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A "Pillared" Process to Construct Graphitic Carbon Nitrides Based Functionalized Mesoporous Materials

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1. Experimental Section

Preparation of pillared g-C_3N_4 nanosheets by nanoparticles

All reagents were analytical grade and used without further purification.

Synthesis of g-C_3N_4 nanosheets: g-C_3N_4 was synthesized by heating dicyandiamide in a muffle roaster at 600 ℃ and holding the sample at the same temperature for another 4 h in air.[S1,S2,S3] g-C_3N_4 nanosheets were prepared according to a previously reported method:[S3] the as-prepared g-C_3N_4 (4 g) was mixed with 52 g of H_2SO_4 (98 wt.%) and 20 g of oleum (with free SO_3 20 wt.% ~ 25 wt.%) in a 100 mL of flask and stirred at 140 ℃ for 3 h. Then the mixture was then heated up to 170 ℃ and held at that temperature for another 3 h before being cooled down to ambient temperature. After that, the mixture was injected into 800 mL of deionized water at 80 ℃ under vigorous stirring, and a suspension was formed. When temperature was lowered down to room temperature, the suspension was filtered with the filtrate collected for further experiments.

Synthesis of silica sol solution(α): As a typical procedure for the synthesis of silica sol solution,[S4] 0.85 g of HNO_3 (68 wt.%), 36 g of H_2O, and 17.5 g of C_2H_5OH were mixed together and a colorless solution was obtained after stirring for 2 min. Then, 20.8 g of tetraethyl orthosilicate (TEOS) was added dropwise to the above solution. The mixture was further vigorously stirred at 70 ℃ for 3 h, and a homogeneous colorless solution was obtained. The silica sol solution obtained with method was referred to α.

Synthesis of silica sol solution(β): In another procedure, 0.43 g of HNO_3 (68 wt.%), 5.76 g of H_2O, and 37.95 g of C_2H_5OH were mixed together and a colorless solution was obtained after stirring for 2 min. Then, 20.8 g of TEOS was added dropwise to the above solution. The mixture was further vigorously stirred at 70 ℃ for 3 h, and a homogeneous colorless solution was obtained, which was referred to β. The size of α silica sol was bigger than that of β silica sol according to the literature.[S4]

Synthesis of SiO_2-xN/g-C_3N_4 composites: In a typical synthesis, the silica sol solution (α (β) samples 2.58 (3.74), 6.45 (9.36), 10.32 (14.98) and 14.19 g (20.6 g) corresponding to 0.2, 0.5, 0.8 and 1.1 g of silicon dioxide, respectively) was added into 100 mL of the as-prepared CNS filtrate and stirred for 2 min. Then the mixture was poured into 100 g of diluted ammonia solution (5 wt.%). After being held in an ice-water bath for about 0.5 h, the solid products were separated by

filtration, washed by water and ethanol, and dried in vacuum at 60 ℃. The final products were obtained after calcination at 300 ℃ for 4 h. The samples were referred to as SiO_2-*xN*/g-C_3N_4 where *x* and *N* denote the ten times weight of silicon dioxide and the silica sol used, respectively.

Adsorption experimenst: Cu^{2+} and Cd^{2+} were used as the pollutants of heavy metal ions pollutants，while malachite green (MG) and methyl blue (MB) were employed as organic pollutant. A mixture of $Cu(NO_3)_2$ and $Cd(NO_3)_2$ aqueous solution (100 mL, 10 mg/L) was administered to flow through a tube (4 mm inner diameter) which was filled with 0.5 g of adsorbent. The residual metal ions in the solution were measured by Inductively Coupled Plasma Optical Emission Spectrometry (Agilent 725-ES, ICP). MG and MB (20 mg/L, 50 mL) were mixed with the adsorbent (30 mg), and the adsorption process was monitored by a UV-vis spectrophotometer (Shimadzu 2550).

Characterization of samples

Nitrogen adsorption-desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 analyzer. Before measurements, the samples were degassed in vacuum at 150 ℃ for at least 6 h. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distributions were determined using Barett-Joyner-Halenda (BJH) model based on the desorption branch.

