{MoS}}$HCDs was quantified by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, SPECTRO, SPECTRO ARCOS, Germany), and the band edge positions of $_{\text{MoS}}$HCDs were measure by cyclic voltammetry (CV, versaSTAT4, Princeton Applied Research, USA). The products for the oxidative coupling reaction of various amines were analyzed by gas chromatography (GC, 6500GC, YoungLin Instrument, Korea) and nuclear magnetic resonance (NMR) spectroscopy (400 MHz, Burker model digital ADVANCE III 400).

2. Experimental Methods

A. Preparation of NMP-CDs

A 20 ml portion of pure NMP in a two-necked round bottom flask was heated up with stirring at 140°C for 3 h under O_2 or Ar atmosphere. The reaction mixture was filtered with alumina membrane filter (20 nm), and the filtrate was concentrated under vacuum at 100°C for 6 h. The concentrated solution was diluted with 20 mL of water, then the product (MNP-CDs) was purified via dialysis with a membrane tube (MWCO 1,000 Da) for 1 day. NMP-CDs were lyophilized at - 40 $^{\circ}$C overnight.

B. Measurement of the band edge positions of $_{\text{MoS}}$HCDs

The Pt disk electrode and Ag wire were used as working, counter and quasi-reference electrodes, respectively. A 20 mg portion of $_{\mathrm{MoS}}$HCDs were dispersed in 10 ml of acetonitrile and NMP (7 : 3) mixture, followed by addition of tetrabutylammonium perchlorate (TBAP) and ferrocene (Fc) as an electrolyte and a standard. The band edge positions of $_{\mathrm{MoS}}$HCDs were measured by sweeping between 2.0 and -2.0 eV at the rate of 100 mV/s.

C. Quantum yield measurement

The quantum yield (QY) of $_{\mathrm{MoS}}$HCDs was measured by using Coumarin 153 solution in ethanol (QY 0.53) as a standard. The $_{\mathrm{MoS}}$HCDs were dispersed in NMP using a probe sonicator to measure their absorption and photoluminescence. The absorption of $_{\mathrm{MoS}}$HCDs was measured at 400 nm, and their photoluminescence was measured under excitation at 400 nm. The absorption remained below 0.1 to minimize a reabsorption effect.

$$\emptyset_x = \emptyset_{ST} \cdot \left(\frac{Grad_x}{Grad_{ST}}\right) \cdot \left(\frac{n_x^2}{n_{ST}^2}\right)$$

$\emptyset$= Fluorescence quantum yield

$Grad$ = The gradient from the plot of integrated fluorescence intensity *vs.* absorbance

n = The refractive index of the solvent

The subscripts ST and X denote standard and sample, respectively.

D. Photoluminescence quenching of $_{\mathrm{MoS}}$HCDs by BA

A 2 mg portion of $_{\mathrm{MoS}}$HCDs were added into a mixture of acetonitrile and NMP (7 : 3, 10 mL), which was redispersed using a probe sonicator. To examine the quenching of $_{\mathrm{MoS}}$HCDs photoluminescence by BA, a certain amount of benzylamine (12.4, 31, 62, and 124 mg) was added to 2 ml of $_{\text{MoS}}$HCDs dispersion. After mixing for 1 min, the photoluminescence of $_{\text{MoS}}$HCDs was measured.

E. Apparent quantum yield measurement

To calculate the apparent quantum efficiency of $_{\text{MoS}}$HCDs, light of 410 nm was irradiated into the reaction solution of benzylamine using a monochrometer. External Quantum Efficiency (EQE) was calculated using following equations (1) – (5).

$$E_p = h \cdot f = h \cdot (c/\lambda) \tag{1}$$

$$N_p = {}^{E}\!/_{E_p} \tag{2}$$

$$E_{QF} = {}^{N_p}\!/_{N_A} \tag{3}$$

$$EQE = \frac{N_{product}}{N_{IP}} \cdot 100(\%) \tag{4}$$

Where E_p is a distinct energy of photons [J], h is a Planck's constant (6.63×10^{-34} J·s), c is a speed of light (2.998×10^{8} m/s), f is frequency [1/s], λ is wavelength [m], N_p is the number of photons [1/ m^2·s], E is a power density of a light source (14.28 mW/m^2), E_{QF} is the photon flux [mol/m^2·s], N_A is the Avogadro's number (6.02×10^{23}/mol), $N_{product}$ is the molar amount of product [20 μmol], N_{IP} is the number of photons of incident light (2114.47 μmol).

F. NMR analysis of various imine products

***N*-Benzyl-1-phenylmethanimine (*N*-benzylidenebenzylamine, NBBA). ^{1}H NMR ($CDCl_3$)** : δ (ppm) = 8.35 (s, 1H), 7.79 – 7.74 (m, 2H), 7.39 (d, J = 2.2 Hz, 3H), 7.32 (d, J = 4.4 Hz, 4H), 7.24 (s, 1H), 4.80 (d, J = 1.3 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ (ppm) = 162.09, 139.40, 136.25, 130.88, 128.72, 128.61, 128.39, 128.09, 127.10, 65.16.

