Supplementary Information

Direct synthesis of palladium nanoparticles on alginic acid and seaweed supports

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Electron microscopy

All electron microscopy images were acquired with the help of Ms Meg Stark at the Technology Facility in the Department of Biology, University of York, UK.

Scanning electron microscopy (SEM) micrographs were recorded using a JEOL JSM-6490LV. Samples were mounted on alumina plates and coated with a 7 nm layer of Au/Pd using a high resolution sputter SC-7640 coating device prior to analysis. Typical magnifications used were x1000, x2000 and x4500.

Tunnelling electron microscopy (TEM) micrograph images were recorded using a Tecnai 12 BioTwin at 120kV. Samples were suspended in ethanol and deposited on to carbon grids via solvent evaporation.

All TEM analysis was carried out with the assistance of Ms Meg Stark, Biosciences Technology Facility, Biology Department, University of York, UK.

Infrared spectroscopy

Infrared analysis was performed using a Bruker Vertex 70 FT-IR fitted with a Specac Golden Gate ATR attachment with diamond top plate analysis window. This was controlled by Opus software. The spectrum was scanned from 4000 – 600 cm^{-1}. The number of background scans and sample scans were set at 32 and 16 respectively. The resolution was selected to be 4 cm^{-1}.

Inductively coupled plasma spectroscopy

Inductively coupled plasma (ICP) analysis was carried out on a Varian ICP with axial OES. The samples were digested in reverse aqua-regia using a CEM mars Xpress microwave.

Porosimetry analysis

Nitrogen adsorption-desorption isotherms, surface area and porosimetry measurements (including pore volumes and porous distributions) were conducted using a Micrometrics ASAP 2010 volumetric adsorption analyser at -196 ^{o}C. Prior to analysis samples were out-gassed at 333 K under reduced pressure for 1 hour, followed by 120 ^{o}C for a further 1 hour.

X-Ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was conducted by Dr Benjamin Johnson, EPSRC XPS service at the University of Leeds, School of Physics and Astronomy, Leeds, LS2 9JT.

XPS spectra were recorded on a Kratos Axis Ultra DLD photoelectron spectrometer using a hemispherical photoelectron analyser with a monochromatic AlKα X-ray source (75-150 W) and analyser pass energies of 160 eV (for survey scans) and 40 eV (for detailed scans). Samples were mounted using double-sided tape. Binding energies were referenced to the C 1s binding energy 285 eV. Prior to analysis samples were degassed overnight at ultrahigh vacuum ($<5x10^{-10}$ Torr). CasaXPS software was used to carry out analysis of the spectra.

Alginic acid catalyst preparation

40 g of alginic acid was added to 800 mL of deionised water and heated at 90 ^{o}C for 2 h. The gel was retrograded for 12 h at 5 ^{o}C. The gel was subjected to 5 solvent exchanges with ethanol to remove the water. The resulting expanded alginic acid (20 g) was added to ethanol (250 ml) in a round bottom flask and subjected to stirring. Once the mixture was well mixed

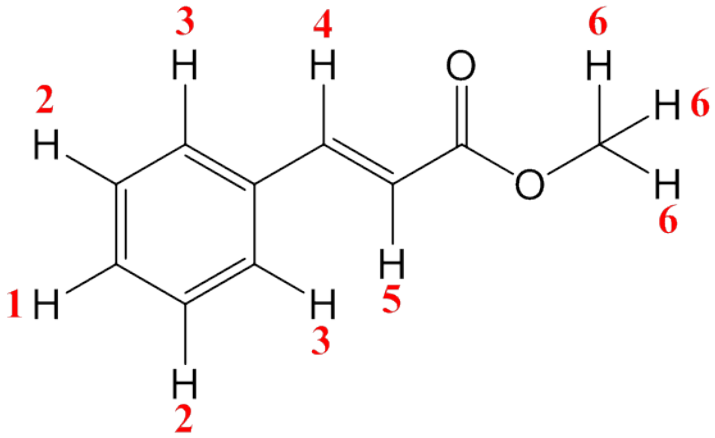
(approximately 10 min) palladium acetate (1 w/w% of expanded alginic acid) was then added. The solution appeared pale orange/yellow due to the dissolved palladium acetate. The solution was stirred until this colour was no longer visible – indicating that all of the palladium had been adsorbed. The expanded alginic acid was dried using a Thar SFE500 supercritical CO_2 extractor operating at 40 ^oC, 100 bar, 40 g min^{-1} for 3 h, followed by carbonisation at 1 ^oC min^{-1} under an inert atmosphere of nitrogen to 300 ^oC.

