Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Starch-derived carbonaceous mesoporous materials (Starbon®) for the selective adsorption and recovery of critical metals

Andrea Muñoz García,[a] Andrew J. Hunt,[a*] Vitaly L. Budarin,[a] Helen L. Parker,[a] Peter S. Shuttleworth,[b] Gary J. Ellis[b] and James. H. Clark[a]

a Department of Chemistry, The University of York, Heslington, York, YO10 5DD, UK. E-mail: andrew.hunt@york.ac.uk; Fax: +44 (0)1904 432705; Tel: +44 (0)1904 324456

b Departamento de Física de Polímeros, Elastómeros y Aplicaciones Energéticas, Instituto de Ciencia y Tecnología de Polímeros, CSIC, c/ Juan de la Cierva, 3, 28006, MADRID, Spain

Experimental

Chemicals: all materials were used as received, without further purification. $AuCl_3$ was purchased from Alfa Aesar (>64.4% purity), $PdCl_2$ was purchased from FluoroChem (80% purity), $PtCl_2$ was purchased from Acros Chemicals (73% purity), $IrCl_3$, $ZnCl_2$, $CuCl_2$ and $NiCl_2$ were purchased from Sigma Aldrich (100, 98, 97 and 98% purity, respectively).

Monolith and Starbon® synthesis: Hylon VII corn starch (5 g) was gelatinized by microwave heating in water (15 ml) at 140 ^oC and 150 W for 10 min. Microwave heating was applied by Discover SP system from CEM. After gelation, the gel was poured into a mould and subsequently cooled to 5 ^oC for at least 48 h. The water was exchanged with ethanol. Afterwards, the ethanol was removed by supercritical CO_2 ($scCO_2$) at 40 ^oC and 150 bar with a flow rate of 30 $g \cdot min^{-1}$ for 4 h. Ethanol was used as co-solvent for the first 2 h. Monoliths were then doped with p-toluene sulfonic acid (10% w/v) for 2 days. Monoliths were dried and subsequently heated under vacuum up to 800 ^0C.

Characterisation: Nitrogen-adsorption analysis was carried out using an ASAP 2020 volumetric adsorption analyser from Micrometrics. Measurements were performed at 77 K. Samples were degased at 130 ^oC for 6 h prior to analysis. The Brunauer-Emmett-Teller (BET) theory was used to determine the surface area, and the Barret-Joyner-Halenda (BJH) equation was applied to determine the mesoporous volume and the pore size. TEM images were taken by a Tecnai 12 BioTwin made by FEI Eindhoven at 120 kV. Samples were wet with ethanol and subsequently placed onto carbon grids via ethanol evaporation. The X-ray photoelectron spectroscopy analysis was performed by using VG Escalab 250. The analysis was carried out by the personnel of the Leeds EPSRC Nanoscience and Nanotechnology Research Equipment Facility. CasaXPS software was used to process the data. Inductively Coupled Plasma Mass Spectroscopy (ICP) was carried out to measure the metal concentration in solution using Agilent 7700x fitted with standard Ni sample and skimmer cones and coupled to a Mass Spectrometer (MS). The samples were run in He mode. The sample introduction line was rinsed for 60 sec between samples using 5% HCl and 2% HNO_3 (30 sec with each compound). Samples were prepared by diluting 1µL of the sample in 10 mL of ultra-pure water. The XRD analysis was undertaken using Bruker-AXS D8 Advance diffractometer with a Kristalloflex 760 X-ray generator. Scans were taken with a 40kV voltage and 30 mA current in the range of 0 - 80 2θ.

Metal adsorption studies: an HCl solution containing a mixture of the six metals was prepared in a volumetric flask using ultra-pure water. Glassware was rinse with a mixture of HCl (37%):HNO_3 (70%) (3:1). The concentration of the metals in solution was 100 $mg \cdot L^{-1}$. Concentration of certain salts was lower due to the low solubility of some of the salts. The pH of the solution was adjusted, when necessary with HCl 1 M, 0.1 M and NaOH 1M and 0.1 M. For the adsorption studies, flasks were filled with 30 mL of solution, the adsorbent and a stir bar. The adsorbent was added in amounts ranging 5 to 50 mg. The experiments were running for 24 h. For the kinetics studies, samples were collected after 10 min, 30 min, 1 h, 2 h, 4 h, 6 h, 22 h and 24 h. The adsorbent was separated from the solution by centrifugation and decantation.