***N*-(4-Methylbenzyl)-1-(*p*-tolyl) methanimine**. **^{1}H NMR ($CDCl_3$)** : δ (ppm) = 8.30 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4, 2H), 7.18 (d, *J* = 8.0, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 2.34 (s, 3H), 2.31 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ (ppm) = 161.18, 141.06, 136.57, 136.45, 133.70, 129.41, 129.26, 128.37, 128.07, 64.87, 21.61, 21.22.

***N*-(2-Methylbenzyl)-1-(*o*-tolyl) methanimine**. **^{1}H NMR (CDCl$_3$)** : δ (ppm) 8.63 (s, 1H), 7.92 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.32 – 7.10 (m, 7H), 4.80 (s, 2H), 2.47 (s, 3H), 2.37 (s, 3H) **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 160.66, 137.84, 137.73, 136.20, 134.34, 130.93, 130.37, 130.23, 128.40, 127.84, 127.17, 126.30, 126.20, 63.41, 19.52, 19.42.

***N*-(4-(tert-butyl)benzyl)-1-(4-(tert-butyl)phenyl) methanimine**. ^{1}H NMR (CDCl$_3$) : δ (ppm) 8.35 (s, 1H), 7.73 – 7.69 (m, 2H), 7.44 – 7.40 (m, 2H), 7.37 – 7.33 (m, 2H), 7.28 – 7.23 (m, 2H),4.77 (s, 2H), 1.33 (s, 2H), 1.31 (s, 9H), 1.30 (s, 9H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) =161.77, 154.18, 149.87, 136.61, 133.73, 129.83, 128.23, 127.89, 127.82, 125.65, 125.50, 64.97, 35.03, 34.60, 31.56, 31.38, 31.22.

***N*-(4-Methoxybenzyl)-1-(4-methoxyphenyl) methanimine**. **^{1}H NMR (CDCl$_3$)** : δ (ppm) 8.26 (s, 1H), 7.72 – 7.66 (m, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.93 – 6.83 (m, 4H), 4.70 (s, 2H), 3.79 (s, 3H), 3.75 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 161.72, 160.99, 158.70, 131.74, 129.89, 129.24, 114.03, 113.95, 64.49, 55.40, 55.33.

1-(Benzo[1,3]dioxol-5-yl)-*N*-(benzo[1,3]dioxol-5-ylmethyl)methanimine. **^{1}H NMR (CDCl$_3$)** : δ (ppm) 8.21 (s, 1H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.83 – 6.78 (m, 2H), 6.76 (d, *J* = 1.0 Hz, 2H), 5.97 (s, 2H), 5.91 (s, 2H), 4.66 (d, *J* = 1.1 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 160.96, 150.03, 148.37, 147.84, 146.62, 133.45, 131.08, 124.67, 121.13, 108.71, 108.31, 108.13, 106.78, 101.57, 101.02, 64.61.

***N*-(4-Fluorobenzyl)-1-(4-fluorophenyl) methanimine**. **^{1}H NMR (CDCl$_3$)** : δ (ppm) 8.33 (s, 1H), 7.78 – 7.74 (m, 2H), 7.32 – 7.21 (m, 2H), 7.12 – 7.04 (m, 2H), 7.03 – 6.96 (m, 2H), 4.75 (s, 2H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 165.65, 163.31,163.26,160.88, 160.62, 135.10, 135.07, 132.48, 132.45, 130.32, 130.32, 129.61, 129.54, 115.93, 115.72, 115.51, 115.30, 64.22.

***N*-(4-Chlorobenzyl)-1-(4-chlorophenyl) methanimine**. ^{1}H NMR (CDCl$_3$) : δ (ppm) = 8.31 (s, 1H), 7.72 – 7.65 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 4.74 (s, 2H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 160.98, 137.76, 137.00, 134.58, 131.02, 129.61, 129.41, 129.07, 128.78, 64.30.

***N*-(2,4-Dichlorobenzyl)-1-(2,4-dichlorophenyl) methanimine**. ^{1}H NMR (CDCl$_3$) : δ (ppm) 8.78 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.29 –

7.21 (m, 2H), 4.86 (s, 2H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 58.98, 137.48, 135.98, 135.47, 134.11, 133.59, 131.66, 130.60, 130.57, 130.45, 129.78, 129.47, 129.30, 128.11, 127.75, 127.37, 61.70.