Seaweed catalyst preparation

To prepare the catalyst, expanded seaweed (20 g) was added to ethanol (250 ml) in a round bottom flask and subjected to stirring. The procedure then continued in the same way as for the alginic acid materials.

Testing catalytic activity

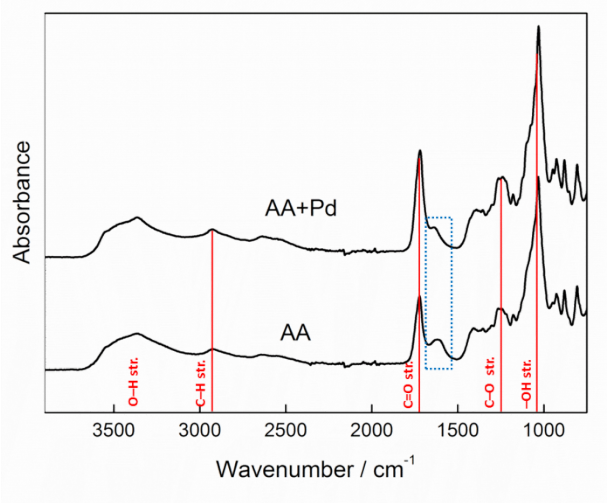
Heck reaction 1 – formation of methyl cinnamate:



