Electronic Supplementary Information

Novel N-doped porous carbon microspheres containing oxygen and phosphorus for CO_2 absorbent and metal-free electrocatalysts

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Experimental Section

Chemicals

Hexachlorocyclotriphosphazene (HCCP) was purchased from Aldrich Chemical Co. Ltd., and sublimated two times before use. 4,4'-oxydianiline (ODA) was purchased from Sinopharm Chemical Reagent Co. Ltd. Triethylamine (TEA), acetonitrile and ethanol were commercially obtained and used as received without further purification.

Synthesis of poly(hexachlorocyclotriphosphazene-co-4,4'-oxydianiline) (PHPODA) microspheres.

HCCP (0.24 g), ODA (0.45 g) and acetonitrile (50 mL) were added into a glass flask. After ultrasonic irradiation for ten minutes, TEA (1.0 mL) was injected to the above solution. And then the solution was maintained at 60 ^{O}C for 8 h under ultrasonic irradiation (150 W, 40 kHz). After the reaction was completed, the product was centrifugated and washed with de-ionized water and ethanol respectively. Then the resulting solids were dried to yield flesh-colored powder.

Synthesis of nitrogen-doped porous carbon microspheres (N-PCMSs) containing oxygen and phosphorus.

The prepared polymer microspheres were mixed with K_2CO_3 at the desired weight ratio (1:1) and then transferred in a quartz boat into a porcelain combustion boat within a stainless steel tube and subjected to carbonization in flowing nitrogen. The temperature program was as follows: temperature was ramped from room temperature to 50 ^{O}C using 5 ^{O}C min^{-1} heating rate and dwelled at 50 ^{O}C for 1 h; then temperature was from 50 ^{O}C to 750 ^{O}C using 1 ^{O}C min^{-1}. The material was kept at the final temperature for 2 h and then cooled to room temperature. Finally, the obtained samples were washed with water and diluted HCl until neutral pH was obtained and finally dried.

Materials Characterization

Scanning electron microscopy (SEM) images of the materials were taken using a JEOL JSM 6700F field emission scanning electron microscopy (FESEM). Transmission electron microscopy (TEM) were performed on a JEOL JEM 2100 transmission electron microscopy with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was obtained on the PHI 5000C spectrometer with a mono - chromated Al X-ray source (h = 1486.6 eV) operated at 250 W. Elemental surface concentration was calculated from peak areas based on the sensitivity factors provided by manufacturer. N_2 adsorption-desorption isotherms were measured at -196 ^{O}C using ASAP 2020 manufactured by Micromeritics, Inc. (Norcross, Georgia, USA).

Prior to adsorption measurements, the samples were outgassed at 300 ^{O}C for 10 h. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.02 - 0.22. Total pore volume (V_t) was estimated from the amount adsorbed at relative pressure $P/P^o = 0.99$. Micropore volume and micropore surface area were obtained from a t - plot. Pore size distributions (PSD) were calculated using the BJH method and the Horvath-Kawazoe (H-K) method. The fourier transform infrared (FT-IR) measurements were conducted on a Perkin-Elmer Paragon 1000 Fourier transform spectrometer. The X-ray diffraction (XRD) patterns of the mesoporous materials were obtained on a Netherlands X'Pert PRO X-ray diffractometer using CuKa (λ=1.54 Å) radiation. Raman spectrum was obtained using a micro-Raman spectroscope (Renishaw-2000) at the excitation wavelength of 632.8 nm.

The CO_2 adsorption-desorption isotherms were measured at 0 and 25 ^{O}C on ASAP 2020. The recyclability measurements were conducted by initial outgassing the sample before adsorption experiment at 300 for 2 h; after that five successive runs of adsorption-desorption isotherms were recorded.

Table S1. Textural properties and elemental composition for the N-PCMSs.

Sample	S_{BET} [a] /m^2 g^{-1}	S_{micro} [b] /m^2 g^{-1}	V_{total} [c] /cm^3 g^{-1}	V_{micro} [b] /cm^3 g^{-1}	Pore size [d] /nm	Element content / at. %			
						C	N	O	P
N-PCMSs	1427	794	1.23	0.36	0.62	83.02	3.65	11.64	1.16

[a] Calculated in the partial pressure (p/p^o) rang of 0.01 to 0.1 which gives the best liner.

[b] Evaluated by the t-plot method.

[c] Total pore volume at relative pressure $p/p^o \approx 0.97$.

[d] Evaluated by H-K method.