1-(Pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanimine. **^{1}H NMR (CDCl$_3$)** : δ (ppm) 8.66 (m, 1H), 8.64 – 8.54 (m, 2H), 8.09 (m, 1H), 7.79 – 7.60 (m, 2H), 7.42 (m, 1H), 7.35 – 7.28 (m, 1H), 7.24 – 7.11 (m, 1H), 5.03 (d, J = 1.4 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 63.87 , 158.65 , 154.29 , 149.44 , 149.30 , 136.64 , 136.50 , 124.89 , 122.33 , 122.09 , 121.43 , 66.54.

1-(Thiophene-2-yl)-N-(thiophene-2-ylmethyl) methanimine. **^{1}H NMR (CDCl$_3$)** : δ (ppm) 8.38 (d, J = 1.2 Hz, 1H), 7.38 (dt, J = 5.0, 1.0 Hz, 1H), 7.29 (dd, J = 3.6, 1.1 Hz, 1H), 7.21 (dd, J = 4.9, 1.5 Hz, 1H), 7.04 (dd, J = 5.0, 3.6 Hz, 1H), 6.99 – 6.92 (m, 2H), 4.92 (s, 2H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 155.52, 142.19, 141.64, 131.13, 129.44, 127.50, 126.99, 125.38, 124.93, 58.61.

1-Phenyl-N-(1-phenylethyl)ethan-1-imine. ^{1}H NMR (CDCl$_3$) : δ (ppm) 7.99 – 7.91 (m, 2H), 7.59 – 7.49 (m, 1H), 7.45 (ddt, *J* = 8.2, 6.6, 1.1 Hz, 2H), 7.39 – 7.26 (m, 4H), 7.26 – 7.17 (m, 1H), 4.10 (q, *J* = 6.6 Hz, 1H), 2.59 (s, 3H), 1.37 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ (ppm) =165.03, 137.15, 133.17, 129.48, 128.63, 128.53, 128.43, 128.37, 128.23, 126.87, 126.85, 126.74, 125.75, 59.90, 25.19, 15.66.

***N*-Heptyl-1-phenylmethanimine**. ^{1}H NMR (CDCl$_3$) : δ (ppm) 8.26 (s, 1H), 7.74-7.70 (m, 2H), 7.44 – 7.35 (m, 3H), 3.62-3.58 (m, 2H), 1.72-1.69 (m, 2H), 1.31-1.24 (m, 8H), 0.88 (t, J = 6.6 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$):** δ (ppm) = 160.88, 136.47, 130.59, 128.71, 128.17, 61.97, 31.99, 31.09, 29.30, 27.49, 22.82, 14.28.

3. Supplementary Figures

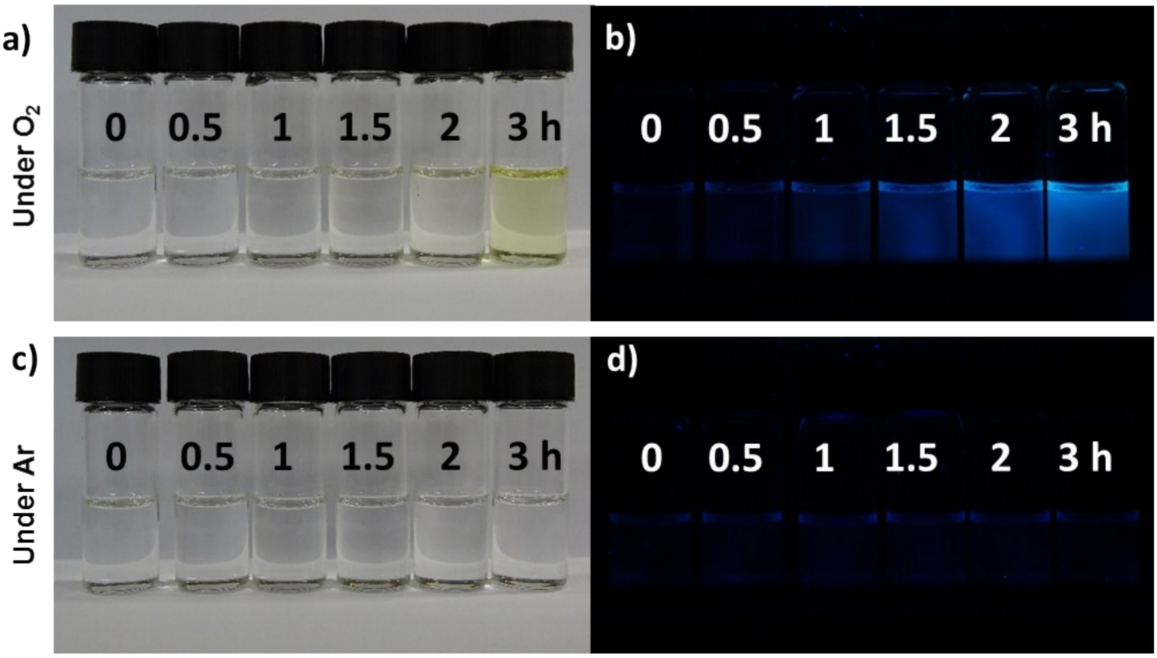

Figure S1. Optical and fluorescence images of pure NMP, not containing MoS_2 nanosheets, as a funciton of heating time (140°C). (a)-(b) under O_2 gas, and (c)-(d) under Ar gas.