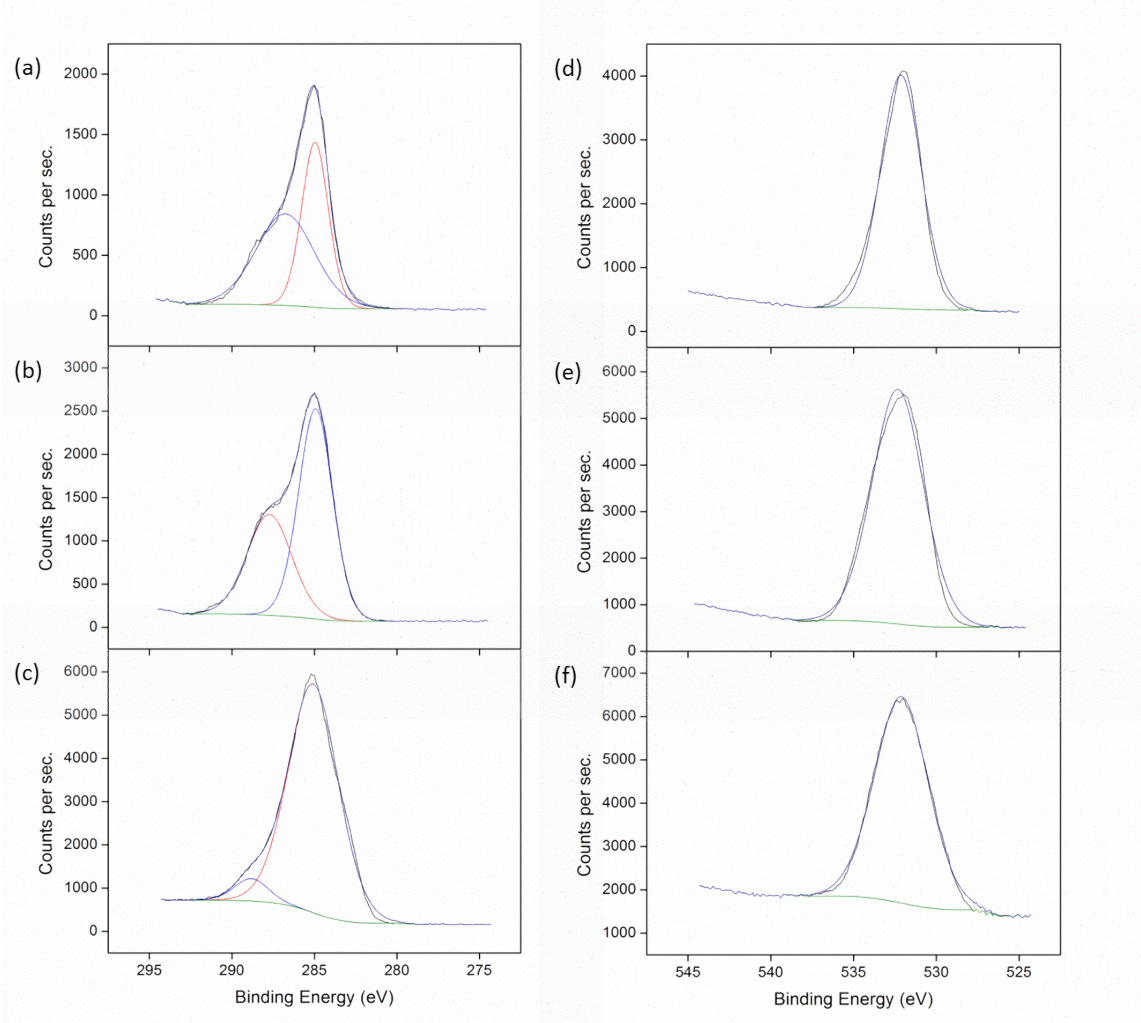
For the reaction of iodobenzene with methylacrylate typical reaction conditions used were: into a 25 ml round bottom flask the following reagents were measured; iodobenzene (20 mmol), methylacrylate (25 mmol), triethylamine (25 mmol). *N*-methylpyrollidone (NMP) (7 ml) was then added and the flask was heated with stirring to 100 ^oC. Once the flask had heated to the required temperature Pd catalyst was added, with the amount of catalyst added equivalent to that needed to achieve a 0.3 mol% Pd concentration (based on iodobenzene concentration). For control experiments un-impregnated materials were added. The reaction was allowed to proceed for 2 hours. Reaction was monitored by GC-FID using diethyl succinate as a standard. Methyl cinnamate: ^1H NMR: (500 MHz, $CDCl_3$): δ [ppm] = 3.82 (s, 3H, 6), 6.47 (d,1H, J = 16 Hz, 4), 7.37-7.57 (m, 6H, 1-3), 7.72 (d, 1H, J = 16 Hz, 5). GCMS: (*m/z*) = 162, 131 (100), 103, 77, 51.

7.5.4 Recycling of the catalysts

The reaction of iodobenzene with methacrylate was used to investigate recyclability of the catalyst. The conditions were the same as previously. After 2 hours the mixture was cooled to room temperature and transferred to a centrifuge tube. The solid and liquid materials were separated by centrifugation at 3000 rpm for 10 minutes. The liquid was decanted and saved for analysis. The solid was washed with NMP. The solid and liquid were again separated. The solid was then washed into a new 25 ml round bottom flask using NMP containing fresh reagents and the Heck reaction was repeated, without adding any fresh catalyst.



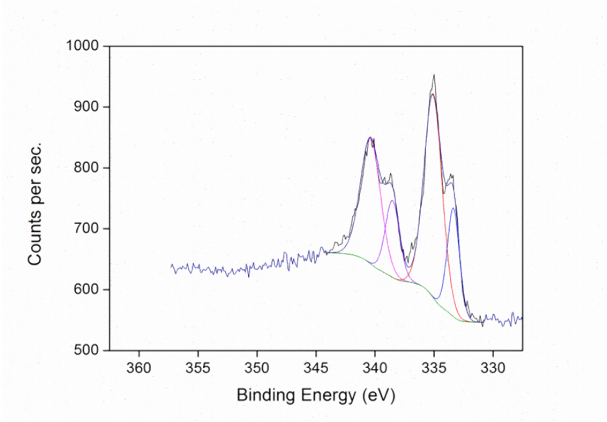
Supplementary Fig. 1 IR spectra of expanded alginic acid (AA) and expanded alginic acid + palladium (AA+Pd).



