Supplementary information

Uniform nanoporous graphene sponge from natural polysaccharides as metal-free electrocatalyst for hydrogen generation

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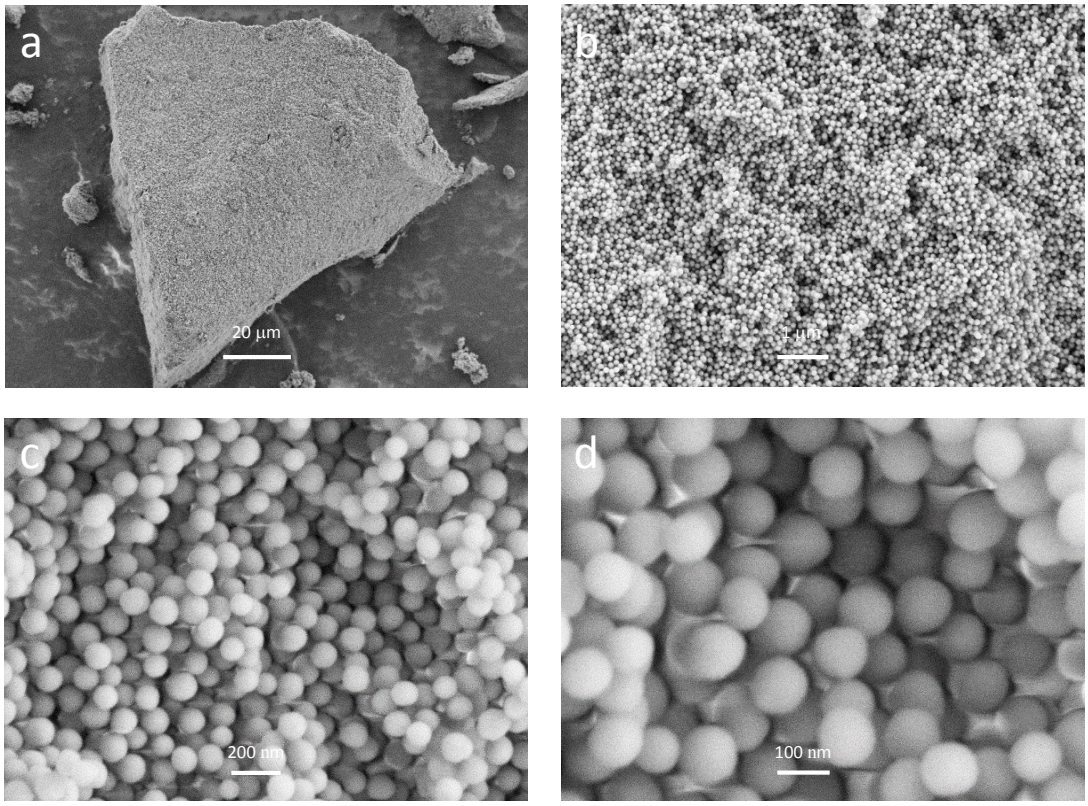

Fig.S1 SEM image of close-packed silica spheres used as template with the diameter of about 80 nm with different magnifications.

