

Supplementary Information

Original Design of Nitrogen-doped Carbon Aerogels from Sustainable Precursors:

Application as Metal-Free Oxygen Reduction Catalysts

Nicolas Brun,^{*1, †} Stephanie A. Wohlgemuth,¹ Petre Osiceanu,² and Magdalena M. Titirici³

¹Max-Planck Institute of Colloids and Interfaces, D-14476 Golm/Potsdam, Germany

²Institute of Physical Chemistry Ilie Murgulescu, R-060021 Bucharest, Romania

³School of Materials Science and Engineering, Queen Mary University of London

Mile End Road, E1 4NS, London, United Kingdom

[†]Current address: Dept. of Chemistry, Graduate School of Science, Kyoto University,

Kitashirakawa, Sakyo-ku, Kyoto 606-8502, Japan

Materials

All chemicals were used as received without further purification.

D-(+)-glucose 99% was purchased from Roth Chemicals. N-acetyl-D-glucosamine (> 99%), D-(+)-glucosamine hydrochloride (> 99%) and cyanuric acid were purchased from Sigma-Aldrich. Gum arabic powder and phloroglucinol 99% anhydrous were purchased from Acros Organic. Nafion® 117 solution (5 wt% in a mixture of lower aliphatic alcohols and water) was purchased from Aldrich. Potassium hydroxide solution (0.1 M) and methanol were purchased from Merck. Platinum catalyst (referred as to Pt@C in the text), nominally 20 wt% on carbon black, was purchased from Alfa Aesar.