The adsorption capacity (q_e) was determined by:

$$q_e = \frac{(C_o - C_e)\cdot V}{m}$$

Where C_o is the initial concentration of the solution ($mg\cdot L^{-1}$), C_e is the concentration of the sample solution ($mg\cdot L^{-1}$), V is the volume of solution employed (L) and m the mass of adsorbent used (g).

Supplementary Tables and Figures

Table S 1 Textural properties of the materials measured by N_2 sorption porosimetry.

Material	BET surface area ($m^2 \cdot g^{-1}$)	Pore Volume ($cm^3 \cdot g^{-1}$)	Pore Size (nm)	Micropore Volume ($cm^3 \cdot g^{-1}$)
Exp. st.	199	0.82	9	0.0001
200 °C	91	0.45	30	0.0003
800 °C	631	0.48	18.2	0.0020

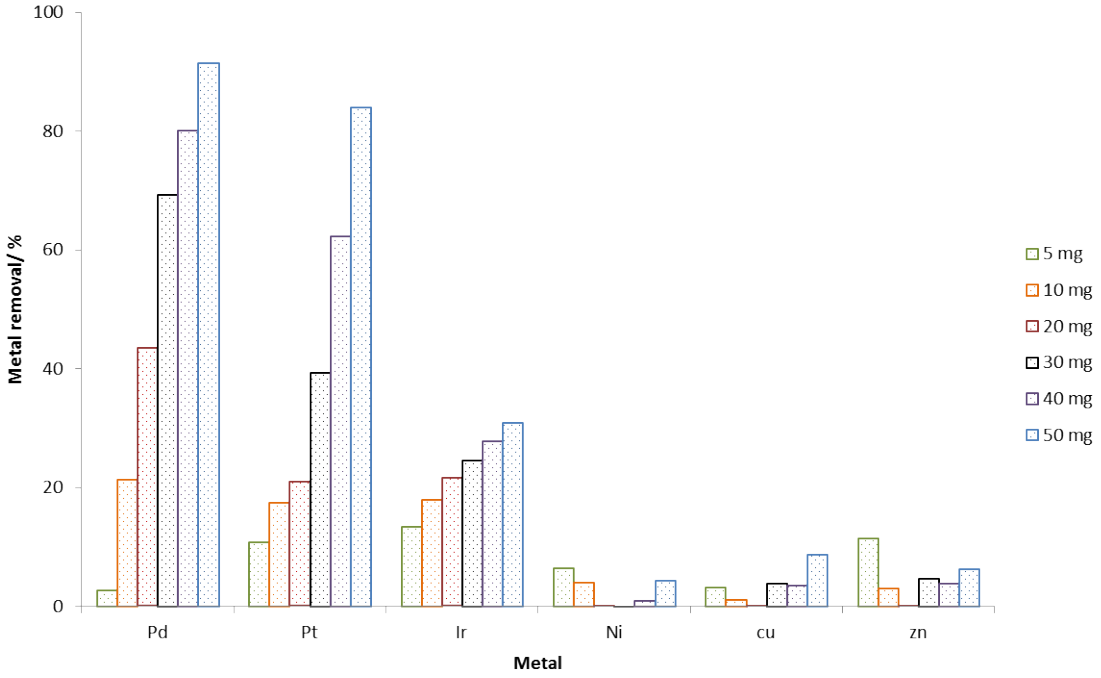

Fig. S 1 Metal removed from 30 mL of an HCl solution when 5 (green), 10 (orange), 20 (red), 30 (black), 40 (purple) and 50 mg (blue) of adsorbent were added.

Table S 2 Elemental analysis from XPS analysis.*Other = Cl, Pd, Au, S.