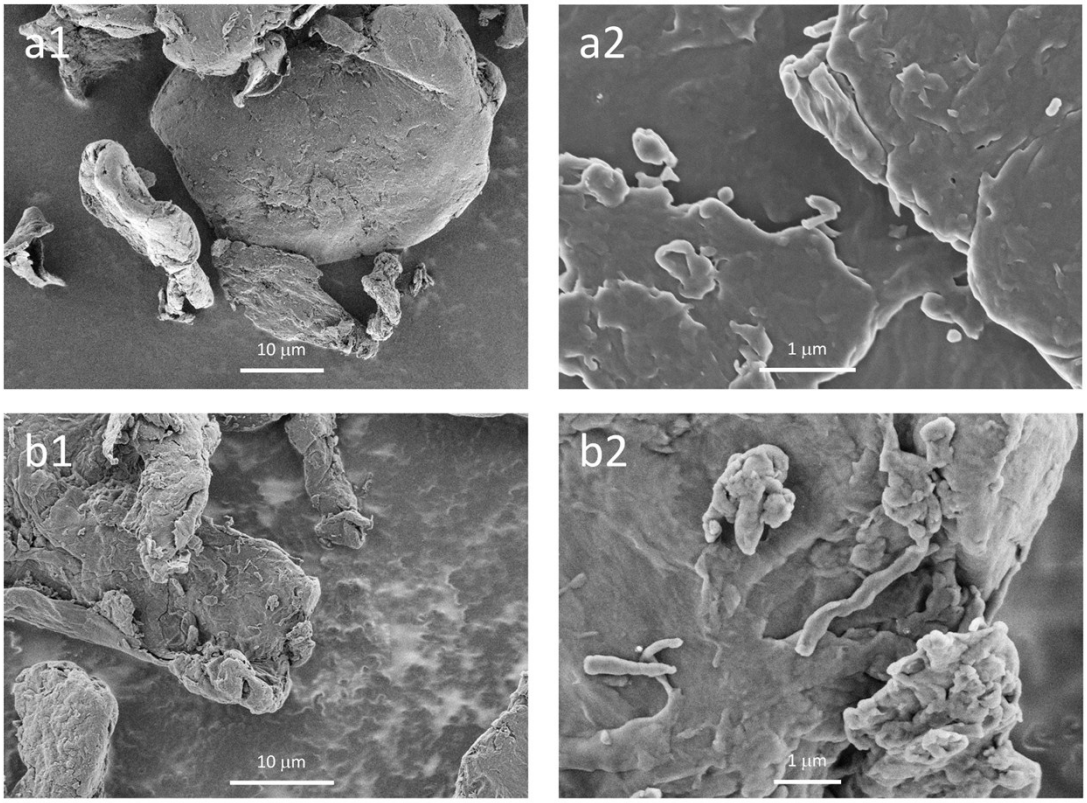

Fig.S2 SEM images of different bulk particles of G-CHI made by pyrolysis of chitosan without silica template, where a2) and b2) are the magnification of the locals of a1) and b1). From the figures, no obvious pores can be found, and the particle size is usual in the micrometre scale.

