Supporting Information

Interfacial Charge Modulation: Carbon Quantum Dot Implanted Carbon Nitride Double-Deck Nanoframes for Robust Visible-Light Photocatalytic Tetracycline Degradation

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Experimental Section

All the chemicals were analytical grade reagents and used directly without any further purification.

Synthesis of pure CN: pure CN was prepared by a thermal polymerization method. Typically, 1 g melamine was placed into a 50 mL ceramic crucible with a cover. Then the crucible was heated to 550 °C at a heating rate of about 5 °C min^{-1} for 4 h in a muffle furnace. Finally, the crucible was cooled naturally to room temperature and CN powders with canary yellow color were obtained.

Synthesis of CQDs: The CQDs were synthesized according to our previous work.[1] Citric acid (2.625 g) and ethylenediamine (837 µL) were dissolved in deionized water (25 mL). Then, the solution was transferred to a 50 mL Teflon-lined autoclave and heated at 180 ºC for 5 h. After the reaction, the reactor was cooled down to room temperature by water or naturally. The product, which was brown-black and transparent, was subjected to dialysis to afford CQDs

Formation of CM-CQDs and CM Complexes: The CM complexes were prepared by mixing 1g melamine, 1g cyanuric acid and a certain amount of carbon quantum dots (CQDs) (0.039g/mL) in 80 mL of DI water in a beaker under an oil bath at 125 ℃ for 4h. Finally, the beaker was cooled naturally to room temperature and white CM-CQDs powders were obtained. The CM-CQDs complexes formed by using melamine and cyanuric acid with different contents of CQDs (20, 40, 100 and 500 μl) were labelled as CM-CQDs-20, CM-CQDs-40, CM-CQDs-100 and CM-CQDs-500 respectively. The CM was obtained by the same method without the CQDs addition.

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Synthesis of CN-CQDs and CNs: A very similar procedure to CN was conducted to synthesize CN-CQDs. The only difference was that CM-CQDs powders were used as precusor for thermal polymerization. The CN-CQDs derived from CM-CQDs-20, CM-CQDs-40, CM-CQDs-100 and CM-CQDs-500 were denoted as CN-CQDs-20, CN-CQDs-40, CN-CQDs-100 and CN-CQDs-500 respectively. The product obtained by calcination CM was denoted as CNs.

Characterizations: The morphologies of samples were acquired by the field-emission scanning electron microscopy (SEM) (Hitachi S-4800). Transmission electron microscopy (TEM) images were characterized by the Hitachi H600 with 200 kV acceleration voltage. Powder X-ray diffraction (XRD) analysis were conducted on a PANalytical X'pert diffractometer operated at 40 kV and 40 mA using Cu Ka radiation. X-ray photoelectron spectroscopy (XPS) was performed by using a Thermo Scientific Escalab 250Xi spectrometer and Fourier transform infrared (FTIR) spectra were carried out a Thermo Nicolet 6700 spectrometer. UV-vis spectroscopy was recorded on a Shimadzu UV-2600 spectrophotometer. Nitrogen adsorption/desorption measurement was measured on -196 °C using a Micromeritics instrument (3Flex Version 3.01). Classic relative pressure range (P/P0 = 0.05-0.20) was performed to determine the specific BET surface area. Photoluminescence (PL) spectra were tested by a Hitachi F-7000 fluorescence spectrometer.

Photoelectrochemical measurement: The photoelectrochemical measurements were carried out by using a standard three-electrode system on a CHI660E electrochemical station in 0.5 M Na_2SO_4 used as the electrolyte. The working electrode consisted of 5 mg photocatalysts, which are loaded on the surface of FTO glass (1 cm × 2 cm) evenly. An Ag/AgCl and a Pt plate were employed as the reference and counter electrode, respectively. In this experiment, a 40 W LED lamp was used as the visible-light source. The applied potential was converted into the RHE scale by using the Nernst equation; $E_{RHE}=E_{Ag/AgCl}+0.059×PH+0.197$. The Mott-Schottky plots were performed by an AC voltage magnitude of 7 mV with the frequency of 1000, 1500 and 2000Hz. Electrochemical impedance spectroscopy (EIS) was recorded in the presence of 5 mM $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ at in the frequency range of 0.01 Hz and 1000 kHz. The photocurrent response of the photocatalysts as light on and off was performed without bias voltage.

