Fabricating carbon nitride based 3D/0D intramolecular donor-acceptor catalyst for efficient photoreduction of CO$_2$

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Characterization

X-ray powder diffraction (XRD) patterns were collected on a Bruker D8 X-ray diffractometer (Germany) in a scanning range of 0.5−50° with a scanning rate of 1° min^{-1}. Fourier transform infrared (FT-IR) spectra of the samples were acquired on a Nicolet Magna-IR 550 spectrometer. The UV–vis diffuse reflectance spectra (UV–vis DRS) of the samples were obtained using a Shimadzu UV-3600 spectrometer with BaSO$_4$ as reference. Photoluminescence (PL) spectra of the samples were collected on a Hitachi F4500 photoluminescence detector (Japan). X-ray photoelectron spectroscopy (XPS) and the XPS valance band (XPS-VB) spectra of the samples were collected using a Thermo Fisher Scientific ESCALAB 250Xi X-ray photoelectron spectrometer. N$_2$ adsorption-desorption isotherm was performed on a Belsorp-Mini analyzer in liquid N$_2$ environment.

The photoelectrochemical properties such as transient photocurrent, electrochemical impedance spectroscopy (EIS) of the samples were performed using a Zahner CHI 852C electrochemical workstation (Germany) with a Xenon lamp (Newport 69920, 300 W). The as-prepared samples were painted on FTO substrates which were used as working electrons, platinum sheet and Ag/AgCl (saturated KCl) were used as the counter electrode and reference electrode, respectively. The working electrode area was 1 cm^2 with 0.5 M Na$_2$SO$_4$ solution as a supporting electrolyte. A bias potential of 0.5 V vs. SCE was applied on the photoanode for the photocurrent test under on-off light conditions. Electrochemical impedance spectroscopy

(EIS) was implemented in 0.5 M Na_2SO_4 solution under the frequency range between 0.1 Hz and 10 kHz at 0.3 V. The amplitude of applied sine wave potential in each case was 5 mV which was carried out using a ZENNIUM electrochemical workstation (Zahner Instruments, Germany), and all electrochemical signals were recorded by a CHI660B electrochemical analyzer (Chen Hua Instruments, Shanghai, China).

The calculation was based on the density functional theory (DFT). The geometry optimization of the catalyst fragments was performed on the Gaussian 09 program equipped with the B3LYP method and 6-311G (d, p) basis set. The HOMO and LUMO of the catalyst fragments were calculated based on the optimized geometry.

Table S1. The structural parameters of the prepared catalysts.

Catalyst	S_{BET} (m^2g^{-1})	Pore Size (nm)	Pore volume (m^2g^{-1})
PY	3.71	16.94	0.03
3D CN	136.02	36.85	1.19
PY-CN-5	91.59	30.84	0.83

Table S2. The surface element composition of the catalyst based on XPS.

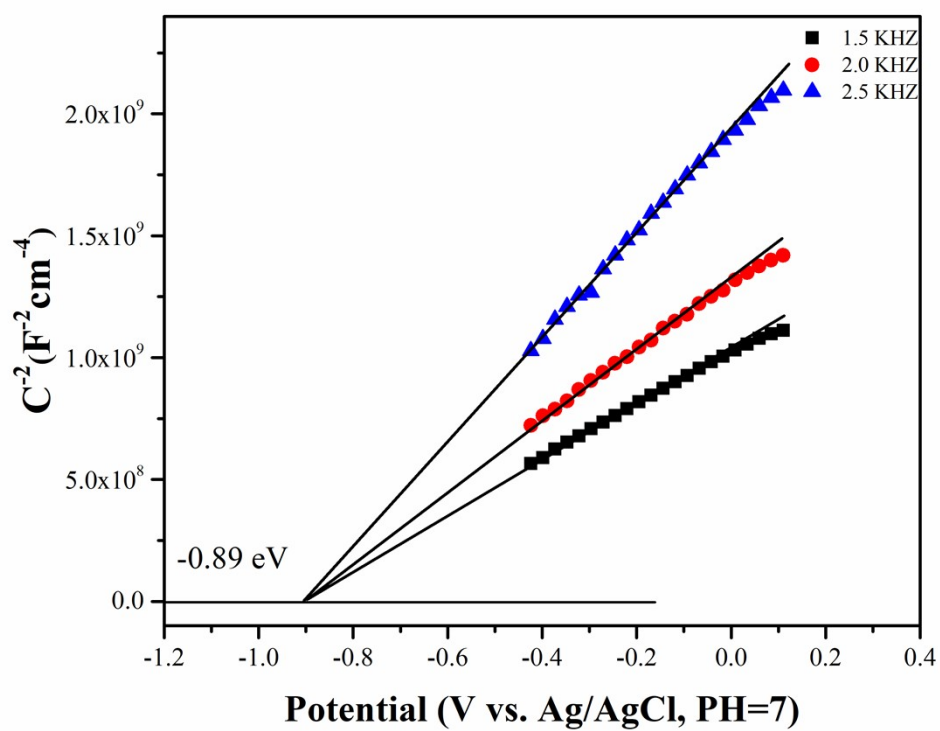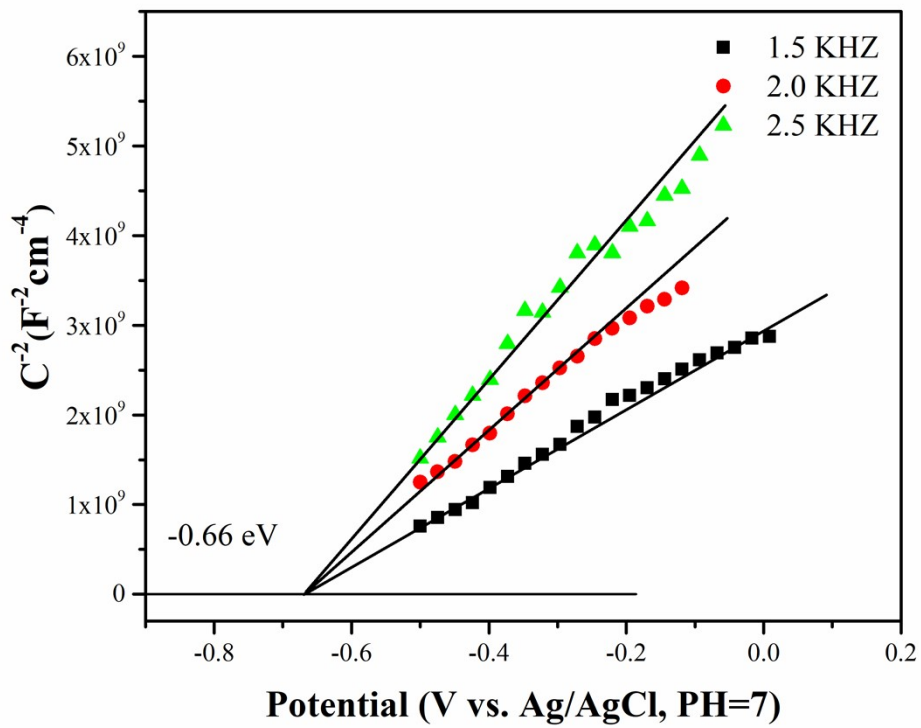| Catalyst	C (atomic%)	N (atomic%)	O (atomic%)
3D CN	44.06	53.37	2.57
PY-CN-5	52.33	41.33	6.33

Figure S1. Mott-Schottky curves of 3D CN.

Figure S2. Mott-Schottky curves of PY-CN-5.