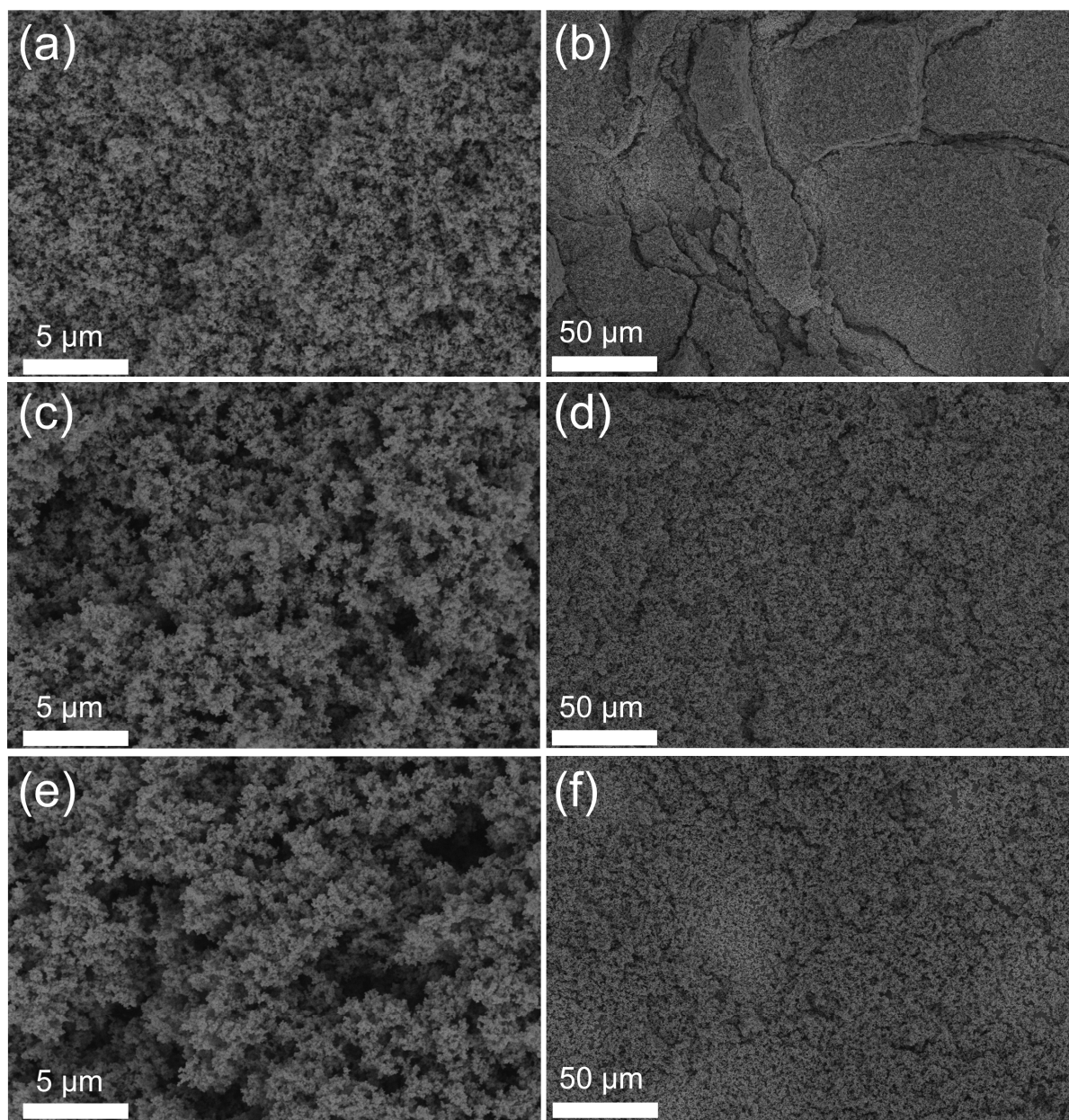


Figure S 1. Scanning electron microscopy (SEM) micrographs of carbon aerogels obtained after further thermal treatment under inert atmosphere at 950°C. (a-b) 950-G1GA1 ; (c-d) 950-AG2 ; and (e-f) 950-AG21CA2.