The photocatalytic activity was assessed by the degradation of tetracycline (TC) or rhodamine (RhB) under a 40 W LED lamp as visible-light source. In a representative photocatalytic degradation

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experiment, TC (40 mL, 40 mgL^{-1}) or RhB (40 mL, 10 mgL^{-1}) with samples (20 mg or 10 mg) were mixed in a glass bottle in the dark with continuous ultrasound for 30 min at room temperature to reach the adsorption-desorption equilibrium between the solvent and sample. During the photoreaction process, 3 mL mixture was gathered in the 0.5 or 1 h intervals. Centrifugal supernatant liquor was measured by a Shimadzu UV-2450 spectrophotometer to log the maximum absorbance at 360 nm for TC and 554 nm for RhB. The degradation ratio (k) of TC or RhB over samples is calculated:

$$k=(1-C_t/C_0) \times 100\%=(1-A_t/A_0) \times 100\% \tag{1}$$

Where C_0 is the primeval concentration of organic pollutants, C_t is the concentration after degrading. A_0 and A_t are the relevant absorbance value.
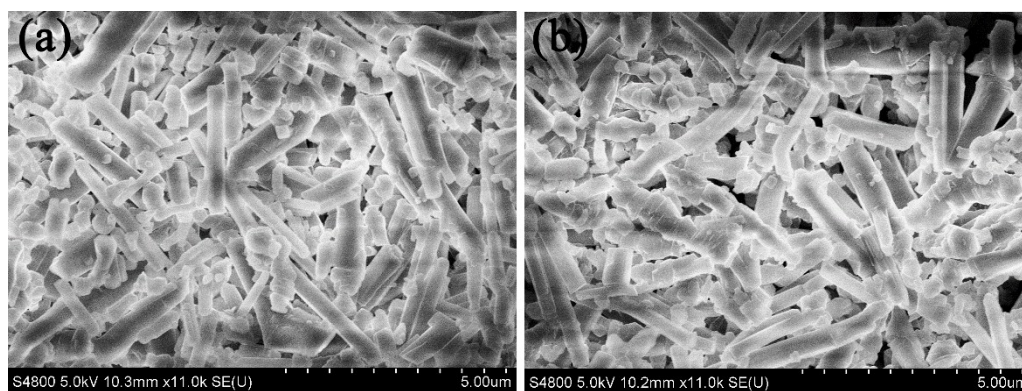

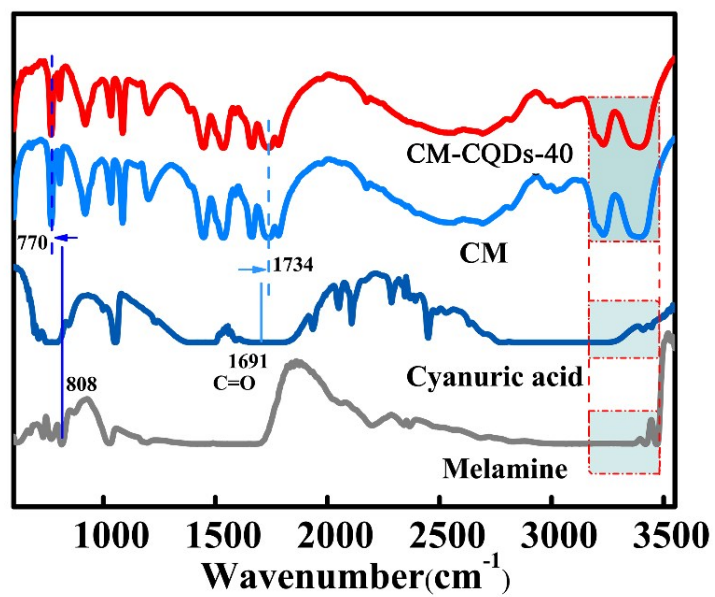**Figure S1.** SEM images of a) CM and b) CM-CQDs-40.