Powder X-ray diffraction (XRD) patterns were recorded with a Shimadzu XD-3D X-ray diffractometer with monochromatized Cu Kα radiation. Fourier transform infrared (FT-IR) spectra were collected on a Nexus 870 spectrophotometer in KBr pellets. X-ray photoelectron spectroscopy (XPS) were collected on a photoelectron spectrometer (VG ESCALAB 210) with a monochromatic X-ray source of Mg Kα ($h\nu$ = 1253.6 eV). Elemental analysis was performed with a VarioE-L cube form Elementar Analysensysteme GmbH to determine nitrogen, carbon, and hydrogen contents in the samples. Transmission electron microscopy (TEM) measurements were performed using a TECNAI G^2 F20 field emission transmission electron microscope operated at acceleration voltage of 200 kV. All samples were ultrasonically dispersed in ethanol and drop-cast onto copper grids covered with carbon film before being transferred into the TEM chamber. Thermal gravimetric (TG) analysis were conducted using a Zetzsch Sta 449F3 in a continuous flow of air (20 mL/min) from room temperature to 700 ℃.

2. Supporting information for XRD

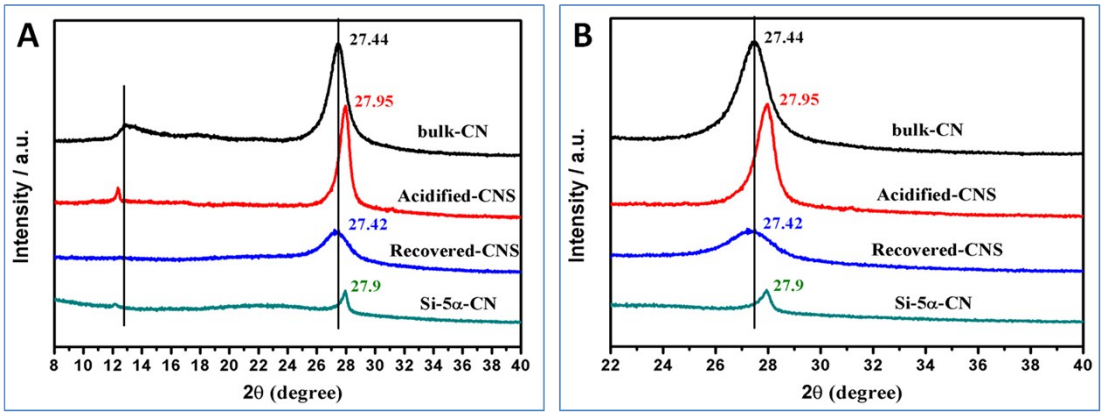

Figure S1. XRD patterns (A) and enlarged partial XRD patterns (B) of bulk g-C_3N_4, acidified g-C_3N_4, recovered g-C_3N_4 that obtained by calcinating acidified g-C_3N_4, and SiO_2-5α-CN.[S3]

3. Flatting effect

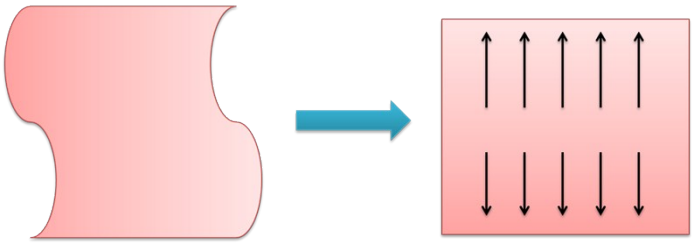

Figure S2. The illustration of flatting effect.

As is known, g-C_3N_4 exhibits slight undulating in the plane of tri-s-triazine cuased by the sp^3 hybridization bridge nitrogen atoms. While when after pillared by SiO_2 nanoparticles, the degree of undulation of g-C_3N_4 decreased, resulted in the strectched properties in-plane and the decrease distance of interlayer packing of g-C_3N_4. We defined this phenomenon as "flatting effect". There are some other evidences, including the weakened absorption intensity of the N-$(C)_3$ group in the IR analysis and the decreased thermal stability of SiO_2-CNS compared to the bulk g-C_3N_4.