Elemental analysis from XPS (%)				
Element	Bef. adsorption	10 mg	30 mg	50 mg
C	97	80	91	93
O	3	17	6	5
Other*	-	3	3	2

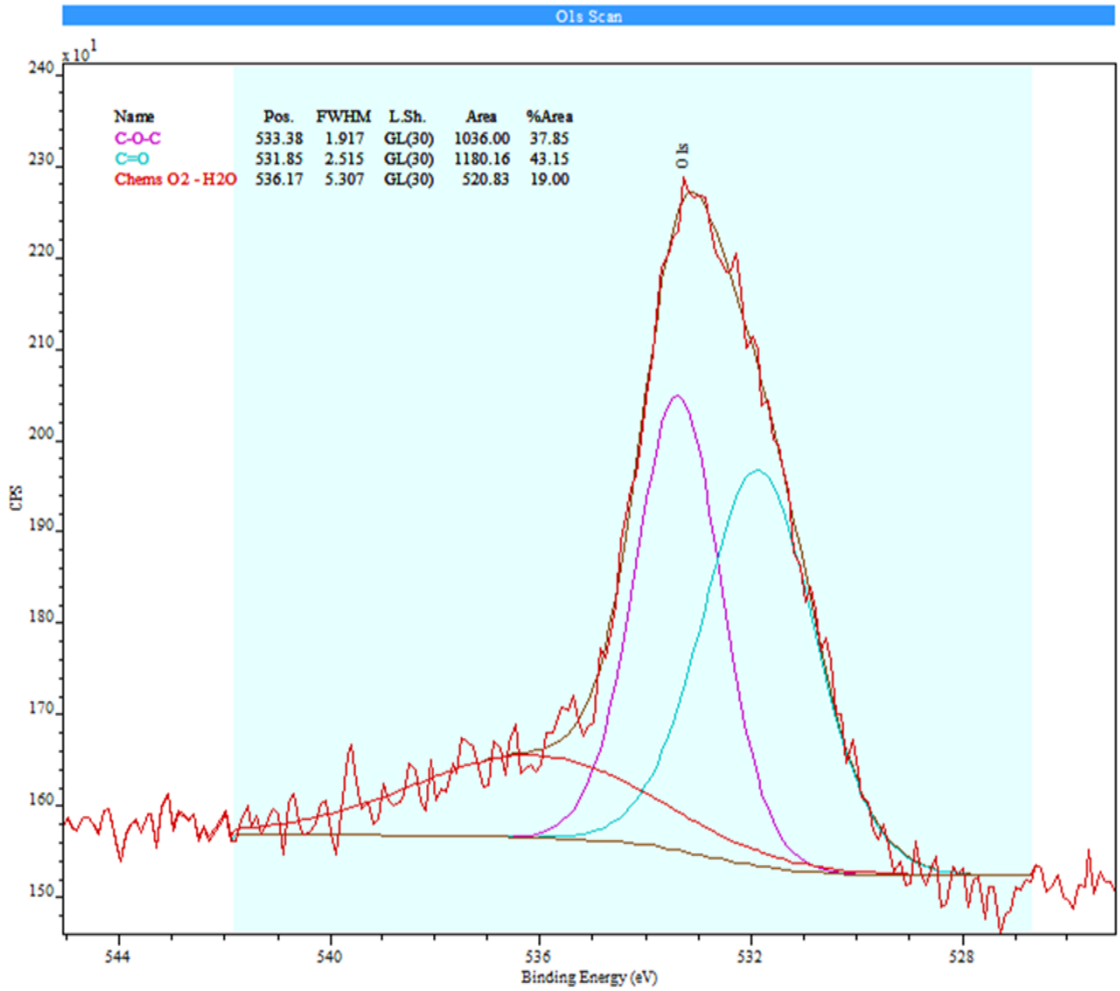

Fig. S 2 XPS deconvolution peaks of oxygen, material before adsorption.