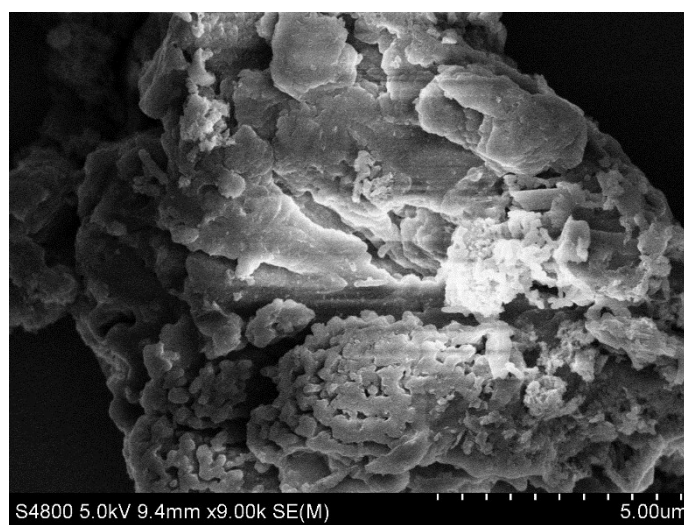**Figure S2.** FTIR spectra of CM, CM-CQDs-40, cyanuric acid, and melamine.

Figure S3. SEM images of pure CN.
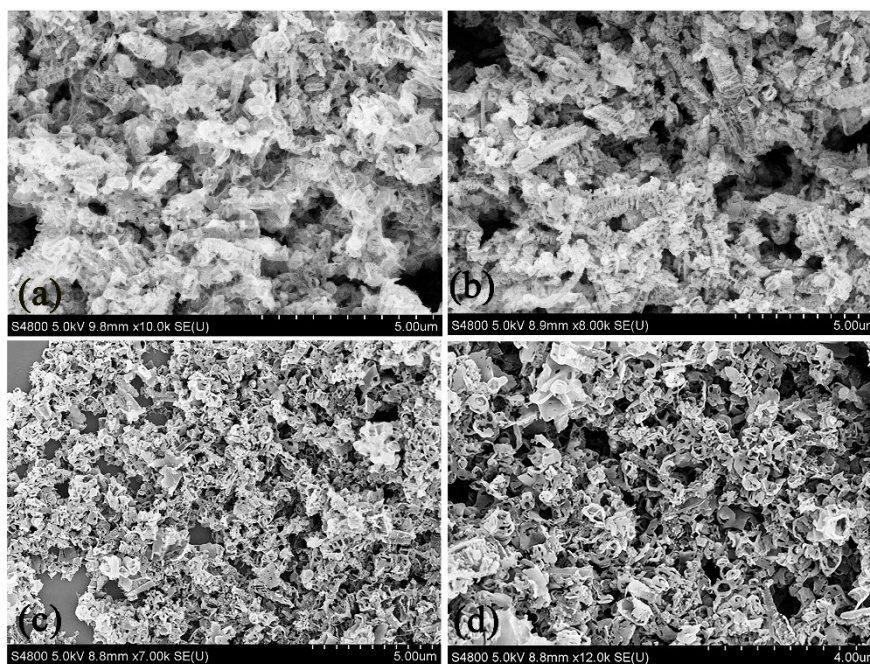
Figure S4. SEM images of a) CN-CQDs-20, b) CN-CQDs-100 and c, d) CN-CQDs-500.

Table S1. Summarized XPS data for CNs and CN-CQDs-40 surface C, N and O atom ratios determined from quantitative analyses are provided.

samples	XPS		
	C	N	O
CNs	45.7%	49.8%	4.5%
CN-CQDs-40	61.1%	30.2%	8.7%

Table S2. Summarized XPS data for CNs and CN-CQDs-40 surface C/N atom ratios determined from quantitative analyses are provided.

samples	XPS
	C/N
CN	0.92
CN-CQDs-40	2.02

Table S3. Band positions of CNs, CN-CQDs-20, CN-CQDs-40 and CN-CQDs-100. All the values in tables are referenced to the electrochemical scale of the reversible hydrogen electrode.

Product	CB, eV (NHE)	VB, eV(NHE)	E_g, eV
CNs	-0.49	2.28	2.77
CN-CQDs-20	-0.41	2.33	2.74
CN-CQDs-40	-0.38	2.35	2.73
CN-CQDs-100	-0.34	2.37	2.71

Table S4. Comparison of TC photodegradation efficiency of CN-CQDs-40 photocatalyst with another CN-based photocatalysts under visible light irradiation.