4. Supporting information for XPS

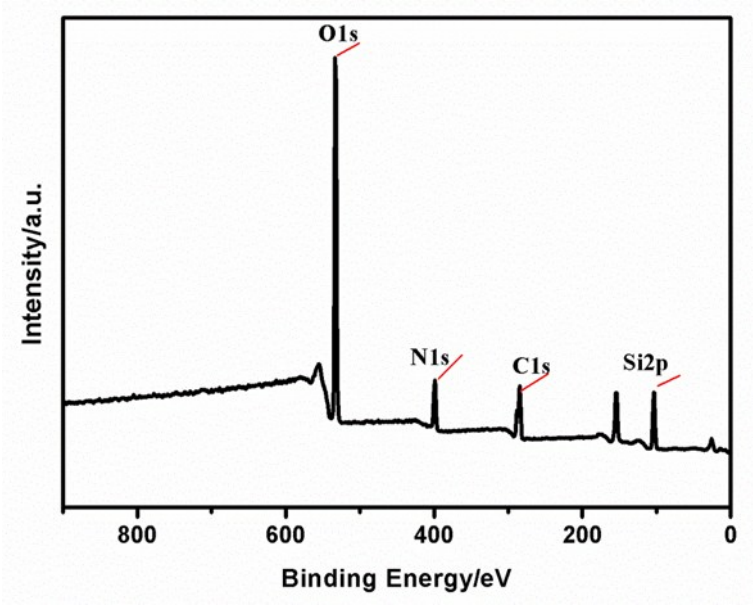

Figure S3. XPS profile of survey of Si-5α-CN sample

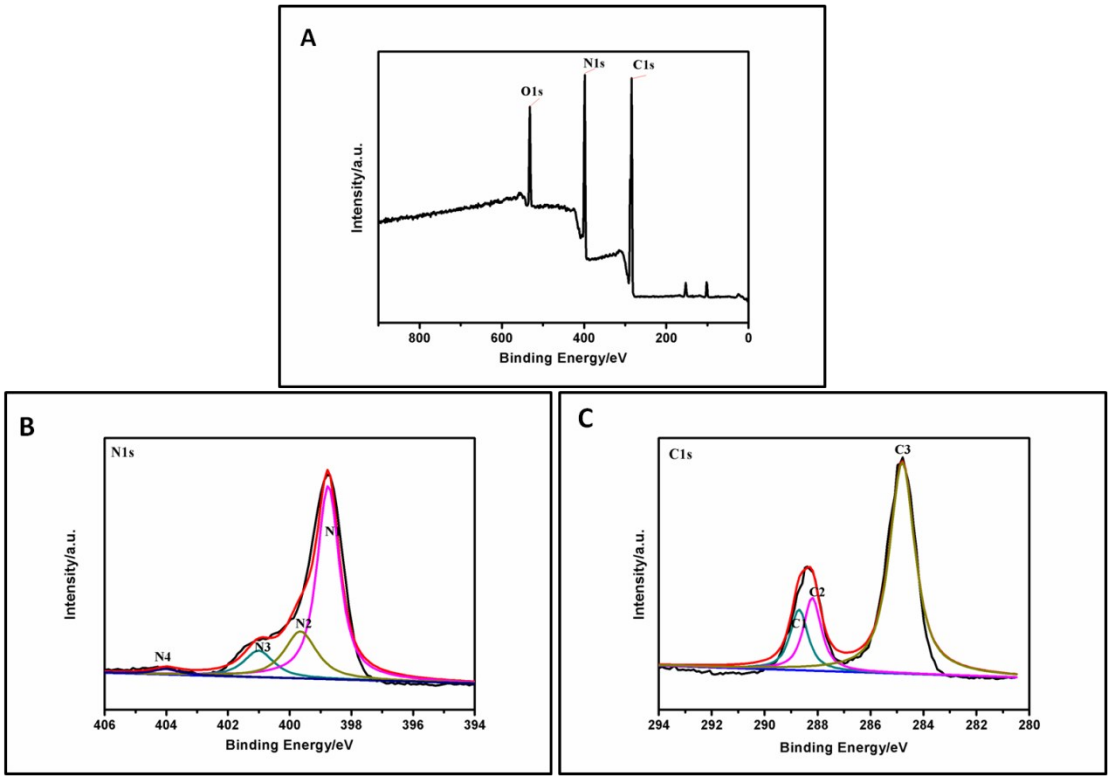

Figure S4. XPS profile of survey (A), N1s (B), C1s (C) of bulk g-C_3N_4

5. Elemental analysis date and the percentage contents of g-C_3N_4 along with SiO_2 contents

Table S1. C, N contents (wt.%) and C/N (molar ratio) of the samples

Samples	Si-2α-CN	Si-5α-CN	Si-8α-CN	Si-11α-CN
N	34.35	19.86	13.05	9.78
C	19.72	11.19	8.35	6.59
C/N	0.66	0.66	0.74	0.77