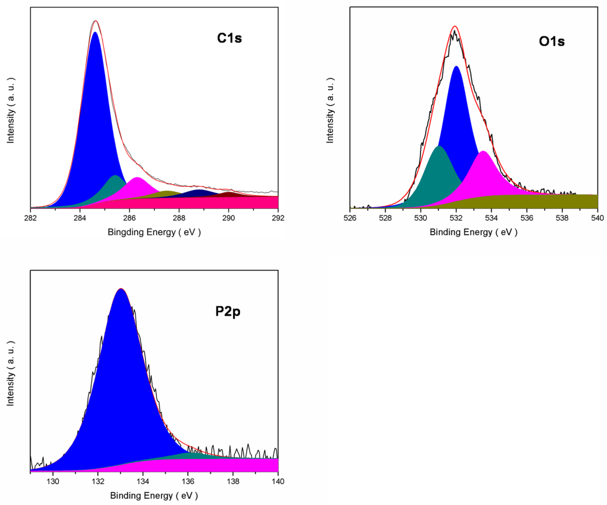

Fig. S1 The fitting XPS spectra of C1s, O1s, and P2p for the N-PCMSs.

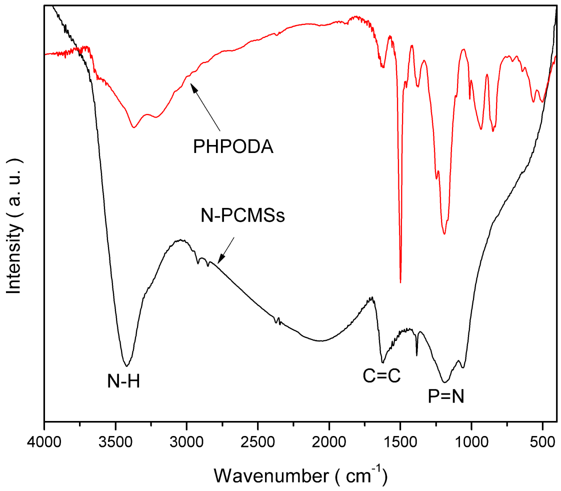

Fig. S2 FT-IR spectra of the PHPODA microspheres and the N-PCMSs.

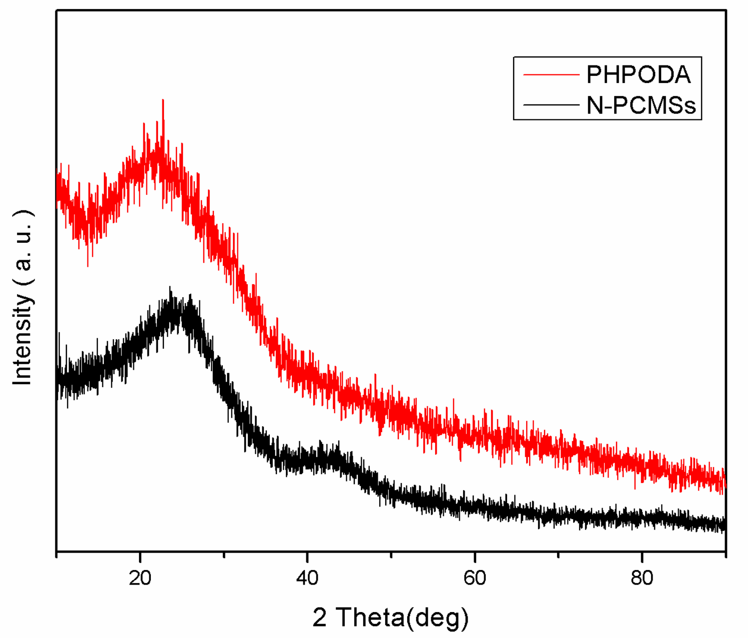

Fig. S3 XRD patterns of the PHPODA microspheres and the N-PCMSs.

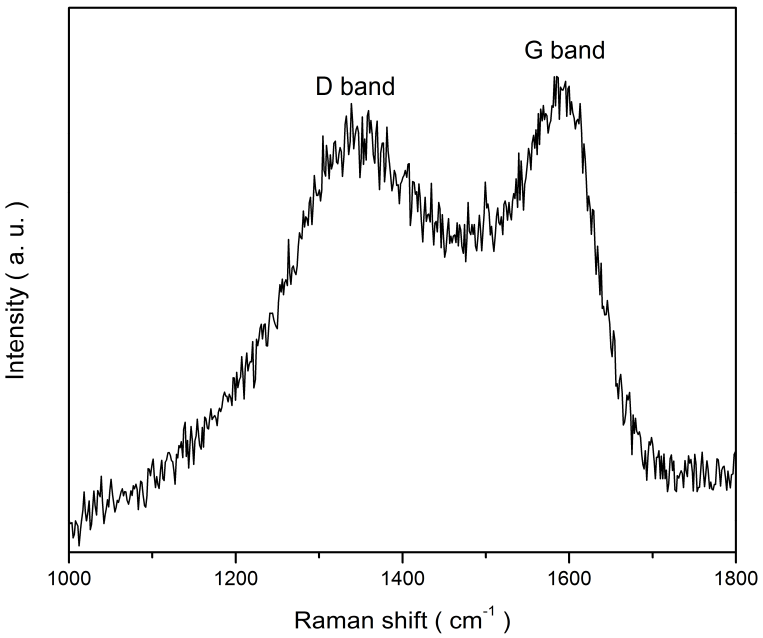

Fig. S4 Raman spectra of the N- PCMSs. The ratio of peak intensity (I_D/I_G) is 0.96.