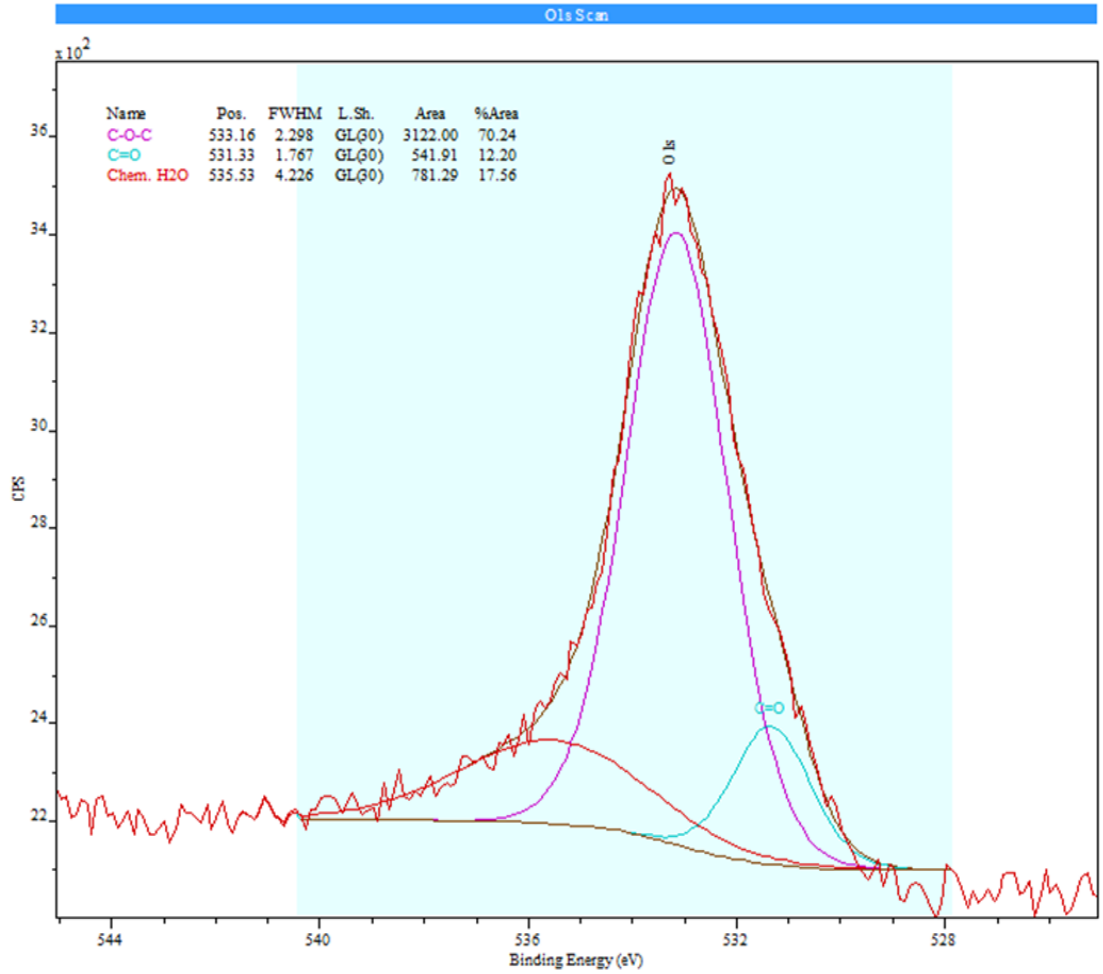

Fig. S 3 XPS deconvolution peaks of oxygen, 50 mg of adsorbent in 30 mL of solution.[i]