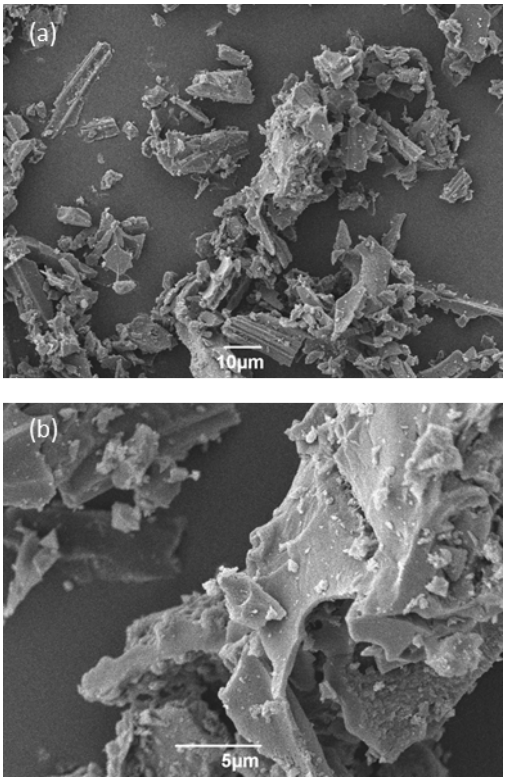
Supplementary Fig. 2 High resolution carbon XPS spectra of (a) AA, (b) AA+Pd and (c) AA-Carbonised and oxygen XPS spectra of (d) AA, (e) AA+Pd and (f) AA-Carbonised

Supplementary Table 1. Composition of expanded alginic acid (AA) and alginic acid + palladium (AA+Pd) components from XPS spectra.

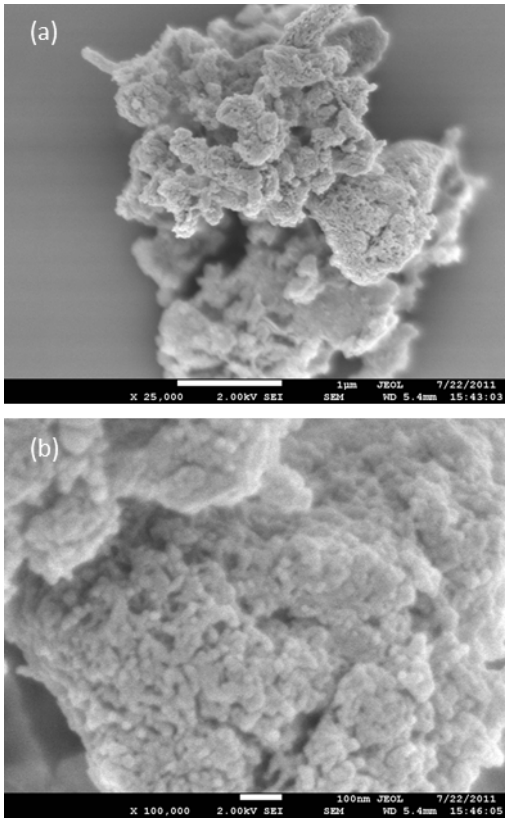
	BE [eV]	Chemical State	%		
			AA	AA+Pd	AA-Carbonised
C	285.2 ± 0.3	C-C (ring)	61	57	94
	288.2 ± 0.5	C=O, O-C-O	39	43	6
O	532.0 ± 0.5	C=O, O-C-O	100	100	100



