# Nanosheet-assembled hierarchical porous flower-like g-$C_3N_4$ for enhanced photocatalytic $CO_2$ reduction activity

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## Experimental

**Materials.** The following chemical reagents involved in the experiment, including dimethyl sulfoxide (DMSO), melamine, urea, and cyanuric acid, were purchased from Aladdin. $C_2H_5OH$ (99.7%) was purchased from Chengdu Kelon Chemical Reagent Factory. All reagents were analytically pure without further purification.

**Synthesis of precursor (CM).** First, 0.5 g melamine and 0.51 g cyanuric acid were dissolved separately in 20 ml DMSO at a 1:1 molar ratio. A clear and transparent solution was obtained after 3 h of stirring. Then, the two solutions were mixed, and the solution turned white immediately. A white precipitate formed after 15 min of stirring. The suspension was centrifuged, washed several times, and then dried in an oven at 50 °C. The resulting white powder product was CM.

**Synthesis of CMN .** A total of 0.6 g precursor (CM) was dispersed in 20 ml ethanol and stirred in a 60 °C water bath for 3 h. The white suspension was then centrifuged, washed several times with deionized water and ethanol, and dried at 50 °C. The white powdery solid was then calcined at 550 °C for 4 h at a heating rate of 2.5 °C/min. A brown fluffy powder was finally obtained and designated as CMN. Two additional samples, CMN-U and CMN-D, were also prepared for comparison. The CMN after sonication for 2 h was marked as CMN-U, and the sample obtained by the direct calcination of the precursor (CM) was denoted as CMN-D. The calcination conditions for the samples were the same as those for CMN.

**Synthesis of CN.** On the basis of a previous report, melamine and urea were uniformly mixed in accordance with an equimolar ratio and then calcined at 550 °C for 4 h at a heating rate of 5 °C/min. The yellow powder prepared was labeled CN.

**Sample characterization.** XRD patterns were collected on DX-2700 X-ray diffractometer with a scanning range of 5°–80°. The step angle was 0.03°, and the sampling time was 0.2 s. FTIR spectra were collected on Thermo Fisher Nicolet Is10. UV-visible DRS was performed on a UV-vis spectrophotometer (PE Lambda 650 s) (250–800 nm) using Teflon as the standard for reflectivity. SEM images were recorded on FEI Inspect F50. Transmission electron microscopy (TEM) images were given by FEI Tecnai G2 F20 at an acceleration voltage of 200 kV. The specific surface area results were recorded on Quantachrome autosorb iQ using Brunauer–Emmett–Teller equation. The sample was degassed at 150 °C for 6 h before the nitrogen adsorption test. Characterization through TGA–MS was completed by Labsys Evo (TGA) equipped with LC-D 200M PRO mass spectrometer (MS). $CO_2$-TPD was conducted through AutoChem II 2920. The temperature was increased to 700 °C under He atmosphere, and the heating rate was 10 °C/min. Transient fluorescence analysis was conducted on Edinburgh instrument FLSP920 at an excitation wavelength of 375 nm and emission wavelength of 460 nm.

**Photocatalytic activity measurement.** Carbon dioxide was photoreduced in a closed glass reactor. Typically, a 30 mg sample was placed in a shallow dish and ultrasonicated for 5 min with 3 ml ethanol. When the sample was dried, 0.5 ml deionized water was added. Prior to the photoreduction experiment, the reactor was emptied to remove excess air. Then, $CO_2$ gas was introduced, and the light source was turned on (300 W Xe arc lamp). The Photocatalytic On-Line Analysis System (Perfect Light Labsolar 6A) was set up for one 30 min cycle. The product of $CO_2$ photoreduction was detected by gas chromatography (FULI 979011).

