Electronic Supplementary Material (ESI) for Chemical Communications

Pd(II) conjugated chitosan nanofibre mats for application in Heck cross coupling reactions

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Supporting Information

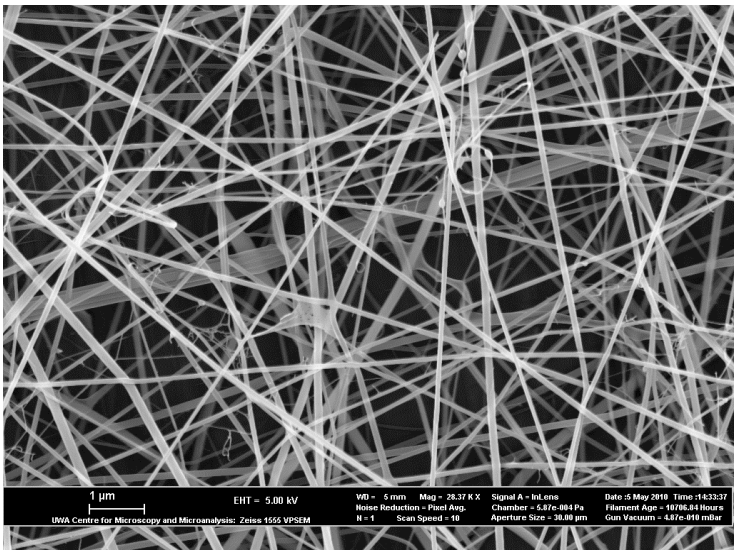

Fig S1.SEM image of electrospun 6 wt% chitosan fibres

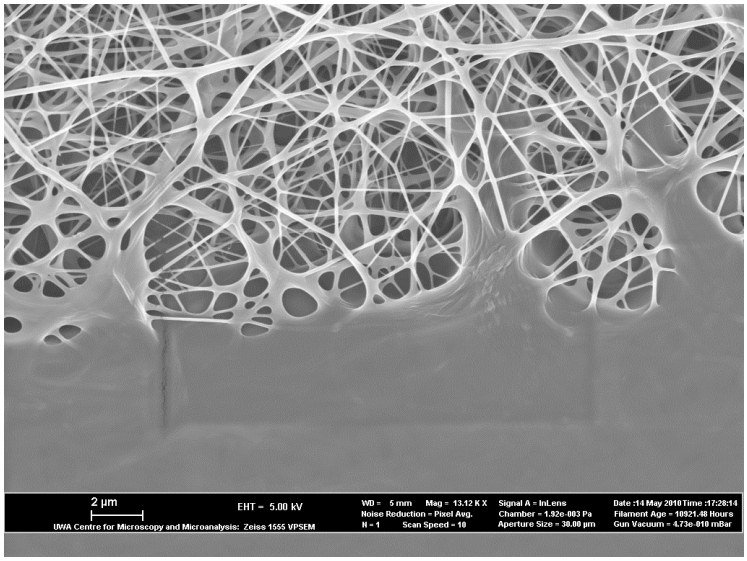

Fig S2. SEM image of fibres not crosslinked following exposure tpdimethyl formamide (DMF)

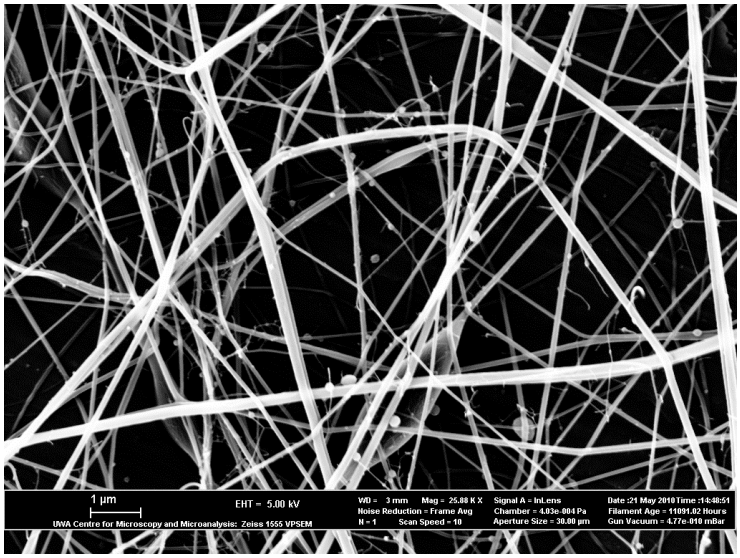

Fig S3. SEM image of intact cross-linked nanofibres after DMF exposure..