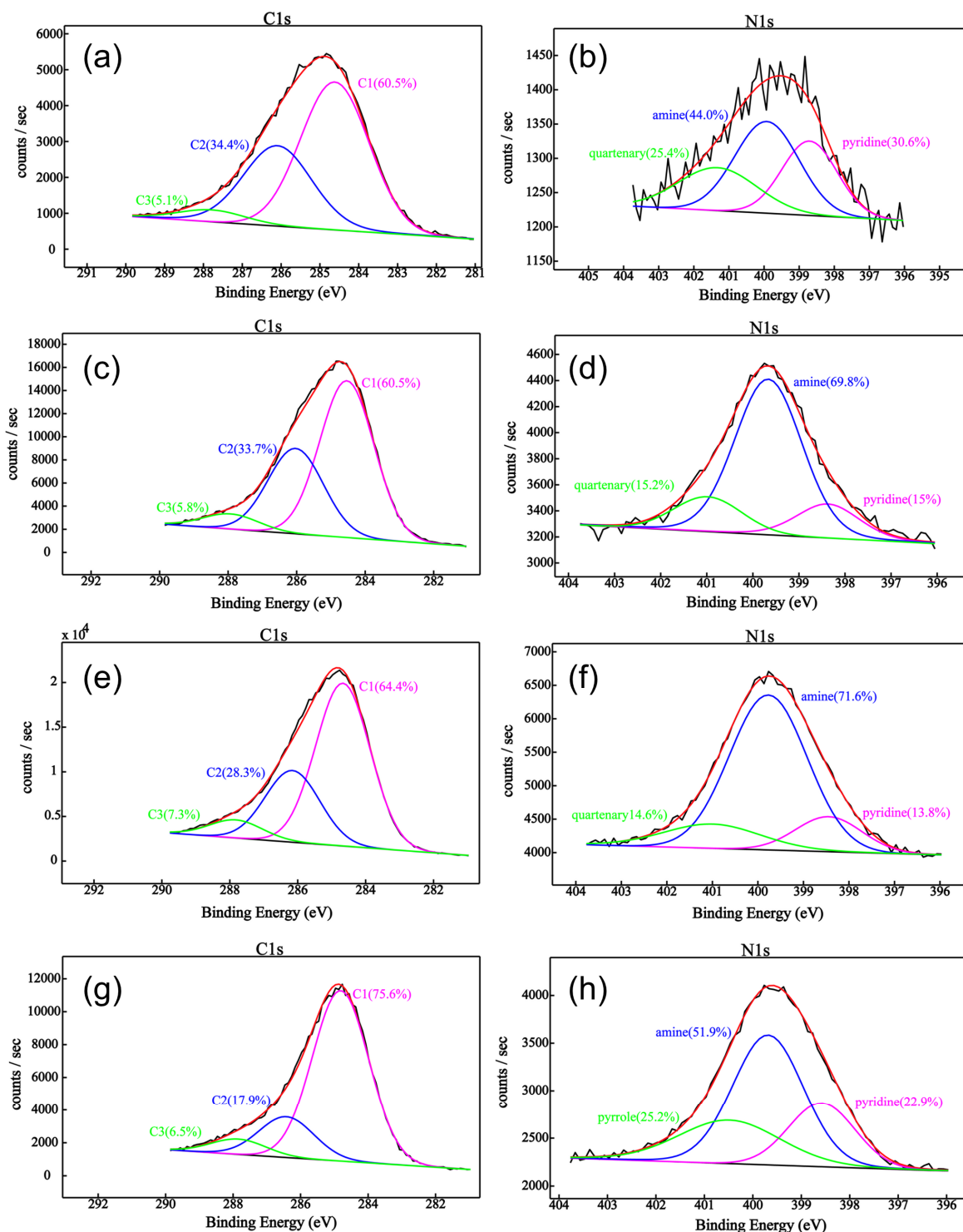


Figure S 2. C1s (left) and N1s (right) X-ray photoelectron spectra (black solid lines) and deconvolution curves (colored solid lines) obtained for the N-containing organic aerogels series. (a-b) HTC-G1GA1; (c-d) HTC-G1AG1; (e-f) HTC-AG2; and (g-h) HTC-AG21CA2. C1, C2 and C3 deconvoluted peaks correspond to $[C-C / CH_n]$, $[C-O / C=N]$ and $[C=O / C=O-N]$ species respectively.