**Photoelectrochemical measurement.** Electrochemical workstations CHI660E (Shanghai Chenhua Co., Ltd., China) were used to characterize the electrochemical impedance and photocurrent properties of the samples. The electrolyte and light source were 0.5 M $Na_2SO_4$ and Xe arc lamp (300 W), respectively. In a typical three-electrode system, Ag/AgCl and Pt wires were used as reference electrodes and counter electrodes, respectively. The working electrode was prepared through the doctor blade method: 30 mg polyethylene glycol and 30 mg sample were mixed with 0.5 ml ethanol, and the ground slurry was coated on the F-doped $SnO_2$-coated glass to keep a coating area of ca. 1 $cm^2$ and maintained at 100 °C for 80 min.

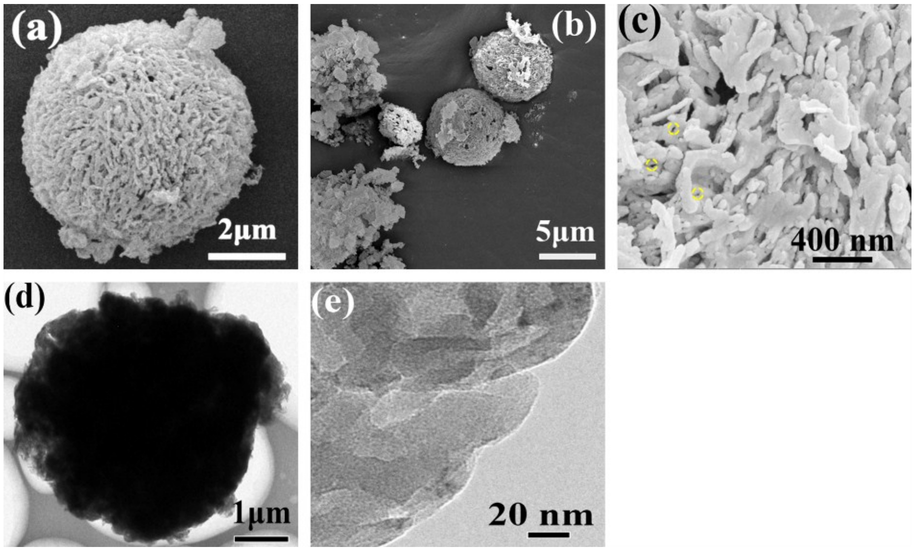


**Fig. S1.** (a–c) SEM images of CMN. (d, e) TEM images of CMN sample.

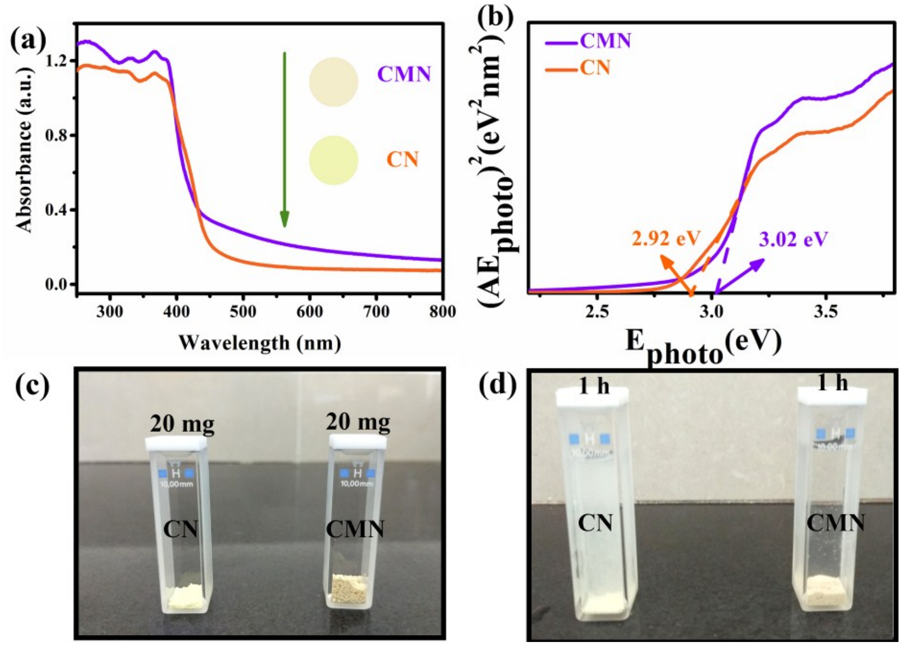


**Fig. S2.** (a) DRS spectra and (b) plots of $(\alpha h\nu)^2$ vs the energy ($h\nu$) of CMN and CN samples. (c) Photograph of CMN and CN samples with a mass of 20 mg. CMN exhibited volume expansion after the insertion of ethanol molecules and polycondensation. (d) CMN and CN samples settled in deionized water for 1 h. CMN showed a better sedimentation performance than CN.

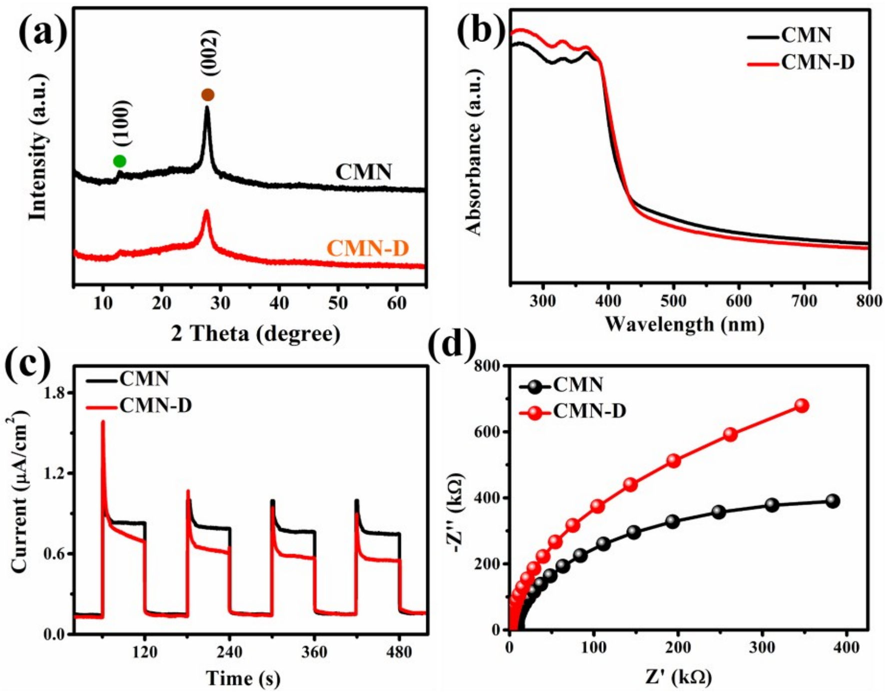


**Fig. S3.** (a) XRD patterns, (b) DRS spectra, (c) Transient photocurrent responses, and (d) electrochemical impedance spectroscopy plots of CMN and CMN-D.

The XRD pattern of CMN and CMN-D (Fig. S3a) showed typical g-$C_3N_4$ characteristic peaks at 13.1° and 27.3°. The diffuse reflectance spectroscopy (DRS) showed the optical properties of CMN and CMN-D (Fig. S3b). Compared with CMN-D, CMN exhibited enhanced light absorption in the ranges of 450–800 nm. The transient photocurrent response (Fig. S3c) indicated that CMN showed a higher photocurrent value than the CMN-D, and the Nyquist plot showed that CMN possessed a smaller arc radius (Fig. S3d). These results indicate that carrier migration and separation of CMN improved compared with those of CMN-D, which are beneficial for photocatalytic activity. The enhanced carrier migration and separation performance is related to the pore structure formed by the intercalation of ethanol molecules. Pore structure promotes the diffusion of carrier.