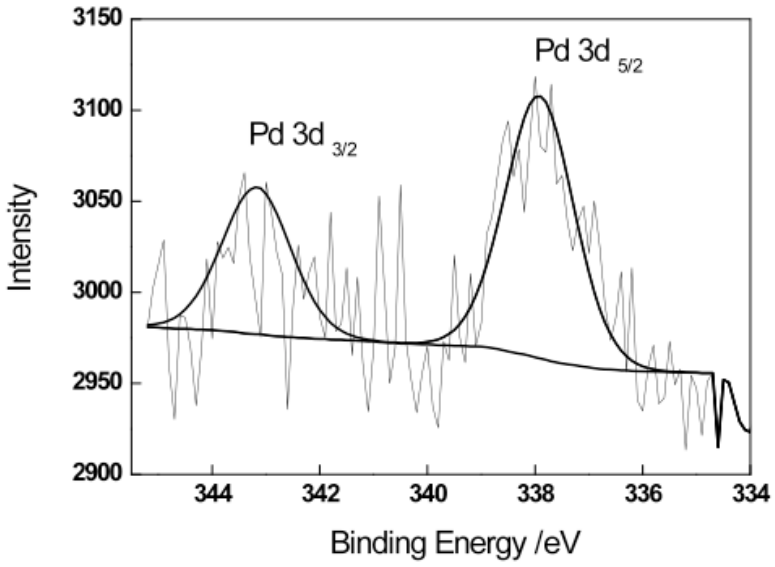

Fig S4. Curve-fitting of the XPS Pd 3d spectra obtained for Pd-chitosan, measured under ultra-high vacuum conditions with a Dual Anode MgKα radiation source.

Experimental

Materials

Chitosan (2-amino-2-deoxy-(1-4)-β-D-glucopyranose), 75-85% deacetylated was acquired from Sigma-Aldrich with an estimated molecular weight of 190,000-310,000. TFA (trifluoroacetic acid) and DCM (dichloromethane) were purchased from Chem Supply. Iodobenzene, glutaraldehyde and butyl acrylate were purchased from Sigma-Aldrich. Triethylamine (Et_3N) was purchased from Fluka. All chemicals were used directly without any further purification.

Synthesis of cross-linked chitosan nanofibres

Electrospinning of chitosan nanofibre: Chitosan nanofibres were synthesised based on a modification of the procedure by Ohkawa, et al.[1] Chitosan was crushed into a fine powder and then added slowly to the TFA and DCM (70:30 v:v%) mixture. The solution was stirred overnight and prior to electrospinning, the viscous chitosan/TFA/DCM solution was sonicated for 15 min to remove any gases and before loading into the syringe.

Electrospinning of cross-linked chitosan nanofibre: The glutaraldehyde method for cross-linking was adapted from Schiffman and Schauer.[2] 2.7 v% glutaraldehyde was added into the 4% chitosan/TFA/DCM mixture before electrospinning.

The final parameters of electrospinning after optimising are a voltage of 18 kV, an 11 cm working distance, 0.5 cm/min traverse speed for the syringe, 0.1 mm/min syringe pump speed (2.5mL/hr), and 1m/min drum rotation speed.

The prepared cross-linked chitosan was placed in a 2 mM aqueous solution of Na_2PdCl_4 and left to soak overnight. After adsorption of the palladium, the solid was washed thoroughly (with MilliQ water) to remove any weakly bound palladium species. The loaded fibres were then freeze-dried for 48 hours to give the catalyst. The loading of palladium was established using ICP-MS, at between 1.75 and 1.89% by mass.

Characterisation of chitosan nanofibres

Solid state ^{13}C NMR analysis was recorded at 100.543 MHz using a Varian 400 NMR spectrometer. Spectra were recorded with a rotor spinning rate of 5 kHz and a cross-polarisation contact time of 2 ms.

High resolution XPS (X-ray photoelectron spectra) measurements were preformed on a Kratos Axis-Ultra spectrometer using a Dual anode Mg Kα X-ray source (1253.6 eV) with 12 kV operational voltage and 12 mA emission current. The pass energies were 80 eV for the survey scan and 20 eV for the Pd 3p, Pd 3d, O 1s and C 1s in the high resolution scans. All spectra were processed by using a Powell peak-fitting algorithm provided by the spectrometer software.

The size and morphology of Pd nanoparticles and chitosan nanofibres were determined using transmission electron microscopy (TEM, JEOL 3000F) operating at 300 kV and scanning electron microscopy (SEM, Zeiss 1555) with an acceleration voltage of 5 kV.

General procedure for Heck reaction

Iodobenzene (0.98 mmol, 1eq), butyl acrylate (1.18 mmol, 1.2eq), Et_3N (2.45 mmol, 2.5eq) in DMF (2 mL) was treated in one portion with Pd-Chitosan catalyst (0.17 mol %). The reaction

mixture was degassed (freeze pump thaw method) before heating to 80°C for 24 h. The ensuing reaction mixture was centrifuged and Pd-Chitosan catalyst was washed three times with DMF (3 × 5mL). The final yield was characterised by GC-MS (gas chromatography and mass spectrometry). For recycling studies, the Pd-Chitosan catalyst was separated by centrifugation, washed by DMF three times, and stored in DMF under argon prior to the next catalytic run.

1. K. Ohkawa, D. I. Cha, H. Kim, A. Nishida and H. Yamamoto, *Macromolecular Rapid Communications*, 2004, **25**, 1600-1605.
2. J. Schiffman and C. Schauer, *Biomacromolecules*, 2007, **8**, 2665-2667.