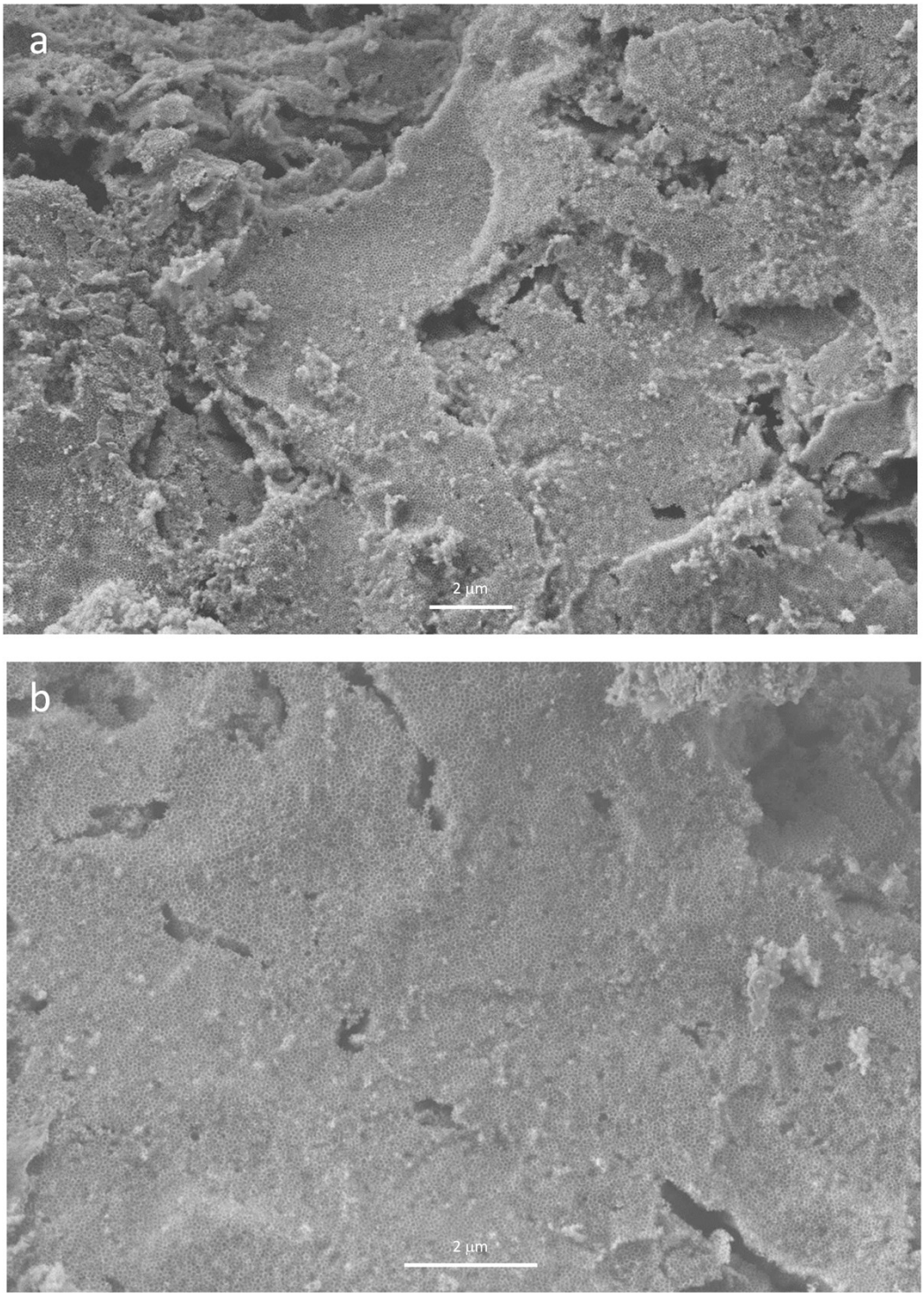

Fig.S3 SEM images of GS-CHI made from chitosan solution with silica template (2 ml 2wt% chitosan solution and 2 g silica template), where a) and b) are different regions of sample. Uniform and plentiful pores with the size about 80 nm can be clearly seen in material.