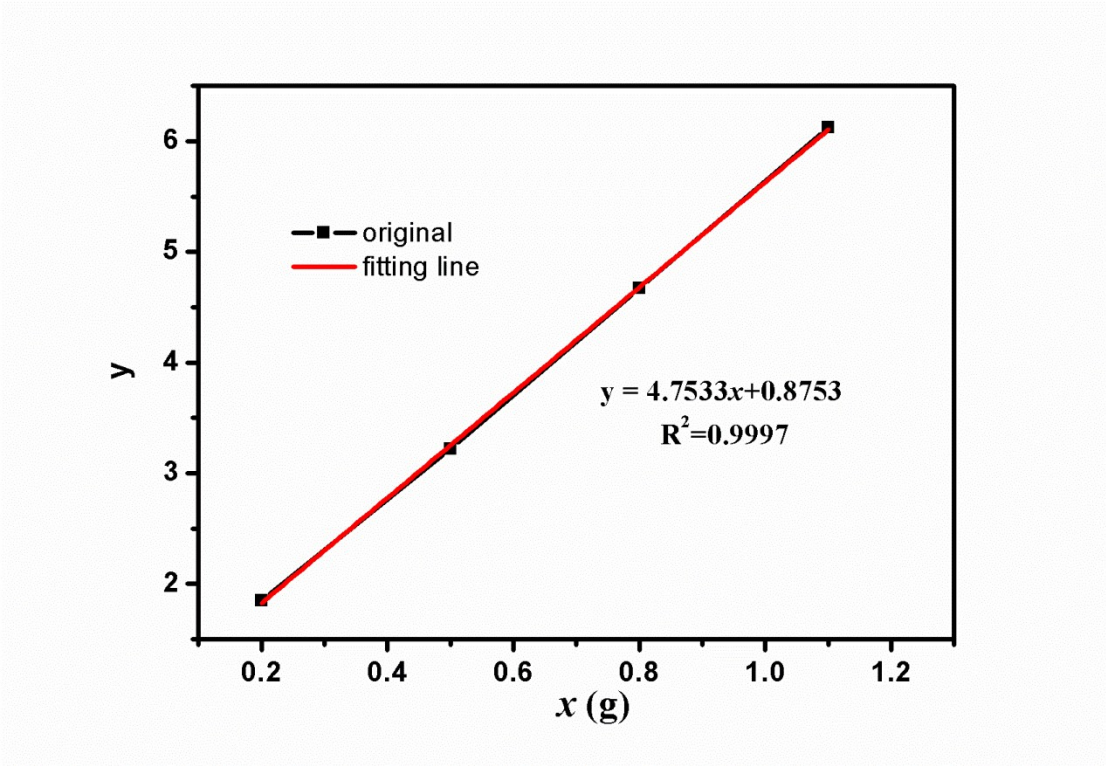

Figure S5. The percentage content of g-C_3N_4 changed with SiO_2 contents (x)

Supposed that the materials were composed only by CNS and SiO_2, the percentage contents of g-C_3N_4 (1/y) can be calculated by the following equation:

$1/y = Wc / (Wc + Ws)$ $\quad$ $y = (Wc + Ws) / Wc$

Where W_C and W_S represent the percentage contents of g-C_3N_4 and SiO_2 calculated with the EA data, respectively. The y axis represents the reciprocal of the percentage content of g-C_3N_4, and the x axis is assigned to the mass of SiO_2 used in the experiments. Curve fit analysis shows the equation is the y=4.7533x+0.8753. By calculated reciprocal of the slope, the mass of g-C_3N_4 in the

samples is about 0.22 g, while 0.5 g of bulk g-C_3N_4 were used as precursors in the experiments. Other g-C_3N_4 has been filtered out during the preparation process of g-C_3N_4 nanosheets.