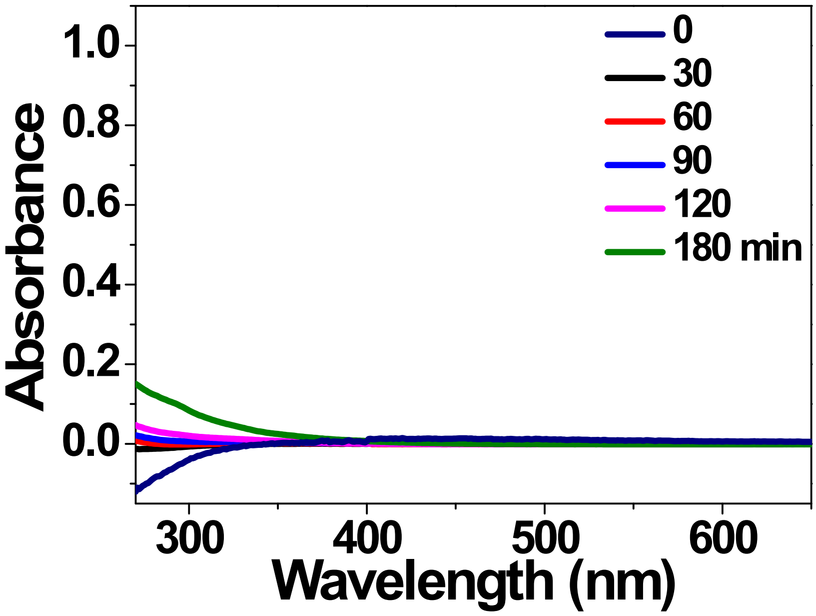

Figure S2. Absorption spectrum of NMP-CDs as a function of reaction time at 140 °C.