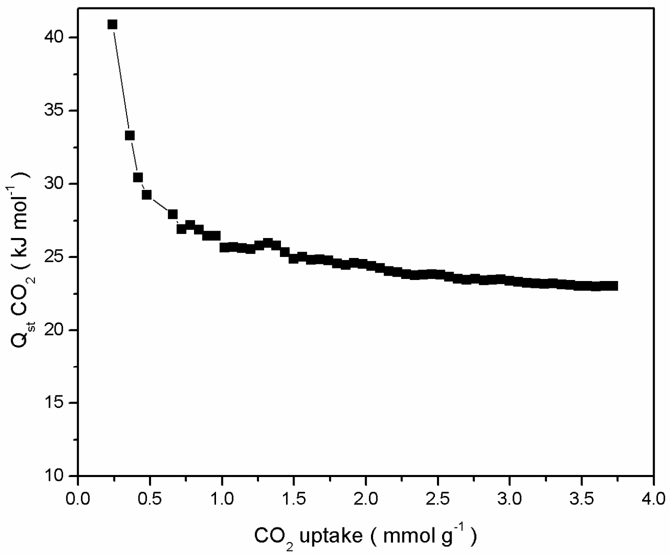

Fig. S5 Isosteric heat of CO_2 adsorption (Q_{st}) for the N-PCMSs as a function of the CO_2 uptake.

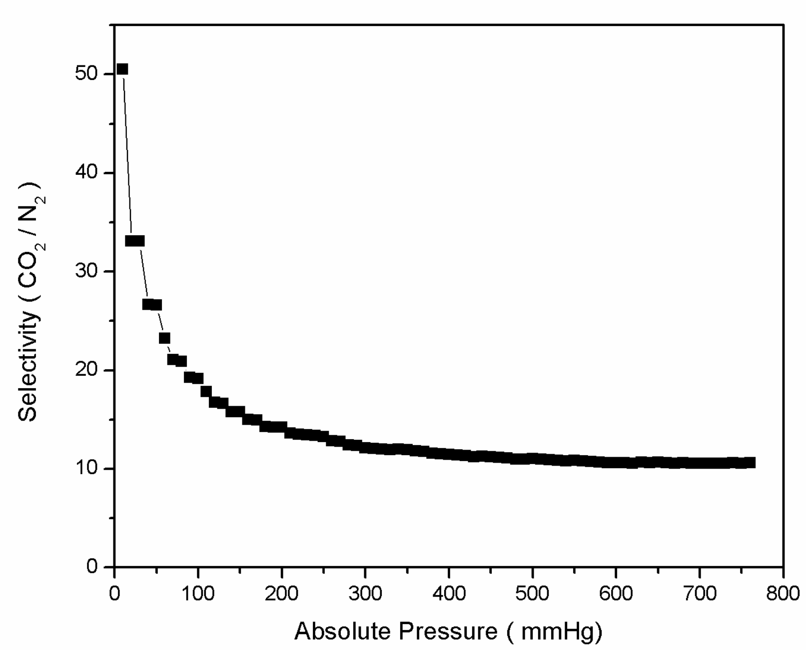

Fig. S6 The selectivity (CO_2/N_2) of the N-PCMSs against the absolute pressure.

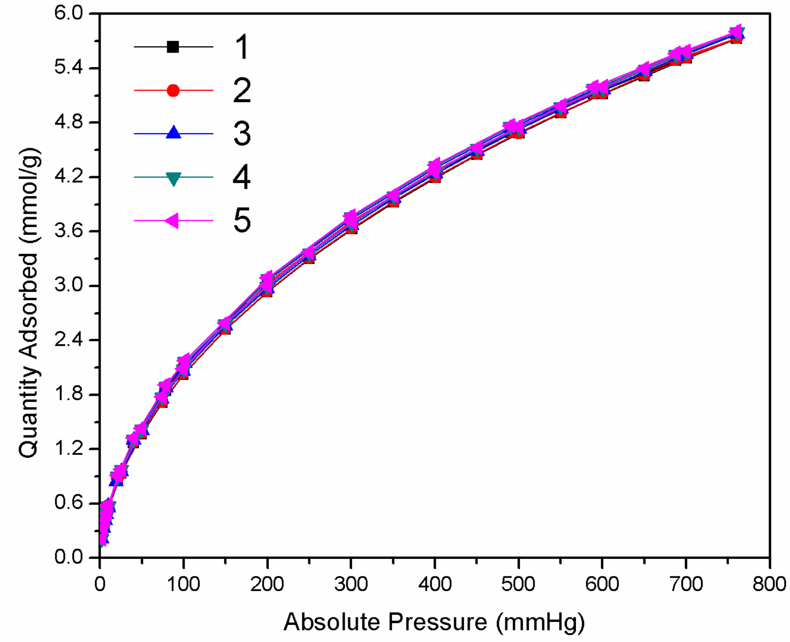

Fig. S7 Multi-cycle CO_2 adsorption - desorption isotherms for the N-PCMSs.