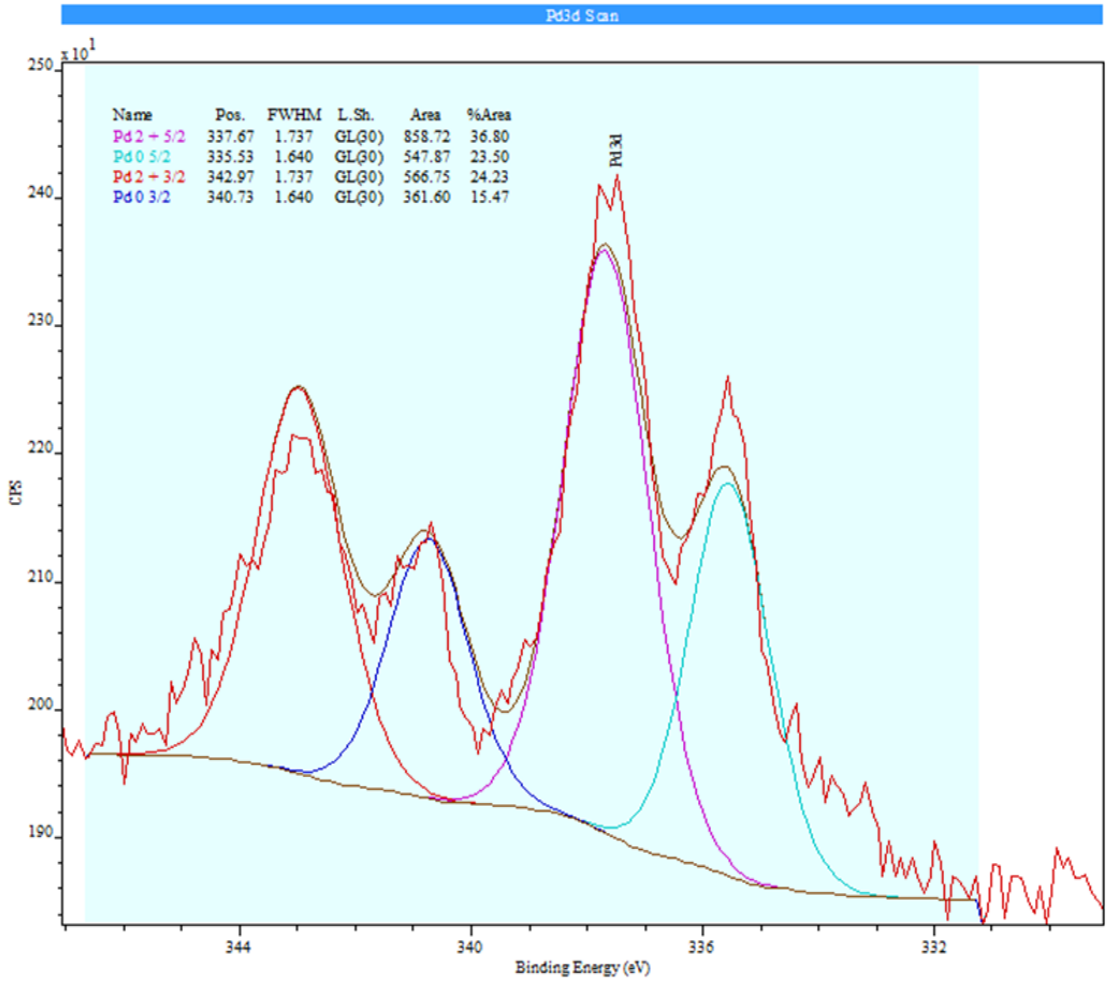

Fig. S 4 XPS deconvolution peaks of palladium, 50 mg of adsorbent in 30 mL of solution.