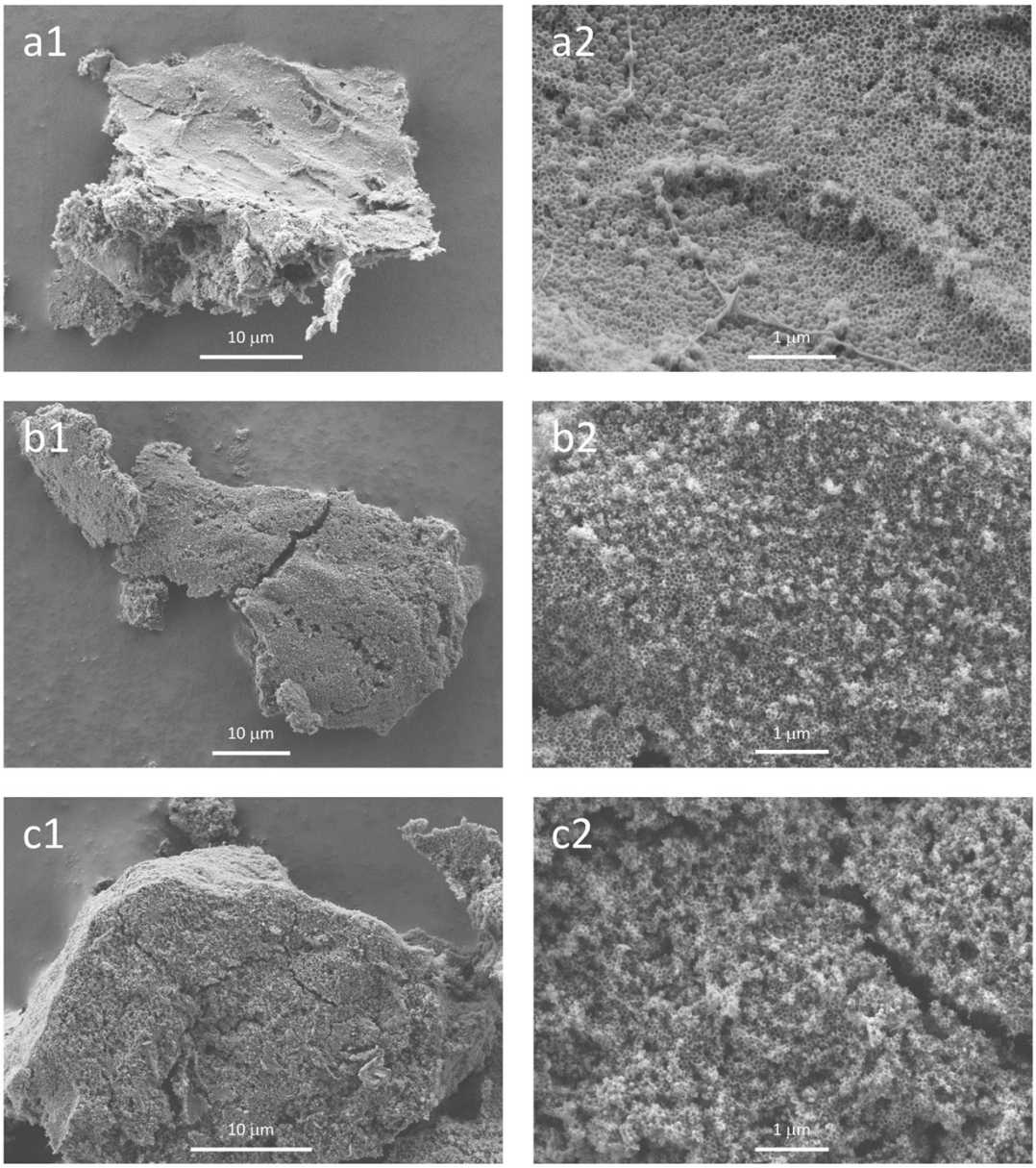

Fig.S4 SEM images of GS-CHI samples obtained using different parameters in the synthesis. a) 1 ml 2 wt% chitosan solution and 2 g silica; b) 5 ml 0.5 wt% chitosan solution and 2 g silica; c) 5 ml 1wt% chitosan solution and 2 g silica. In our studies, different concentrations of chitosan solution and liquid/solid ratios have been investigated, and no obvious difference among these porous GS-CHI particles obtained in different synthesis parameters can be found. However, in some samples especially made at high liquid/solid ratios and/or high chitosan solution concentrations, nonporous part can be inevitably found.