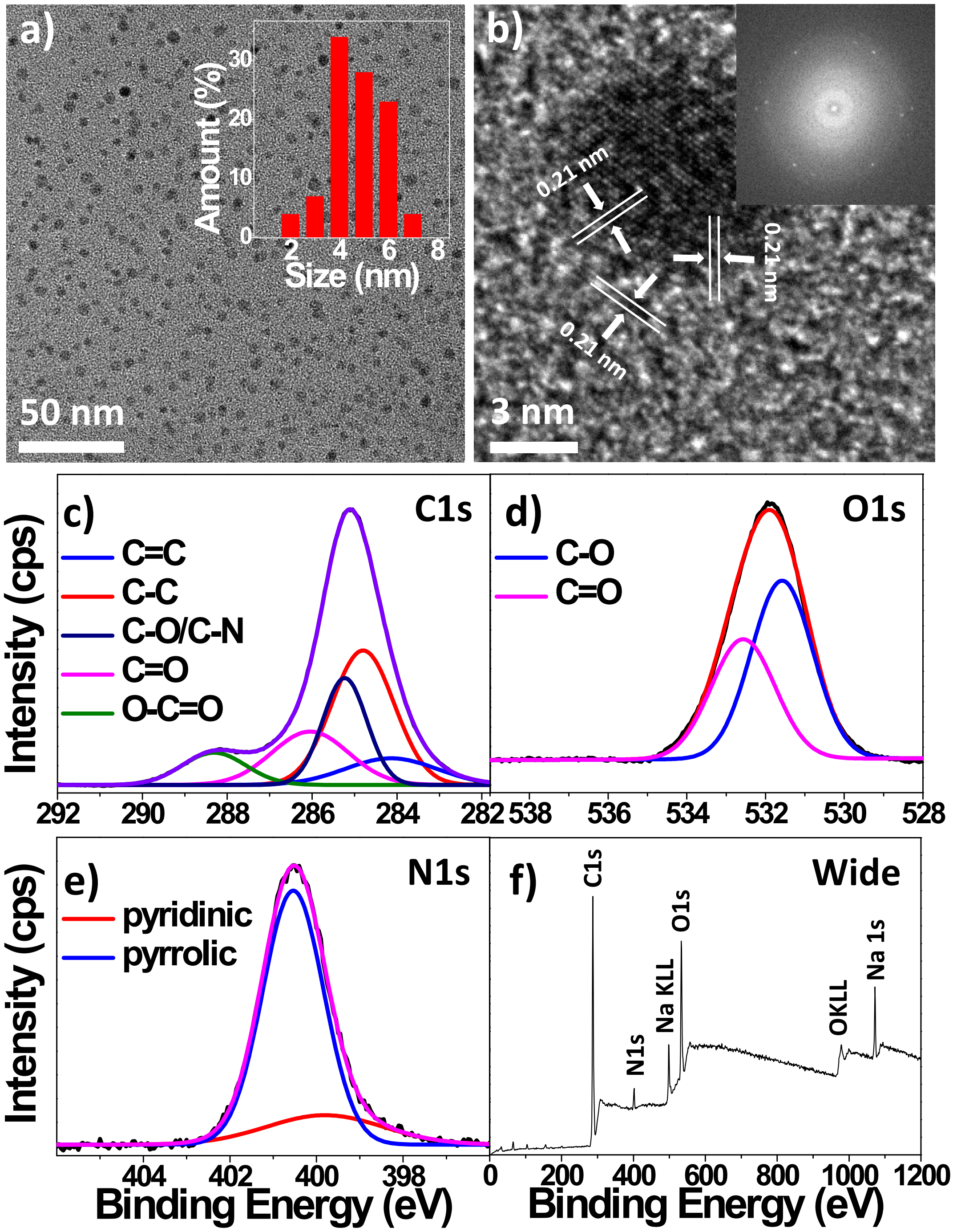

Figure S3. Characterization of NMP-CDs. (a) TEM image of NMP-CDs (Inset : size distribution). (b) HR-TEM image of NMP-CDs (Inset : FFT pattern). (c) C1s, (d) N1s, (e) O1s and (f) wide XPS spectra of NMP-CDs.

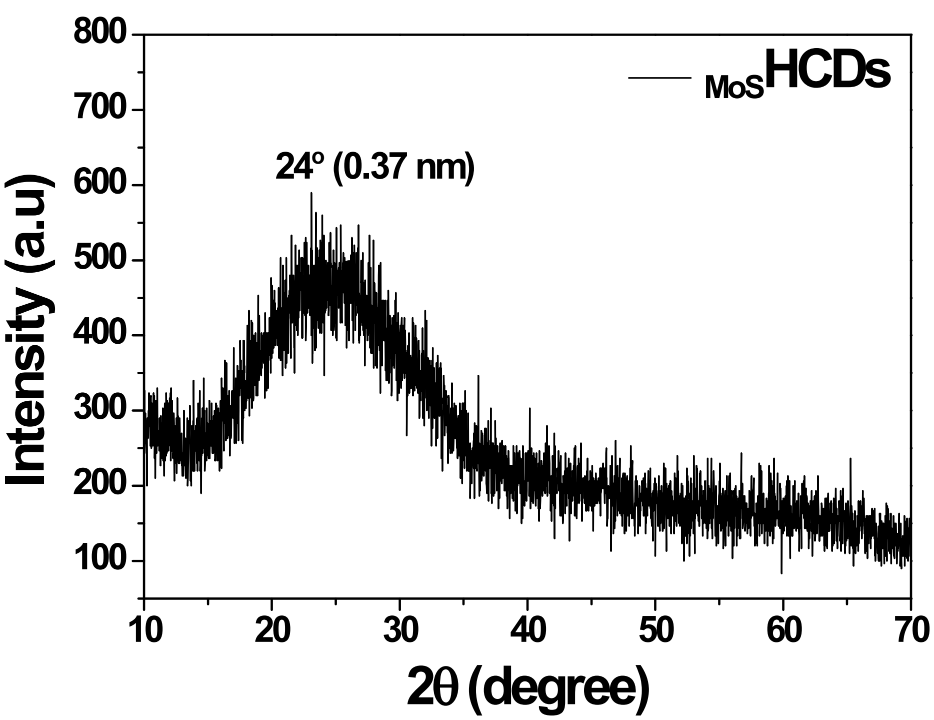

Figure S4. XRD spectrum of $_{MoS}$HCDs.