Photocatalyst	Photocatalyst dosage [g/L]	Light source	Concentration [mg/L]	Photodegradation Removal efficiency	Photodegradation efficiency (h^{-1})	Ref.
CN-CQDs-40	0.5	40W LED lamp	40	60min, 74%	1.2	This work
B-CN	0.5	Xe lamp	10	180min, 98%	1.37	[2]
α-Fe$_2$O$_3$-CN	0.4	500w Xe lamp	20	-	1.2	[3]
GO/CN/BiOI	0.3	LED lamp	30	100min, 74%	-	[4]
S doped CQDs-CN	1	300W Xe lamp	20	60min, 83%	1.75	[5]
CN/Ag/P3HT	1	100W LED lamp	20	-	0.3168	[6]
Cl-CN	0.5	300W Xe lamp	10	120min, 92%	1.2	[7]
BiOI/CN/CeO$_2$	-	300W Xe lamp	20	120min, 92%	1.2	[8]
ZnIn$_2$S$_4$/CN	0.4	500W Xe lamp	50	120min, 85%	0.6	[9]
Fe-CN-graphite	0.5	300W Xe lamp	20	120 min, 99%	-	[10]
carbon nanotube-CN	0.5	300W Xe lamp	20	-	2.88	[11]
carbon plane/CN/TiO$_2$	1.0	500 W Xe lamp	10	180min, 94%	1.8	[12]
CQDs/CN	0.5	250W Xe lamp	10	240min, 80%	0.3852	[13]
Ag/Fe$_3$O$_4$/CN	0.5	300W Xe lamp	20	90min, 98%	1.308	[14]
RGO/CdIn$_2$S$_4$/CN	1.0	500 W Xe lamp	10	180 min, 74%	0.462	[15]
WO$_3$/CN/Bi$_2$O$_3$	1.0	300W Xe lamp	10	60 min, 80%	1.422	[16]
Acid modified CN	0.5	300W Xe lamp	40	60min, 86%	1.944	[17]
Ag/Bi$_5$FeTi$_3$O$_{15}$/CN	0.5	300W Xe lamp	20	40min, 90%	2.79	[18]
CN/CdS	0.5	35W Xe lamp sunlight	50	60min, 80%	1.17	[19]

Table S5. Comparison of RhB photodegradation efficiency of CN-CQDs-40 photocatalyst with another CN-based photocatalysts under visible light irradiation.

Photocatalyst	Photocatalyst dosage(mg)	Light source	Initial concentration (mg/L)	Photodegradation efficiency (h^{-1} 10 mg^{-1})	Ref.
CN-CQDs-40	10	40W LED lamp	10	2.04	This work
Red P-CN	40	300W Xe lamp	10	0.78	[20]
MIL-88A-CN	100	1000W iodine lamp	10	0.96	[21]
CN nanosheets	100	300W Xe lamp	10	0.31	[22]
B/P-CN	100	300W Xe lamp	10	0.19	[23]
CdS-CN	30	300W Xe lamp	7	1.67	[24]
SnO_2-CN	100	visible light source	50	0.27	[25]
Oxalic acid/N-GQD-CN	50	500W Xe lamp	15	2.05	[26]
N-deficient CN	50	150W Xe lamp	5	0.59	[27]
Ni-Mn-LDH-CN	100	Hg lamp	50	0.18	[28]
WO_3-CN	100	XG500 Xe lamp	10	0.09	[29]
BiOCl-CN	30	300W Xe lamp	10	0.82	[30]
Flake-like CN	100	300W Xe lamp	10	0.13	[31]
P doped CN	50	250W sodium lamp	10	0.08	[32]
Na-CN	50	250 W sodium lamp	10	0.08	[33]
Ka-CN	50	250 W sodium lamp	10	0.13	[34]
Ka-Na/CN	50	250 W sodium lamp	10	0.20	[35]
$[WO4]^{2-}$/CN	100	300W Halogen lamp	10	0.13	[36]
YVO_4/CN	100	350W Xe lamp	10	0.23	[37]
TiO_2/In_2O_3/CN	80	300W Xe lamp	10	0.35	[38]

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