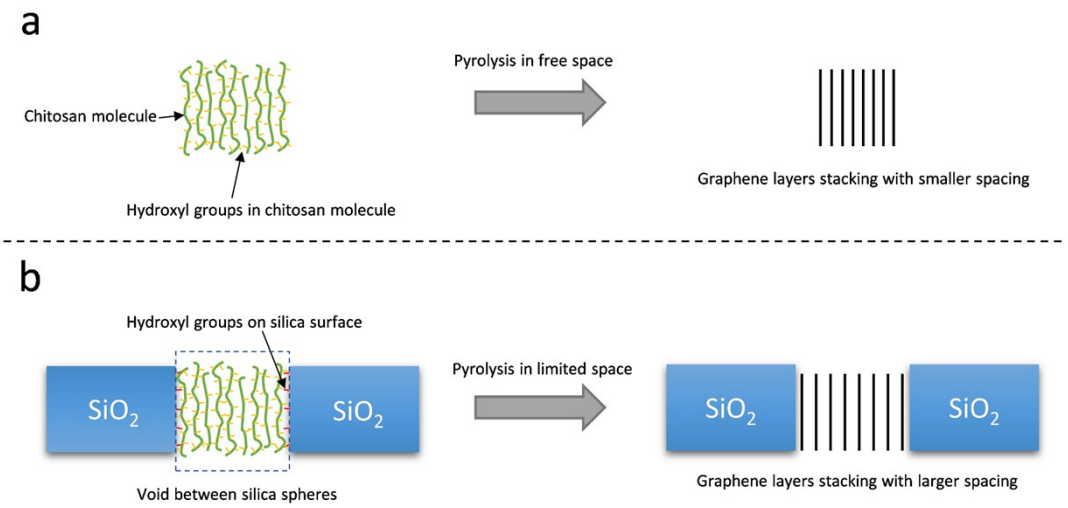

Fig.S5 Schematic shrinkage of graphene interlayer spacing during chitosan pyrolysis in a) free space and b) limited void between silica spheres. Compared to the situation in free space, chitosan molecules close to silica surface are attracted by the hydroxyl groups and unsaturated oxygen atoms on silica surface through hydrogen bond and VDW forces. When pyrolysis, silica surface polymerizes with chitosan and the attractive force is passed into the deeper layer by layer, resulting larger spacing between graphene layers. And this spacing can be maintained even if silica spheres are further etched, due to connected structure of 3D framework.

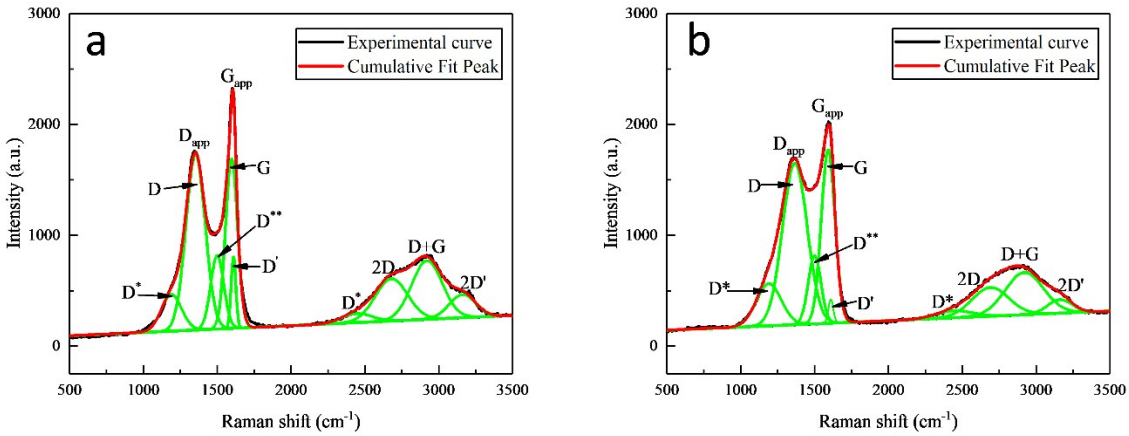

Fig.S6 Raman spectra of a) GS-CHI and b) G-CHI with deconvolution of typical peaks (514 nm excitation)