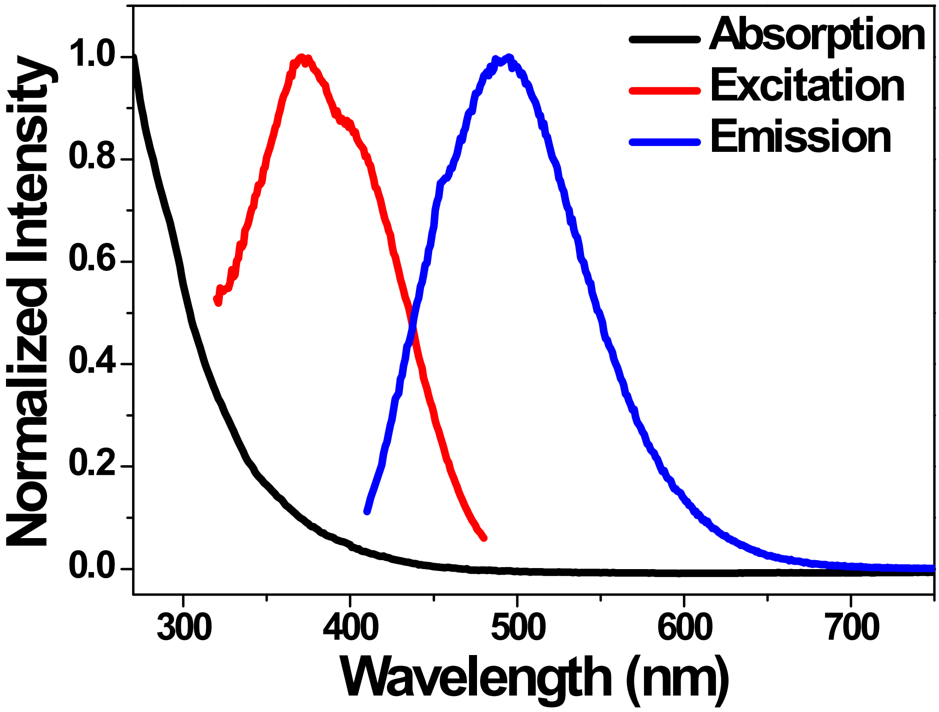

Figure S5. Optical properties of NMP-CDs. UV-vis absorption spectrum (black), photoluminescence excitation (PLE) spectrum at an emission of 500 nm (red) and photoluminescence (PL) spectrum of NMP-CDs at an excitation of 400 nm (blue).