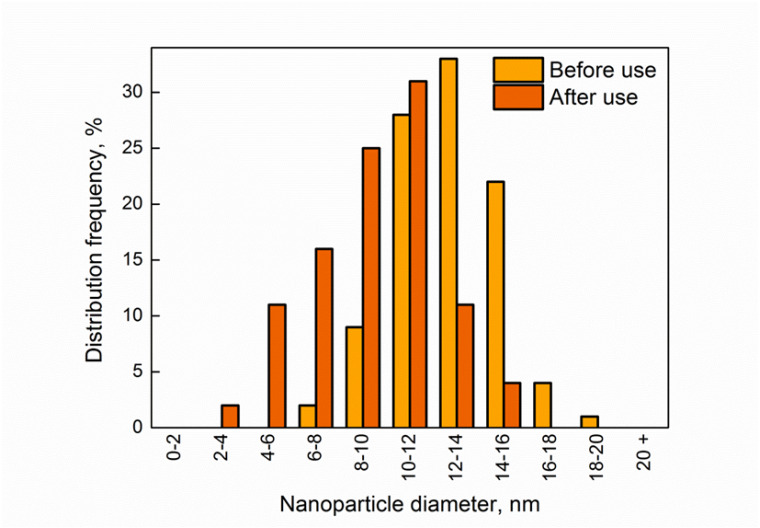
Supplementary Fig. 3 High resolution Pd XPS spectra of Pd/C 1%.



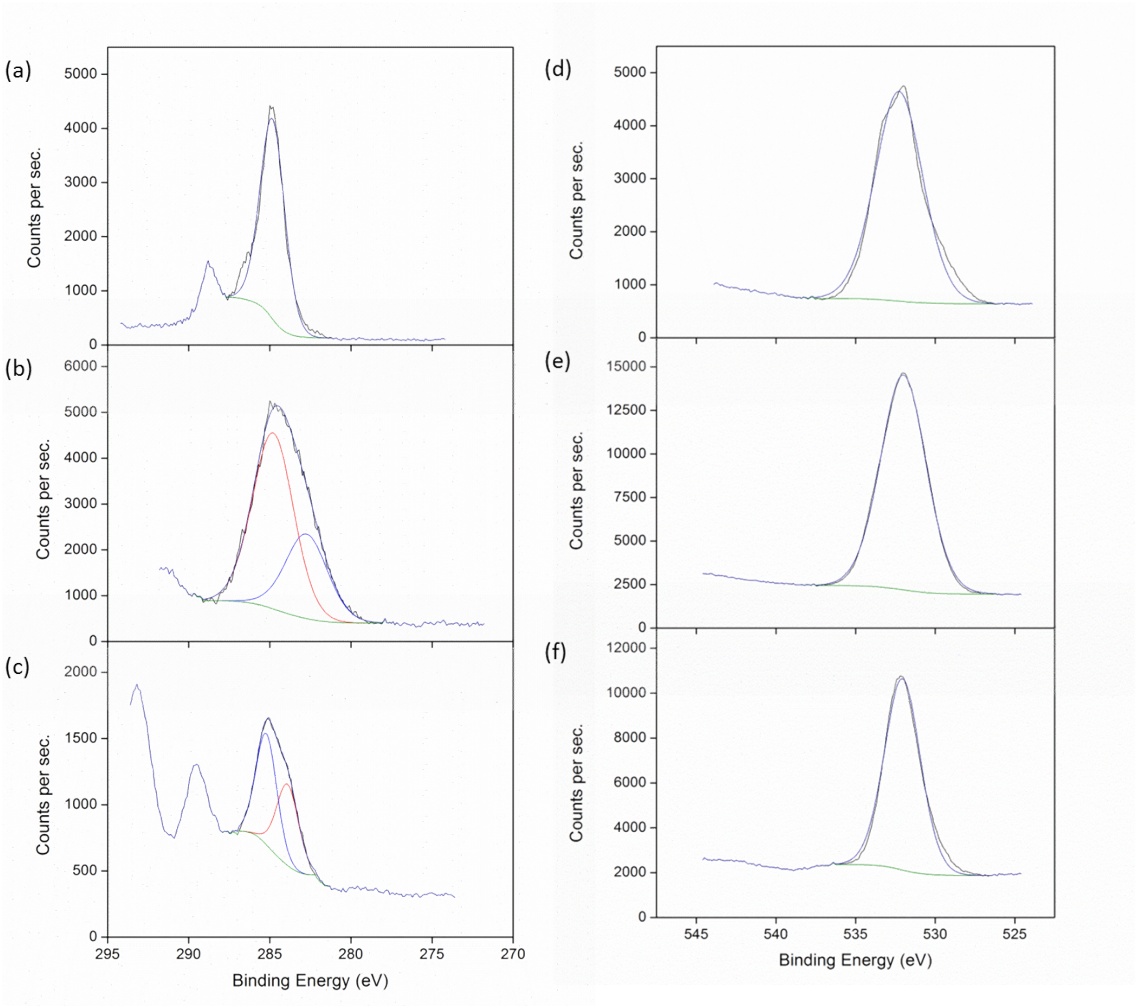
Supplementary Fig. 4 SEM images of Pd/C 1% at (a) x1000 and (b) x4500 magnification.