6. TEM images

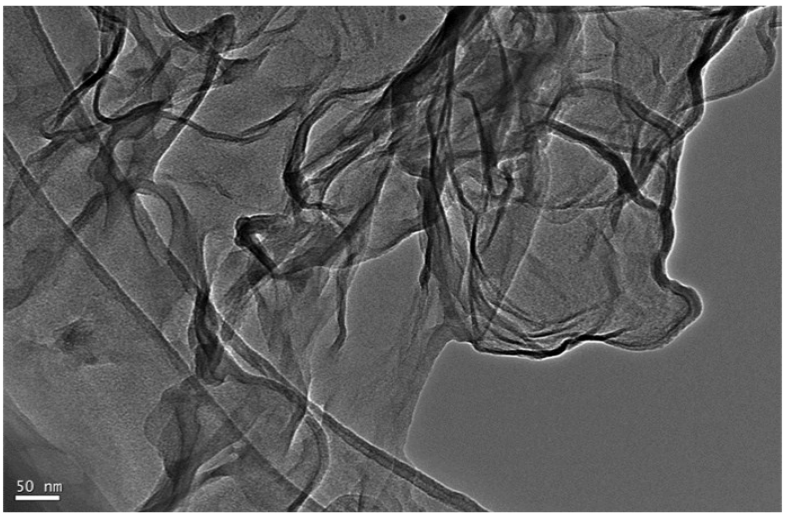

Figure S6. TEM images of g-C_3N_4 nanosheets

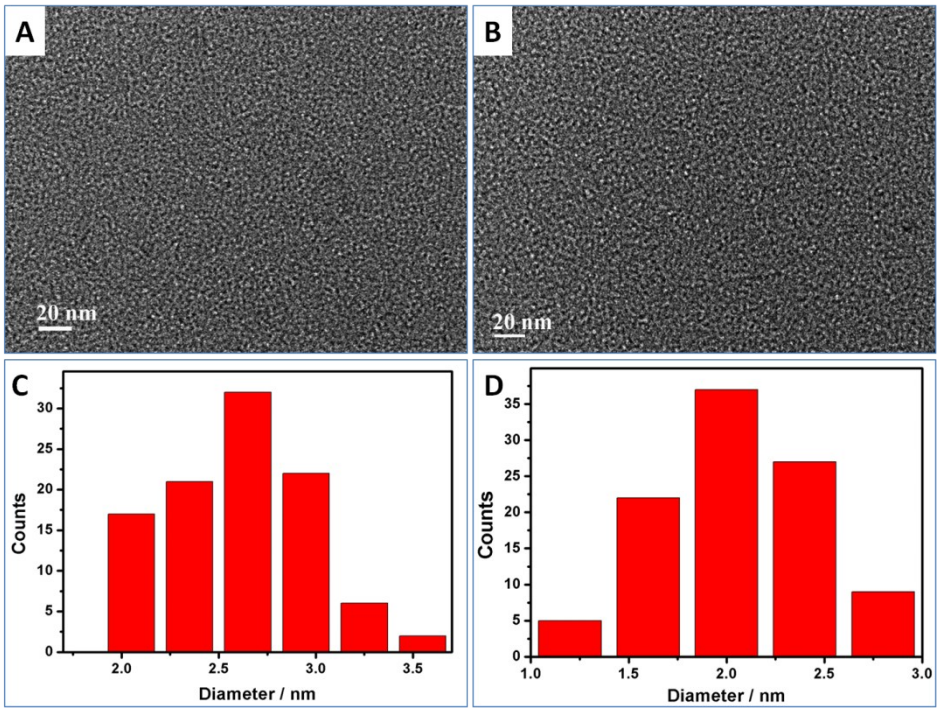

Figure S7. SiO_2 nanoparticles of α (A), β (B) and the corresponding size distribution (C) and (D)

7. Textural parameters, TG and DSC thermograms of Si-*x*N-CN

Table S2. Textural parameters of Si-*x*N-CN

Sample	$S_{BET}(m^2/g)$	Pore size(nm)	$V_p(cm^3/g)$
Si-2α-CN	259	11.9	0.79
Si-5α-CN	407	11.6	1.21
Si-8α-CN	416	11.6	1.25
Si-11α-CN	444	9.99	1.10
Si-2β-CN	227	14.0	0.79
Si-5β-CN	324	11.2	0.79
Si-8β-CN	324	8.6	0.53
Si-11β-CN	355	8.9	0.50

Pore size determined by the desorption branch of isotherm.