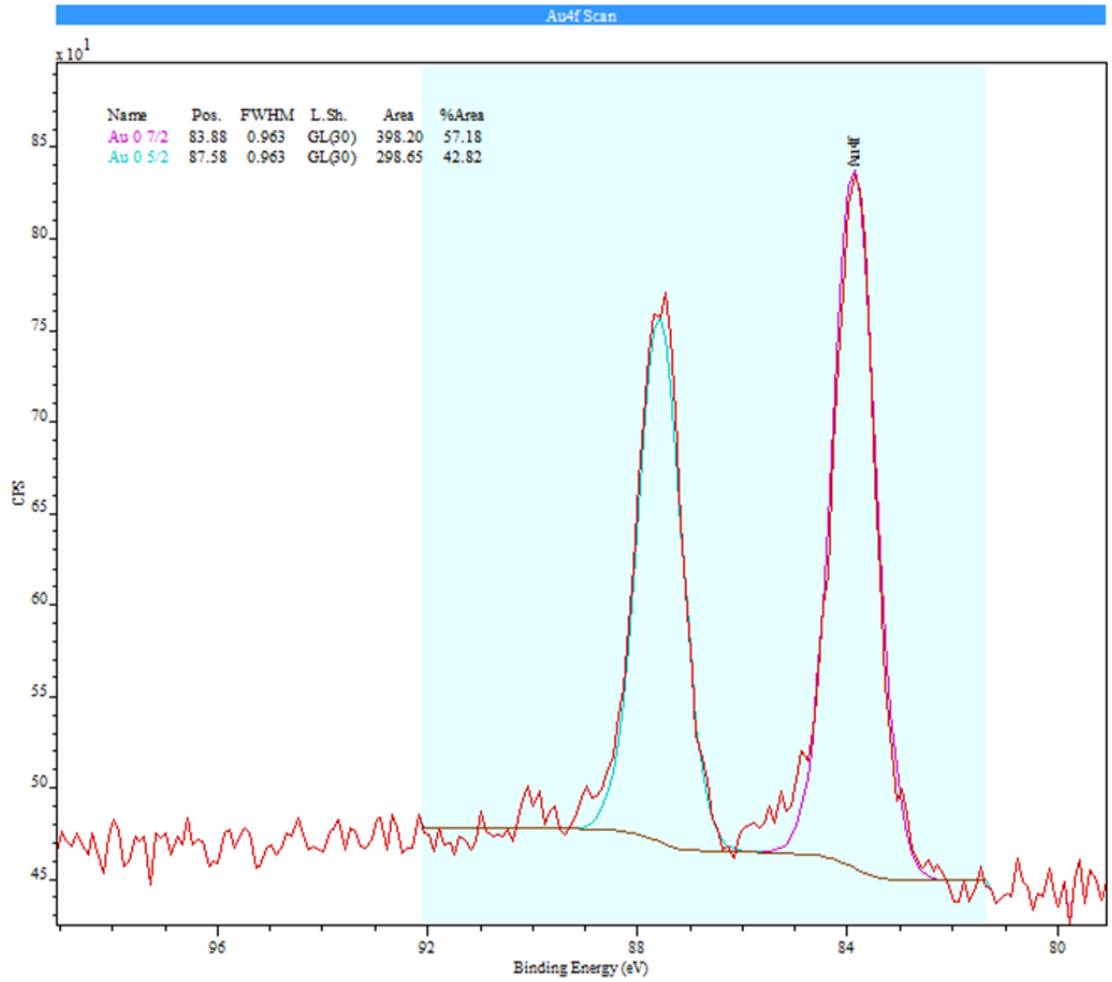

Fig. S 5 XPS deconvolution peaks of Au, 50 mg of adsorbent in 30 mL of solution.

Table S 3 XPS deconvolution peaks: binding energy, chemical state and abundance (%).*Background noise interference made quantification difficult.

		Abundance (%)			
Be (eV)	Chemical state	Bf. Ads.	10 mg	30 mg	50 mg
284.4 ± 0.2	Graphitic carbon	55	50	64	62
285.2 ± 0.1	Defects	18	11	10	14
286.2 ± 0.1	C-OH	-	28	11	10
287.6	C=O/C-O-C	-	6	-	-
288.7 ± 0.5	O=C-O	27	5	15	14
530.4 ± 0.5	C-O-C	38	7	4	12
533.2 ± 0.2	C=O	43	93	92	70
535.9 ± 0.6	Chemisorbed O_2	19	-	3	18
84.0 ± 0.2	Au^0 (4f 7/2)	-	50	53	53
85.9 ± 0.2	Au^{3+} (4f 7/2)	-	7	4	4
87.6 ± 0.2	Au^0 (4f 5/2)	-	38	40	40
89.6 ± 0.2	Au^{3+}(4f 5/2)	-	5	3	3
335.5 ± 0.3	Pd^0 (3d 5/2)	-	*	19	23
337.7 ± 0.3	Pd^{2+} (3d 5/2)	-	*	41	37
340.7 ± 0.3	Pd^0 (3d 3/2)	-	*	13	16
343.0 ± 0.3	Pd^{2+} (3d 3/2)	-	*	27	24