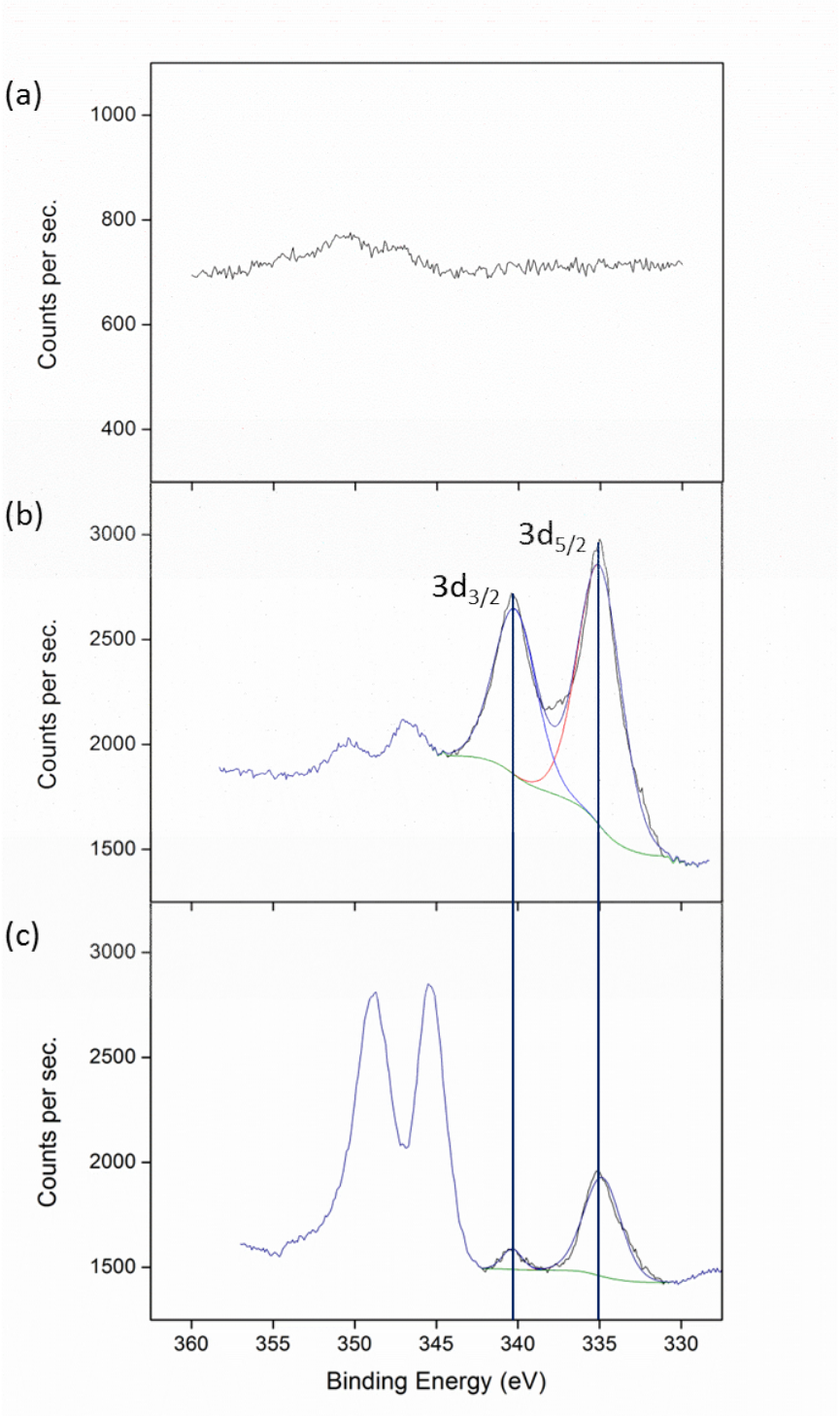
Supplementary Fig.5 High resolution SEM images of AA-SLOW.



