Supporting Information

Surface oxygen triggered size change of palladium nano-crystals impedes catalytic efficacy

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**Synthesis and characterization of Pd-PVP nanospheres:**

Pd-PVP nanospheres were synthesized by using spinning disc processing (SDP) as a facile one step method with hydrogen gas as the reducing agent at room temperature. SDP (Scheme S1) is a process intensification strategy which offers continuous flowing film (1 to 200 μm) on a rapidly rotating disc surface (usually up to 3000 rpm). The wavy thin film generated on the spinning disc surface has been reported to enhance hydrogen gas uptake in the solution. In a typical experiment, the aqueous solutions of H2PdCl4 (0.6mM) were mixed with PVP (polyvinylpyrrolidone) with the molecular ratio of PVP to palladium10, and then fed through a jet feed onto the spinning disc, and hydrogen gas as reducing agent was fed through another jet feed, which resulted in the formation of palladium nano-spheres of uniform size and shape (Figure S1). The resulting mixture was collected from the outlet and washed three times with MilliQ water, then freeze-dried before use in the Heck reaction. A large number of 5 nm palladium particles (Figure S1) spontaneous assembly into nano-spheres within the dynamic thin films on the surface of disc in the presence of PVP, rather than discrete individual palladium nanoparticles. PVP acts as a scaffold entangled with the small palladium nano-particles within the dynamic thin films under intense shearing in the dynamic thin films, as well as stabilising the Pd-PVP
nano-spheres in solution.

Scheme S1. Schematic representation of a spinning disc processor (SDP).

Figure S1.TEM image and high resolution TEM image of Pd-PVP nano-spheres. Quasi-spheroidal 5 nm palladium nano-crystals indicated in dotted box.
Figure S2. XRD patterns of the nano-catalyst, prior to the first cycle, (a), and after the 10th recycling, (b).
Figure S3. Energy dispersive spectra (EDS) of palladium nanospheres. a) pristine; b) after the 5\textsuperscript{th} recycling in the absence of oxygen; c) after the 10\textsuperscript{th} recycling in the presence of oxygen.