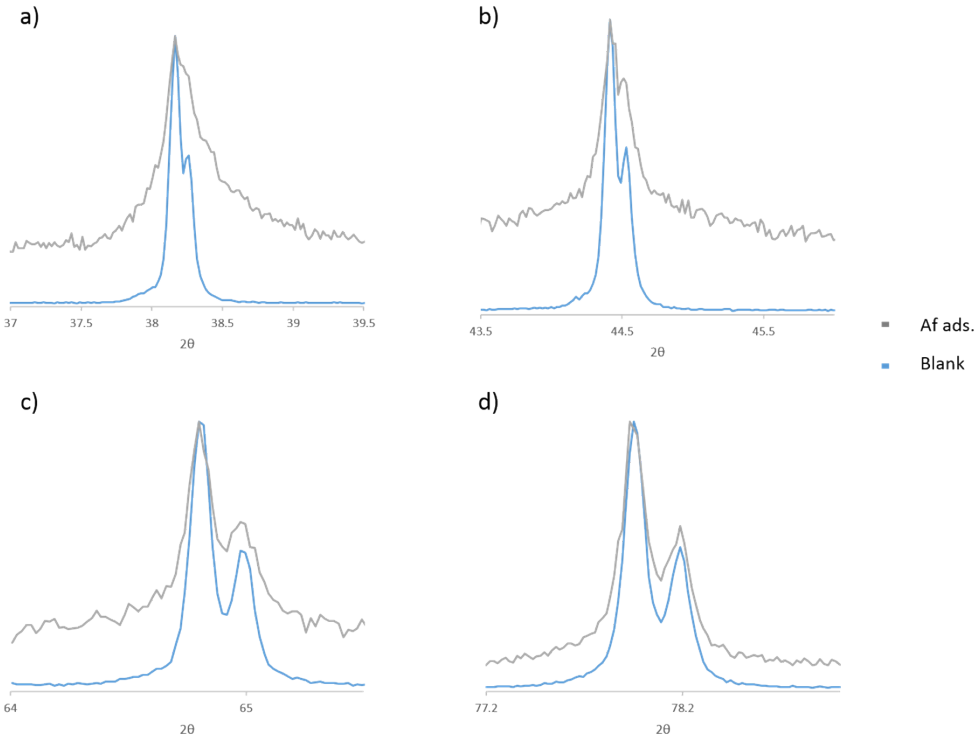

Fig. S 6 XRD pattern of Starbon® after adsorption of metals (grey) and aluminium sample holder only (blue). The main peaks at a) 38°, b) 44.5°, c) 64.9° and d) 78° corresponds to the aluminium holder.[1]

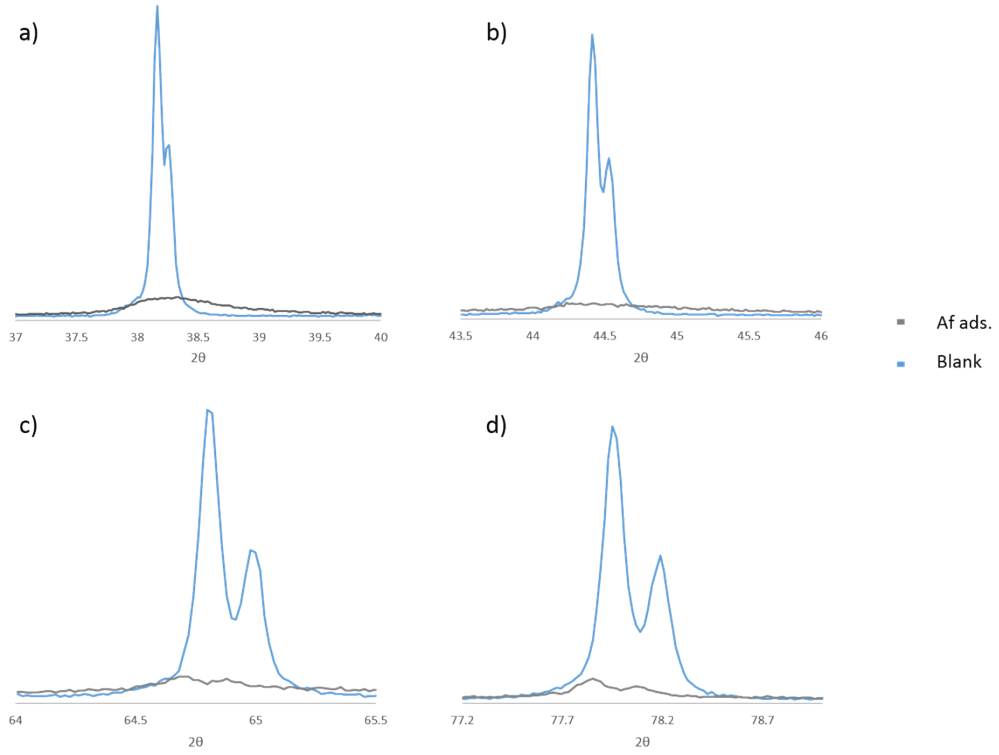

Fig. S 7 XRD pattern of Starbon® after adsorption of metals (grey) and aluminium sample holder only (blue). The aluminium peaks at a) 38°, b) 44.5°, c) 64.9° and d) 78° were not present in the Starbon® sample when the amount of analysed sample was increased. However, it is neither possible to detect gold nor palladium peaks, due to the low concentration of those metals in the surface of the material, as established by XPS.

Fig. S 8 Monolith of Starbon® after carbonisation at 800 °C.

References

1. X.-F. Lei and J.-X. Ma, *Journal of the Brazilian Chemical Society*, 2010, 21, 209-213.

[i] XPS deconvolution peaks of O, Au and Pd are exemplified by the 50 mg sample.