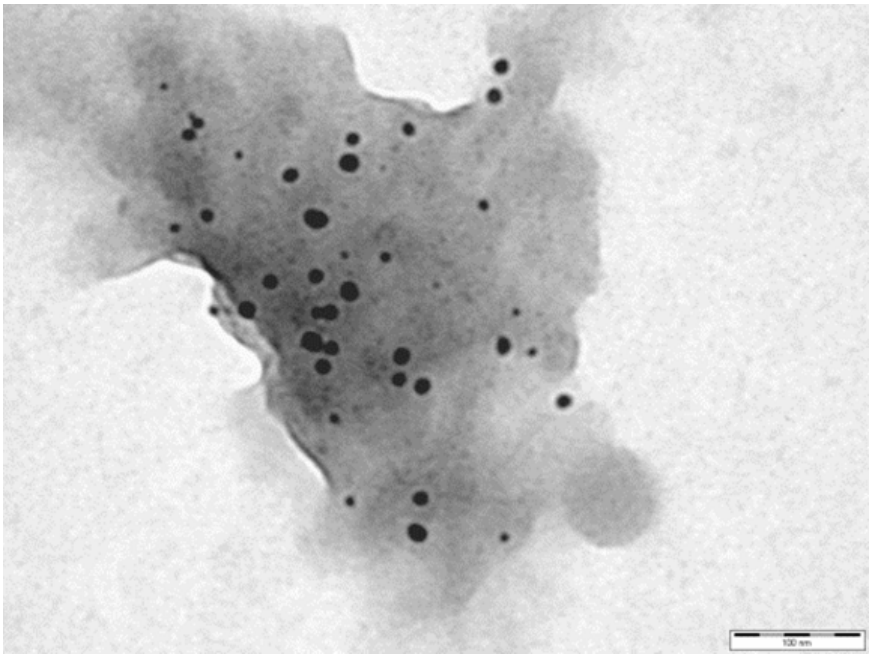
Supplementary Fig. 6 NP size distribution of AA-SLOW before and after use.



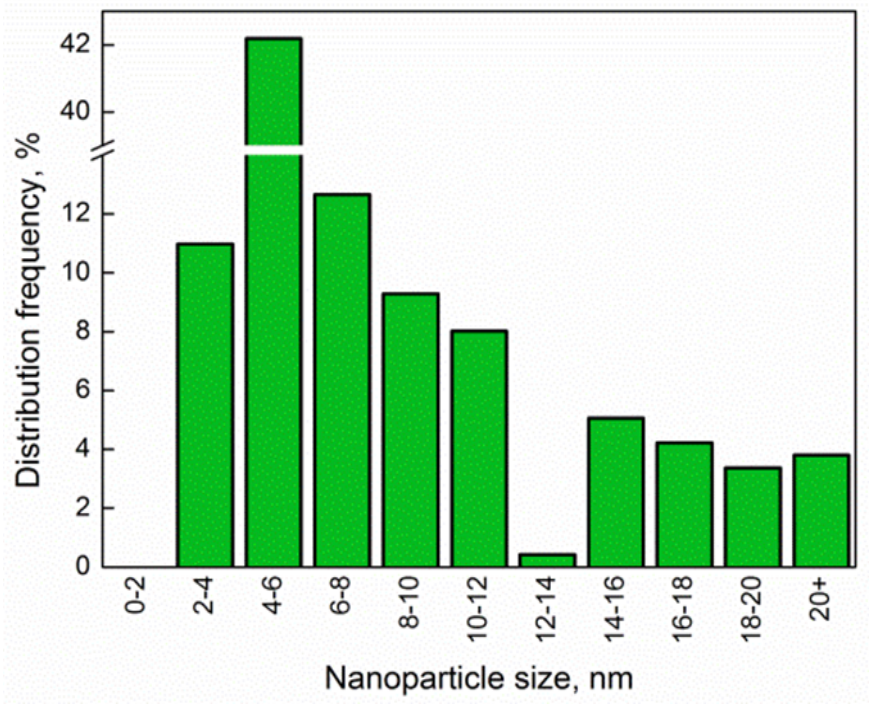
Supplementary Fig. 7 High resolution carbon XPS spectra of (a) SW, (b) SW+Pd and (c) SW-Carbonised and oxygen XPS spectra of (d) SW, (e) SW+Pd and (f) SW-Carbonised