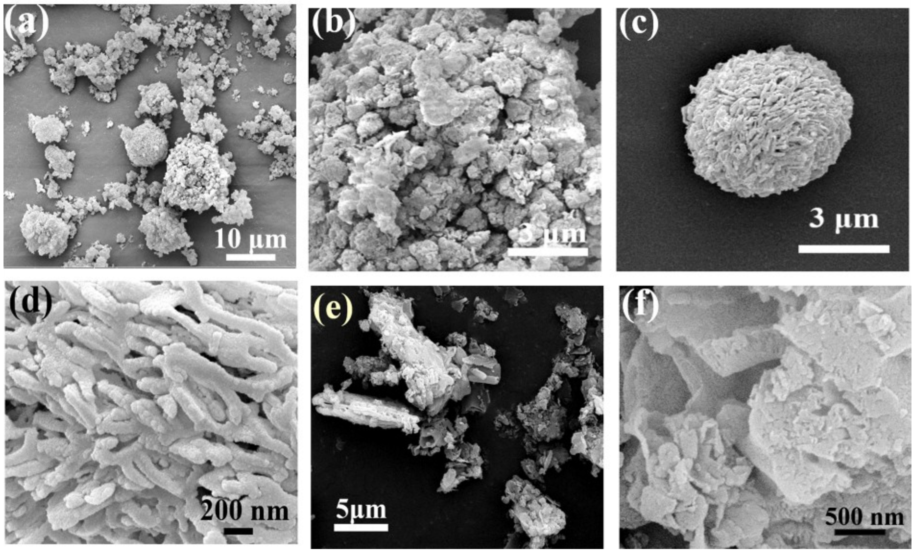


**Fig. S4.** (a, b) SEM images of CMN-U. (c, d) SEM images of CMN-D. (e, f) SEM images of CN.

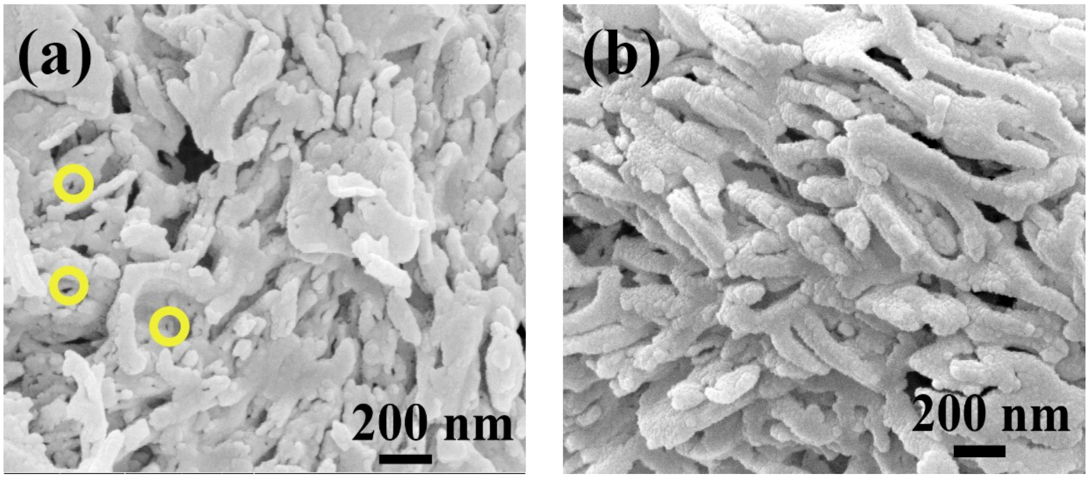
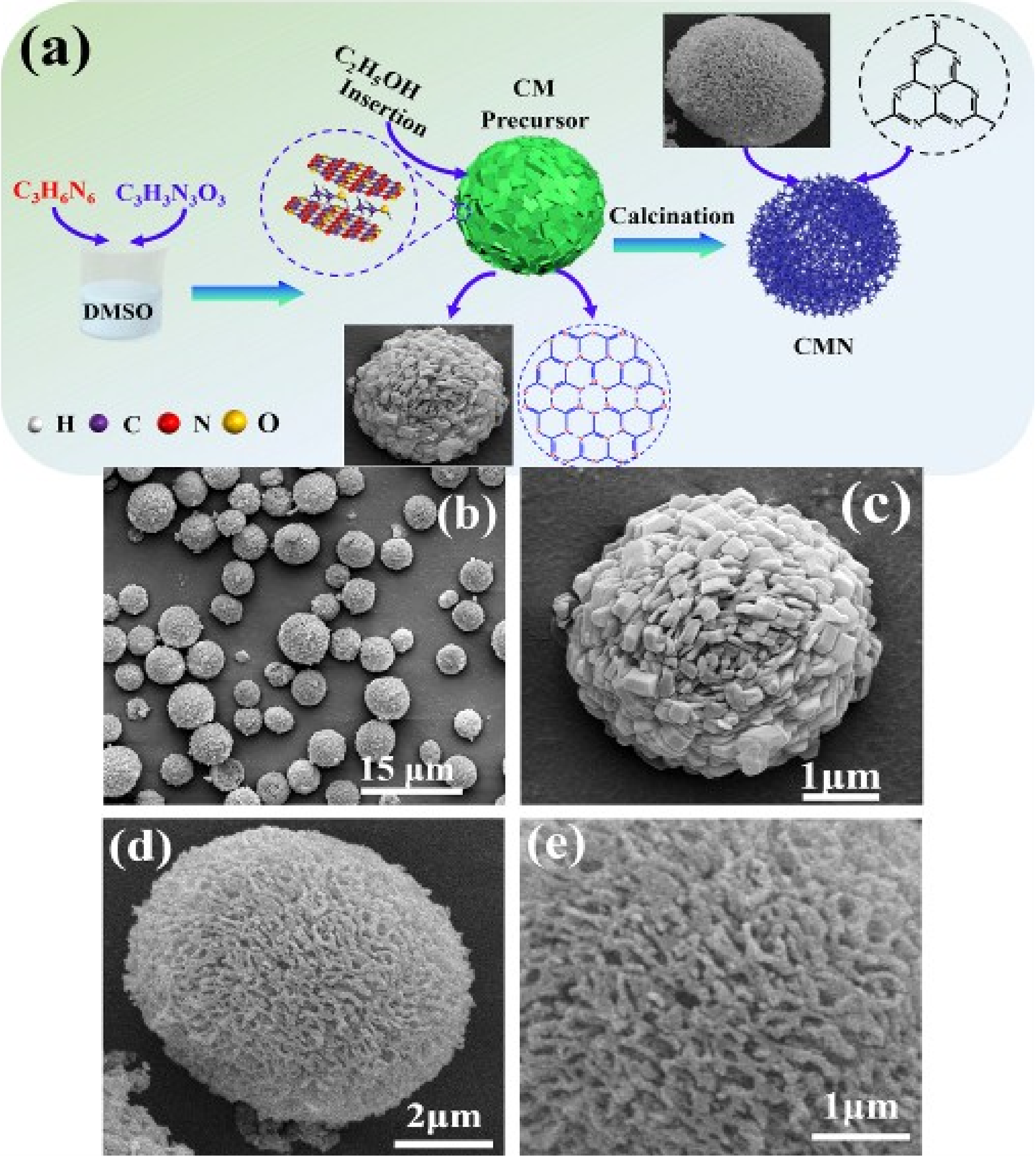


**Fig. S5.** (a) SEM images of CMN. (b) SEM images of CMN-D sample. Compared with CMN, the absence of inserted ethanol molecules can result in thickened monomer sheet and zero pores on the sheets of CMN-D.



**Enlarged Fig. 1.** Schematic of the synthesis of CMN (a). SEM images of CM (b, c) and CMN (d, e). The insertion of ethanol molecules into the supramolecular complex CM formed by the self-assembly of melamine and cyanuric acid resulted in structural expansion during polycondensation, and the final CMN was obtained after thermal exfoliation.