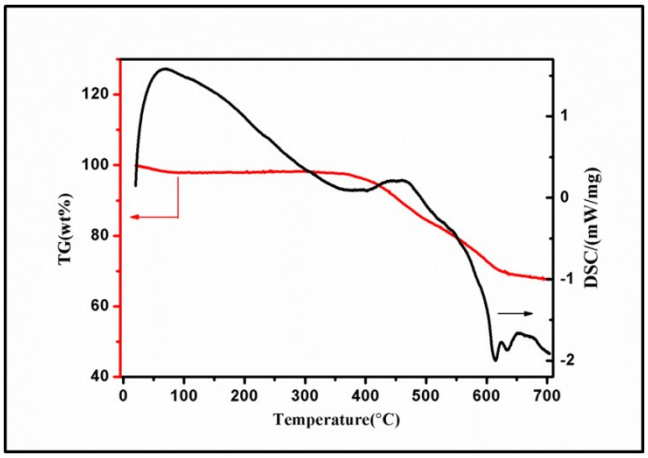

Figure S8. TG and DSC thermograms of Si-5α-CN

8. Supporting information for absorption properties

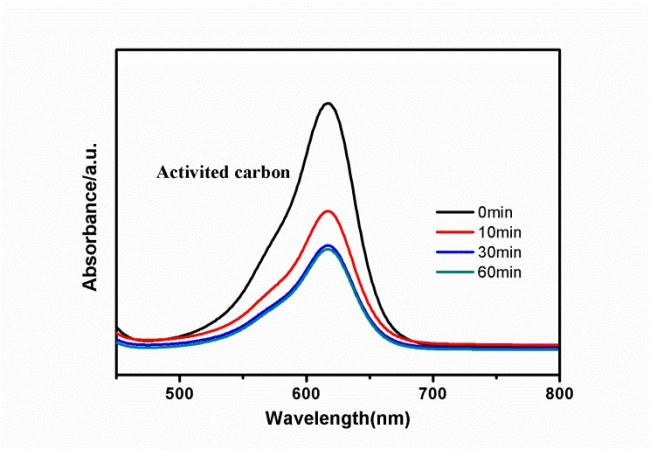

Figure S9. Absorption spectra of activated carbon for MG

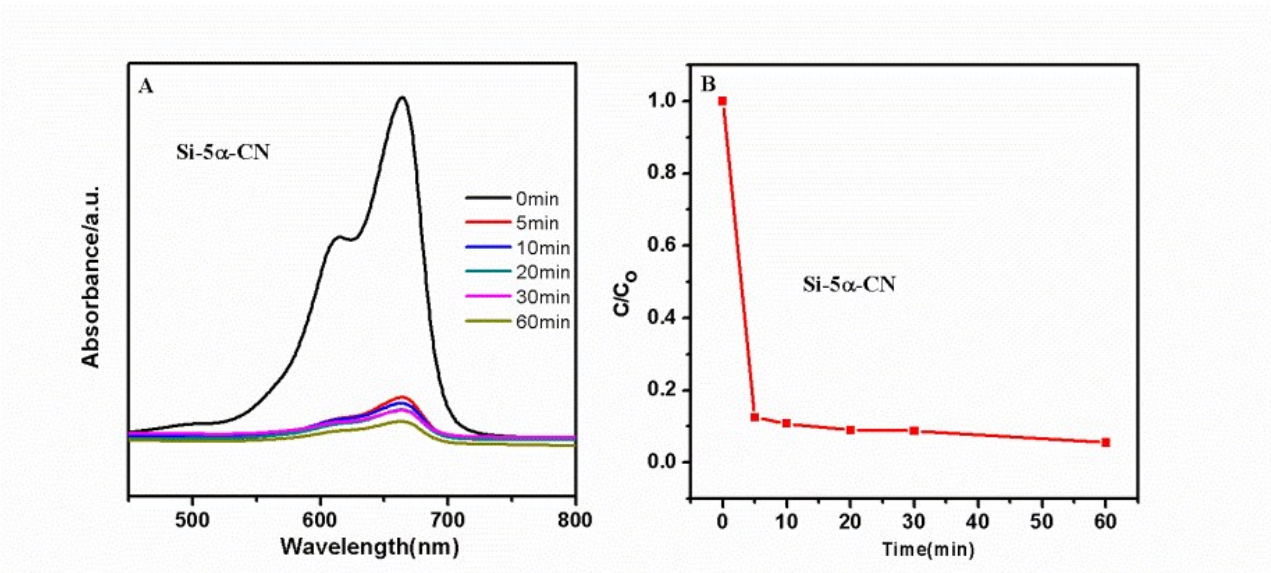

Figure S10**.** Absorption spectra (A) and adsorption rate (B) of an aqueous solution of MB (20 mg L^{-1}, 50 ml) after treatment with Si-5α-CN (50 mg) at different time intervals

References

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S4. Y. Jing, *Journal of Xi'an Polytechnic University*, 2009, **23**, 556-561.