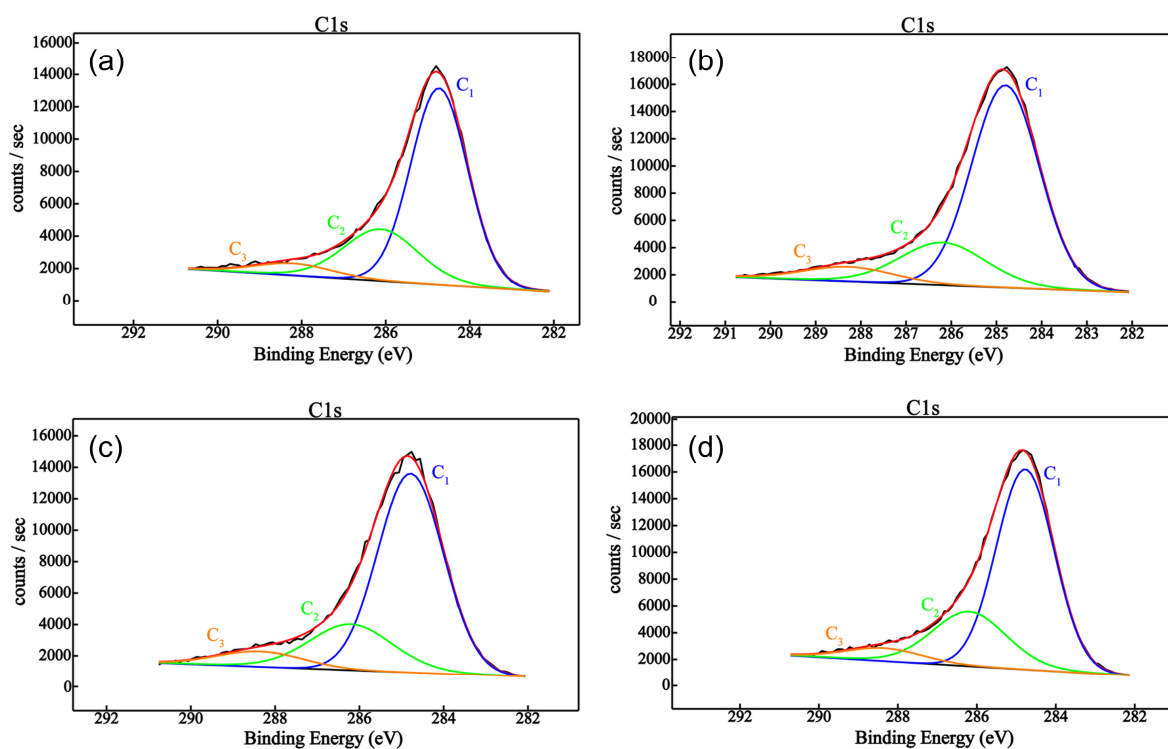


Figure S 3. C1s X-ray photoelectron spectra (black solid lines) and deconvolution curves (colored solid lines) obtained for the N-doped carbon aerogels obtained after pyrolysis at 950°C. (a) 950-G1GA1; (b) 950-G1AG1; (c) 950-AG2; and (d) 950-AG21CA2. C₁, C₂ and C₃ deconvoluted peaks correspond to [C-C / CH_n], [C-O / C=N] and [C=O / C=O-N] species respectively.

Aerogel obtained from gum arabic

Synthesis. In a typical synthesis, 0.89 g of gum arabic (from acacia tree; Sigma) and 0.31 g of phloroglucinol were mixed into a hydroalcoholic mixture of 4.75 g of water and 4.75 g of absolute ethanol. After vigorous stirring for few minutes, the hydroalcoholic solution was then added in a glass inlet (30 mL volume) sealed in a Teflon lined autoclave (45 mL volume) and placed in a laboratory oven preheated to the desired temperature (*e.g.* 180 °C) and left for the desired reaction time (*e.g.* 20 h at 180 °C). The as-synthesized gum arabic gel was then removed from the autoclave, washed a first time with a mixture water/ethanol, and then several times with ethanol, till the gel was saturated in alcohol. Then, the gel was dried by extraction with supercritical CO₂ as described in the manuscript (see experimental section).