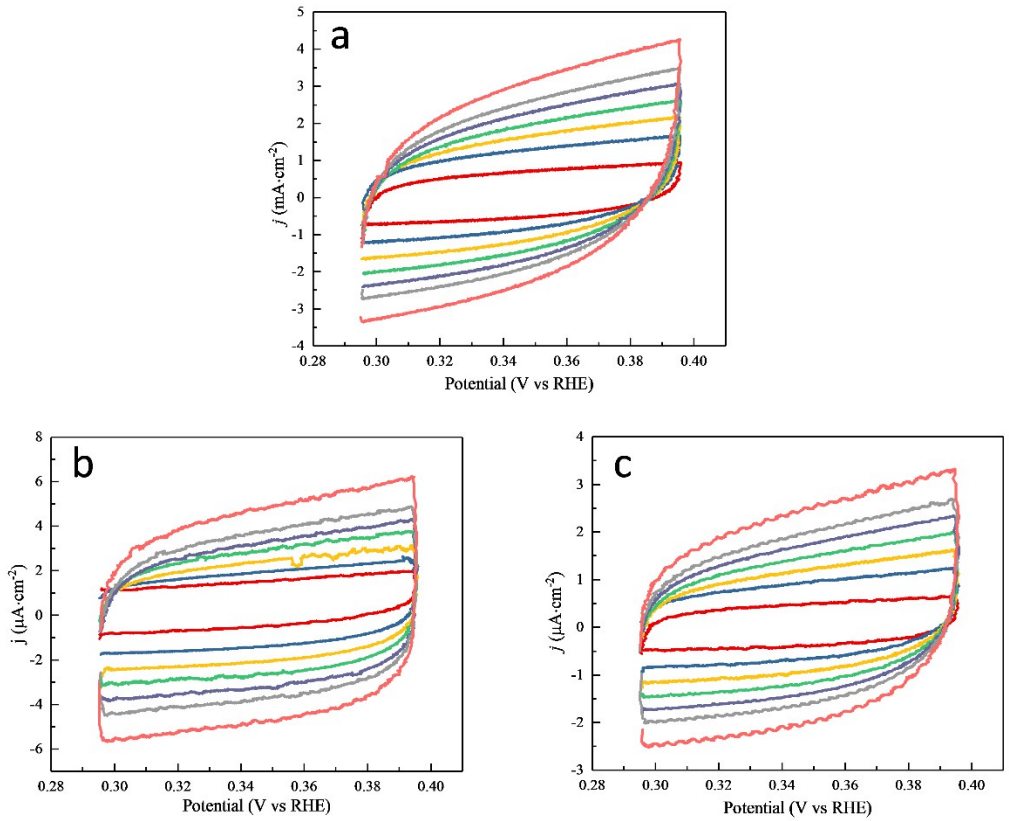

Fig.S7 Cyclic voltammograms in the region of 0.30-0.40 V (vs. RHE) for the a) GS-CHI, b) G-CHI, c) blank GCE at the scan rate of 25, 50, 75, 100, 125, 150 and 200 mV/s.

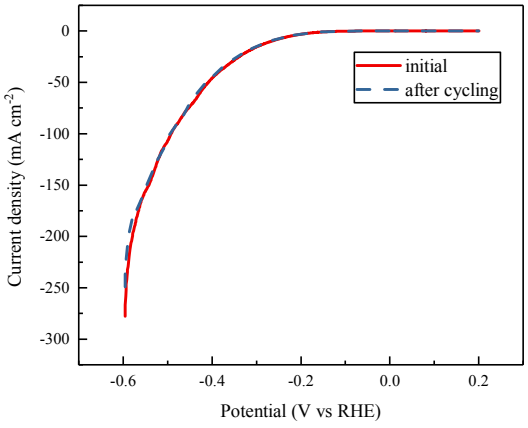

Fig.S8 Stability test for GS-CHI with the initial LSV polarization curve (line) and after 1000 cycles (dash) in 0.5 M H_2SO_4 at a scan rate of 5 mV/s.

Table S1 Curve fitting data of D and G Raman bands for GS-CHI and G-CHI

Peak	Position (cm^{-1})	FWHM (cm^{-1})	Intensity (a.u.)	Area (a.u.)	Integrated area ratio A_D/A_G
GS-CHI					
D*	1190	162	331	57001	
D	1354	153	1580	257046	
D**	1500	105	665	74140	1.66
G	1597	95	1528	155004	
D’	1610	38	644	25730	
G-CHI					
D*	1190	198	380	80023	
D	1367	196	1456	304362	
D**	1500	102	613	66602	1.69
G	1592	108	1564	180519	
D'	1610	39	213	8907	

The D* and D** peaks may be related to the phonon frequencies at K and M point of graphite equivalent Brillouin zone. The D peak is caused by the breathing modes of six-atom rings requiring a defect for its activation. The G peak is related to the E2g phonon at the Brillouin-zone center. The D’ peak originating from the double resonance intervalley process.[1]

References

[1] R. Hawaldar, P. Merino, M. R. Correia, I. Bdikin, J. Grácio, J. Méndez, J. A. Martín-Gago, M. K. Singh, *Sci. Rep.* **2012**, *2*, 2.