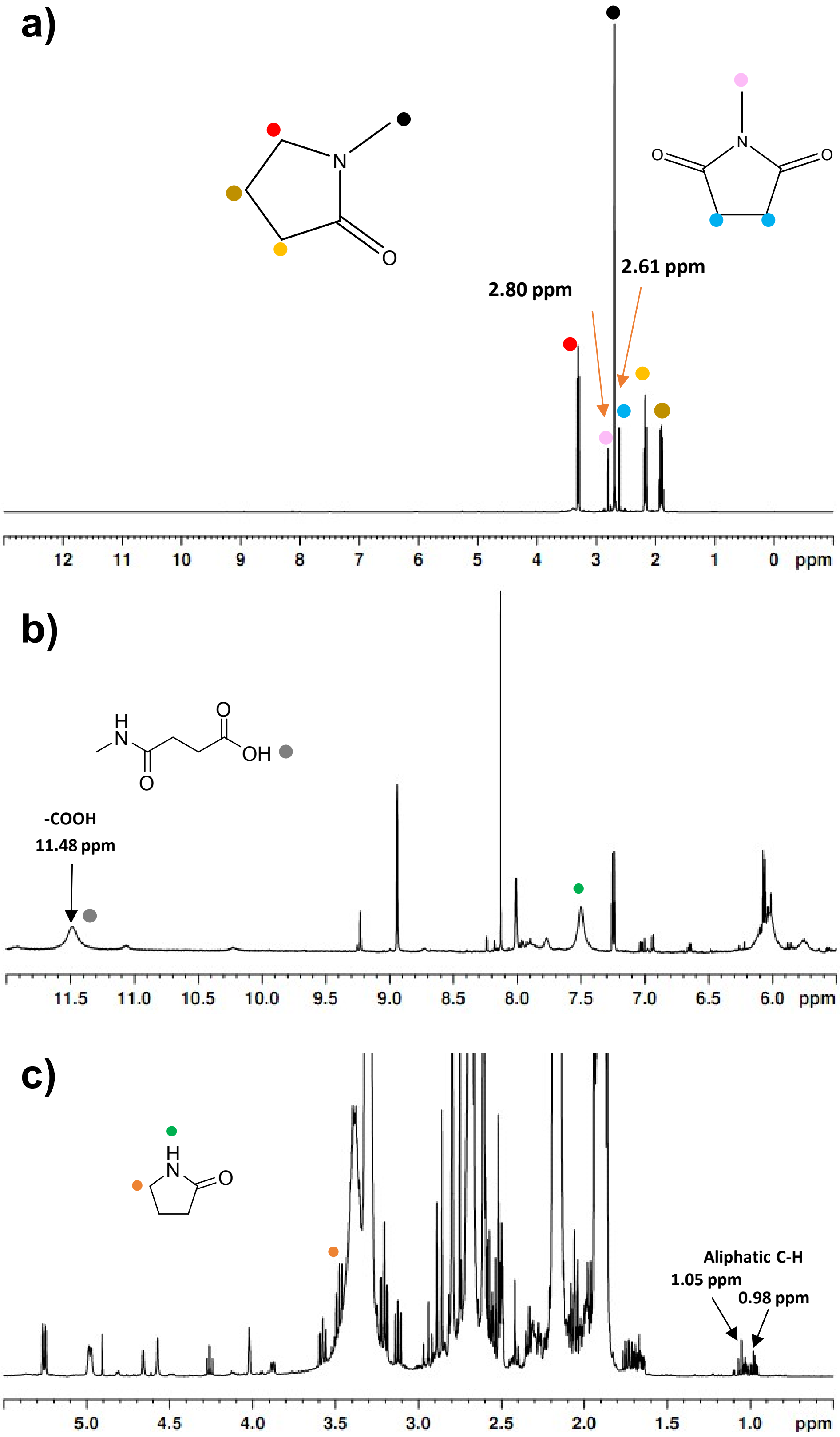

Figure S6. (a) ^{1}H-NMR spectra of a MoS_2 nanosheets/NMP solution after heating for 3 h at 140°C under O_2 atmosphere before purification. (b)-(c) Magnified spectra.

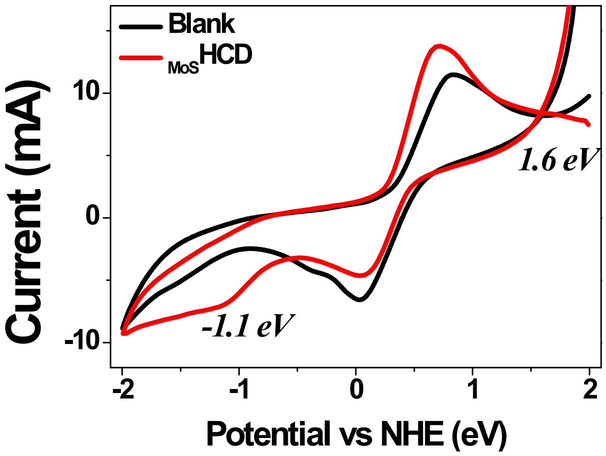

Figure S7. Cyclic voltammogram of $_{MoS}$HCDs. A Pt disk electrode and silver wire w ere used as working, counter electrode and quasi-reference electrodes, respectively, in TBAP solution. Fc was used as a standard and a scan rate was 100mV/s.

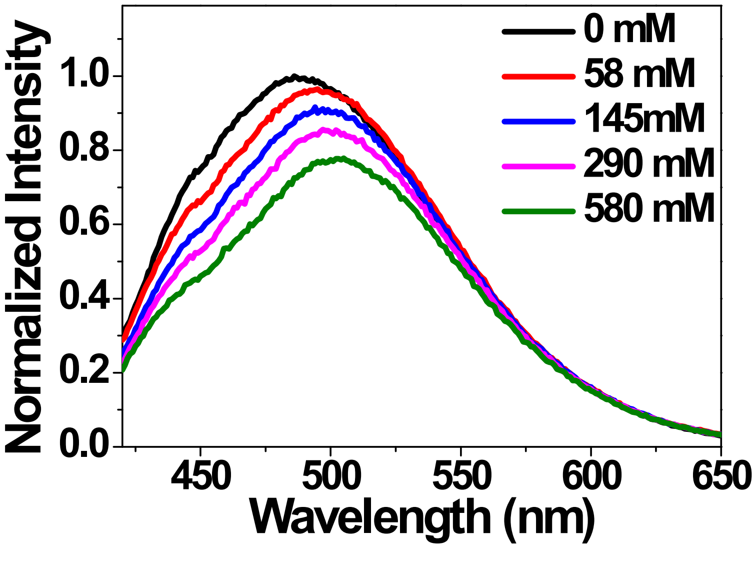

Figure S8. PL response of $_{MoS}$HCDs to benzylamine at various concentrations (58, 145, 290, and 580 mM).