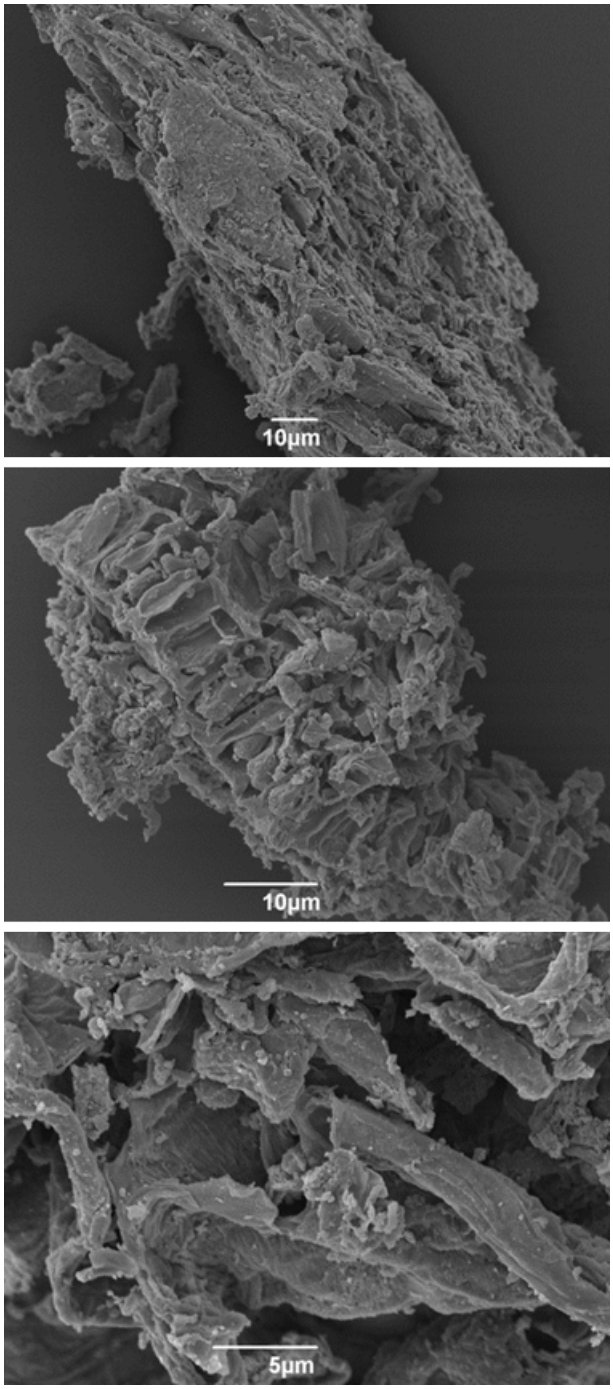
Supplementary Fig. 8 Pd XPS spectra for (a) SW, (b) SW+Pd and (c) SW-Carbonised.



Supplementary Fig. 9 TEM Image of SW-Carbonised with PdNPs visible.



Supplementary Fig. 10 NP size distribution for SW-Carbonised material.



Supplementary Fig. 11 SEM images of SW-Carbonised at (a) x1000, (b) x2000 and (c) x4500 magnification.