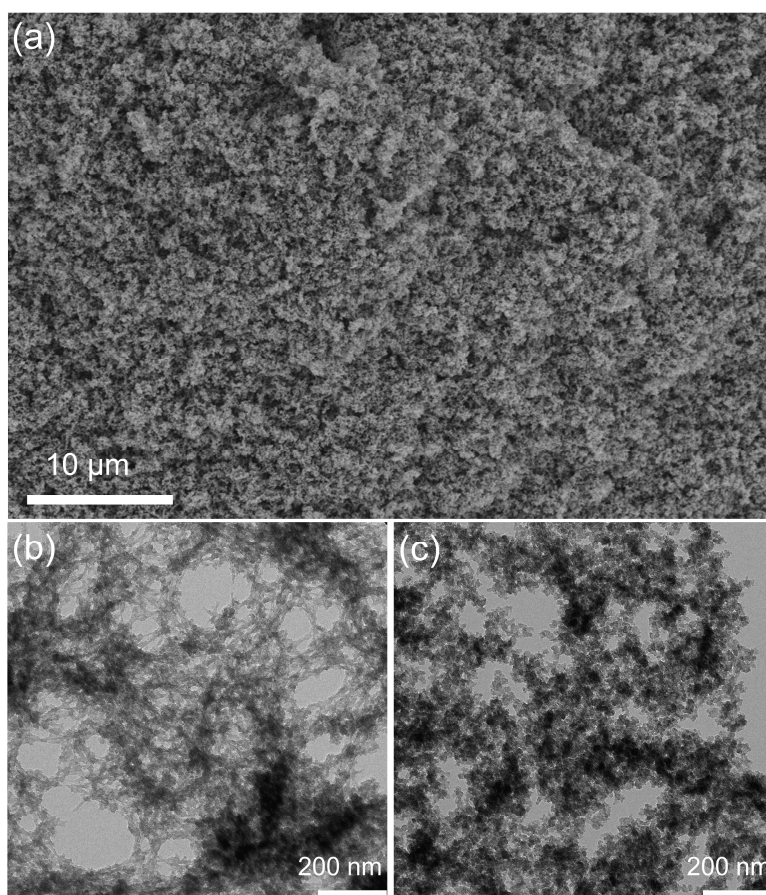


Figure S 4. (a) SEM and (b) TEM micrographs of the gum arabic-based organic aerogel. (c) TEM micrograph of the same aerogel after pyrolysis at 950°C.

Table S 1. Elemental analysis and nitrogen sorption data extracted from gum arabic aerogel before and after pyrolysis.

Samples	Elemental analysis			BET surface area $\text{m}^2 \cdot \text{g}^{-1}$	
	wt.%	C	N		N/C
Gum arabic aerogel - HTC		57.9	2.3	4.0	/
Gum arabic aerogel - 950°C		81.9	1.1	1.3	340

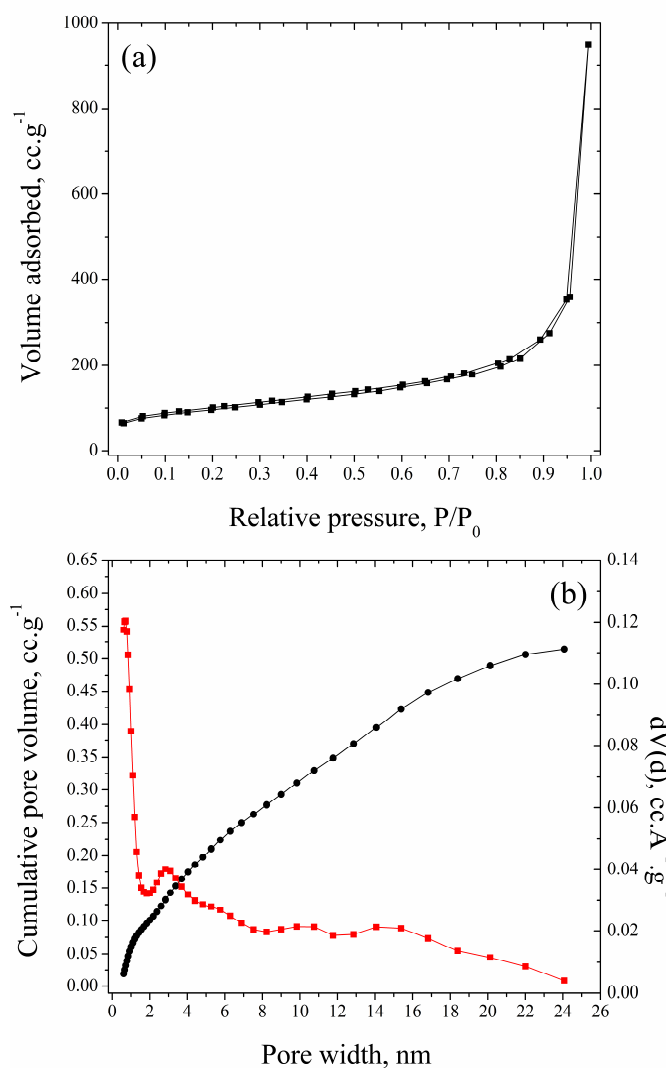


Figure S 5. (a) Nitrogen sorption isotherms and (b) pore size distribution (DFT method, QSDFT equilibrium model) of the gum arabic-based aerogel after pyrolysis at 950°C.