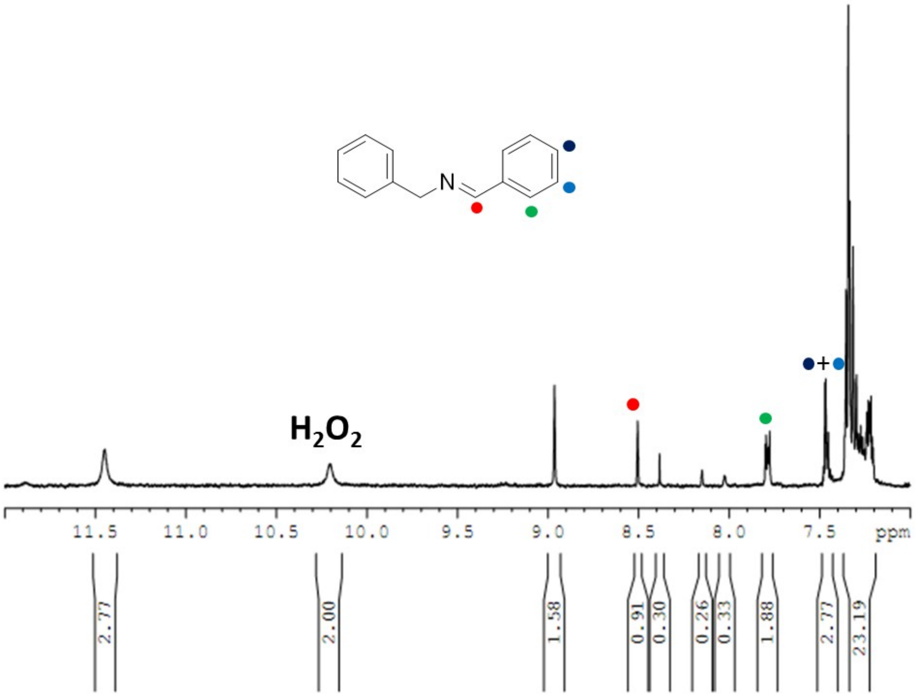

Figure S9. ^{1}H-NMR spectrum of the reaction mixture for the oxidative coupling of benzylamine photocatalyzed by $_{\mathrm{MoS}}$HCDs for 12 h at 25^{o}C.

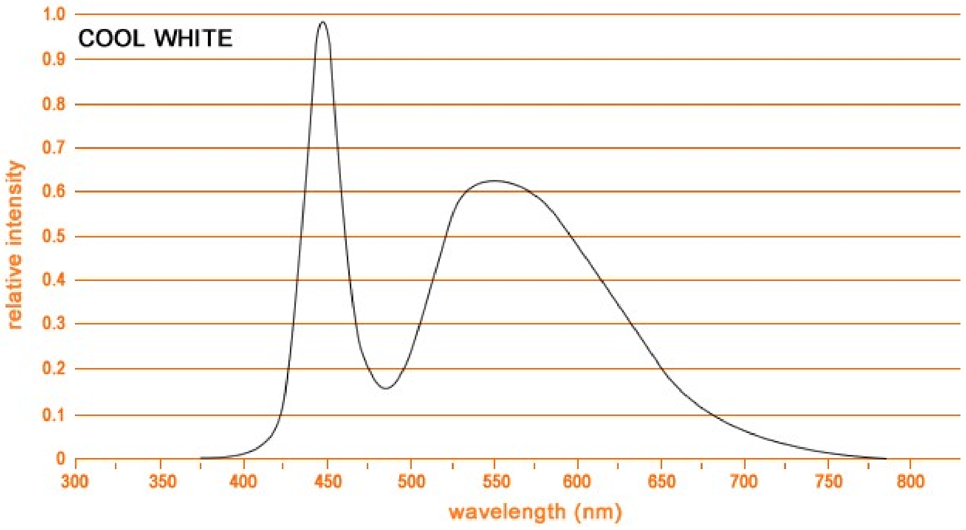

Figure S10. Emission spectrum of a cool white LED lamp.

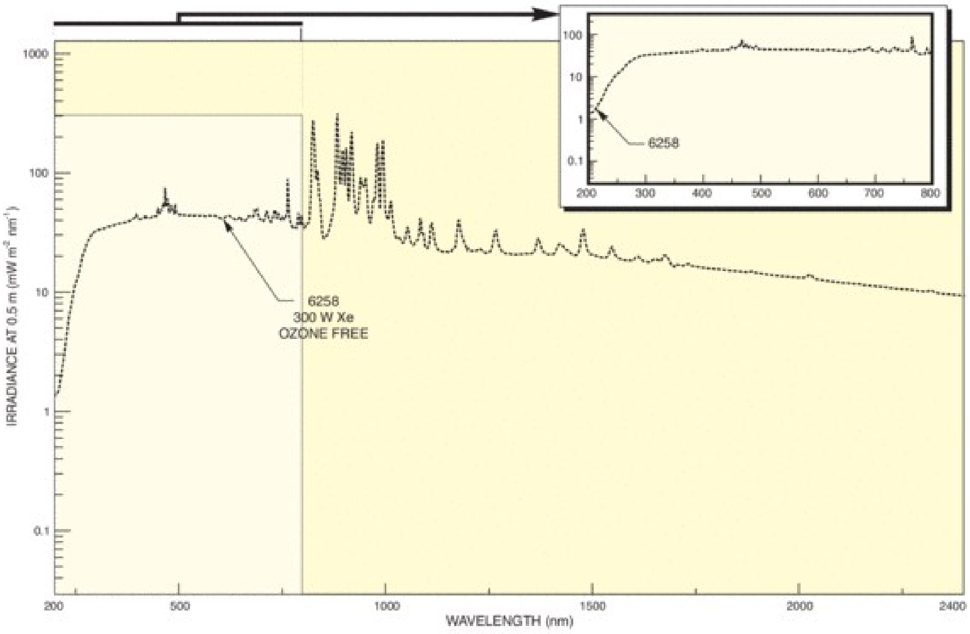

Figure S11. Emission spectrum of a 300 W Xe lamp.