Supporting information for

Noble Metal Aerogels — Synthesis, Characterization, and Application as Electrocatalysts

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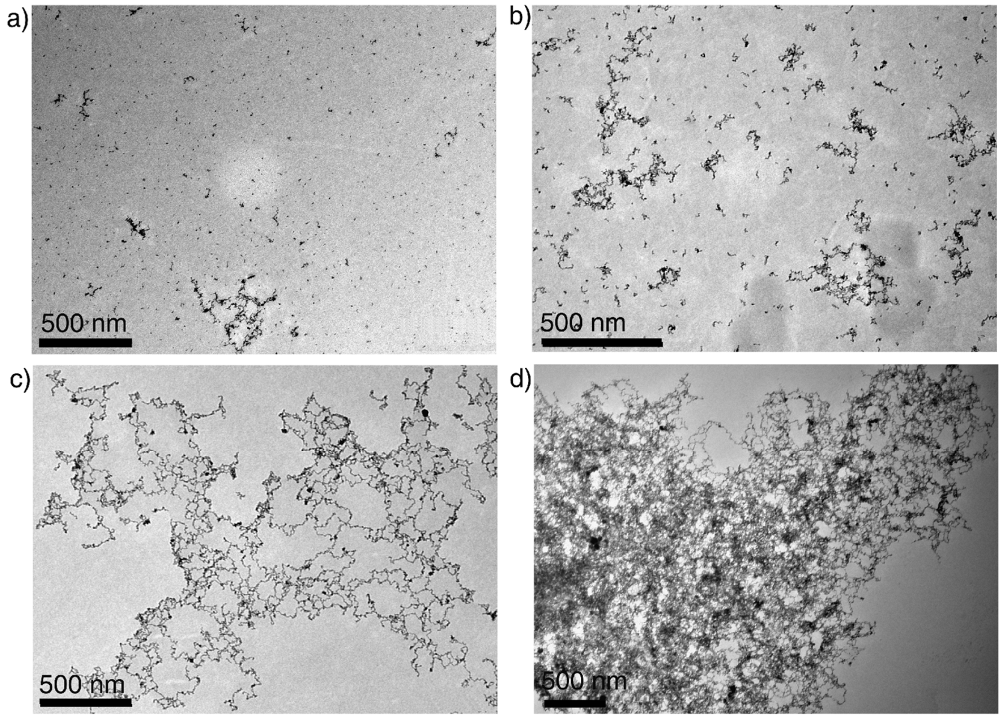

FIGURE S1. TEM monitoring of the formation of $Pd_{\beta\text{-CD}}$ hydrogel: images for the reaction solution at 30 s (a), 20 min (b), 2 h (c) after adding $NaBH_4$ into the K_2PdCl_4/β-CD aqueous solution, and for the $Pd_{\beta\text{-CD}}$ hydrogel formed 3 days later (d). Reprinted with permission from ref. 1, copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Depending on the nature of the noble metal NPs, the nanochains in the noble metal aerogel networks may appear in the form of fused nanowire-like structures or in the form of necklace-like chains, as can be seen from Figure 2 and Figure S2-S4.[1-4]

Take the noble metal aerogels obtained via strategy (I) up to now for example, the Pt, Au-Ag, Au-Pd and Pt-Pd aerogels prepared via this strategy (Figure 2 (a)-(d)) consist of interconnected nanowire network structure resulting from the coalescence of the initial spherical metal nanoparticles into nanowire-like structures with the diameter of the nanowires similar to the diameter of the initial nanoparticles. Notably, no pre-agglomeration or formation of secondary particles occurs during the gelation. Exceptionally, the silver and gold monometallic aerogels obtained via strategy (I) so far are composed of grains with a diameter of around 50 nm to hundreds of nanometers. It seems that these two kinds of metal NPs are prone to form pre-agglomerated secondary or tertiary particles and not of the original colloidal particles during gelation (Figure S2-S3).

The noble metal aerogels prepared via strategy (II) up to now are also mostly composed of interconnected fused nanowire-like structure with several nanometer diameter, e.g., the $Pd_{\alpha,\beta,\gamma\text{-}CD}$ and Pt-Pd aerogels (Figure 2 (e) and (f)). The Pt aerogel synthesized by this strategy shows necklace-like network structure composed of small nanoparticles or short nanowires with interspace between them (Figure S4). The Pd aerogel (Figure S4) obtained via this strategy is composed of more irregular agglomerates with less longer nanowires and less larger pores, as compared with those in the $Pd_{\alpha,\beta,\gamma\text{-}CD}$ aerogel (Figure 2 (e)).

Our initial results indicate that the detailed morphology of the noble metal aerogels is related to many factors, such as the initial morphology of the preformed noble metal NPs, the nature of the noble metals in the case of synthetic strategy (I), and the noble metal precursors, the stabilizers and the noble metal ratios in terms of synthetic strategy (II). More detailed and systematic investigations are under progress to better understand the growth mechanism and finally to realize the design of more controllable synthesis approaches for the noble metal aerogels.

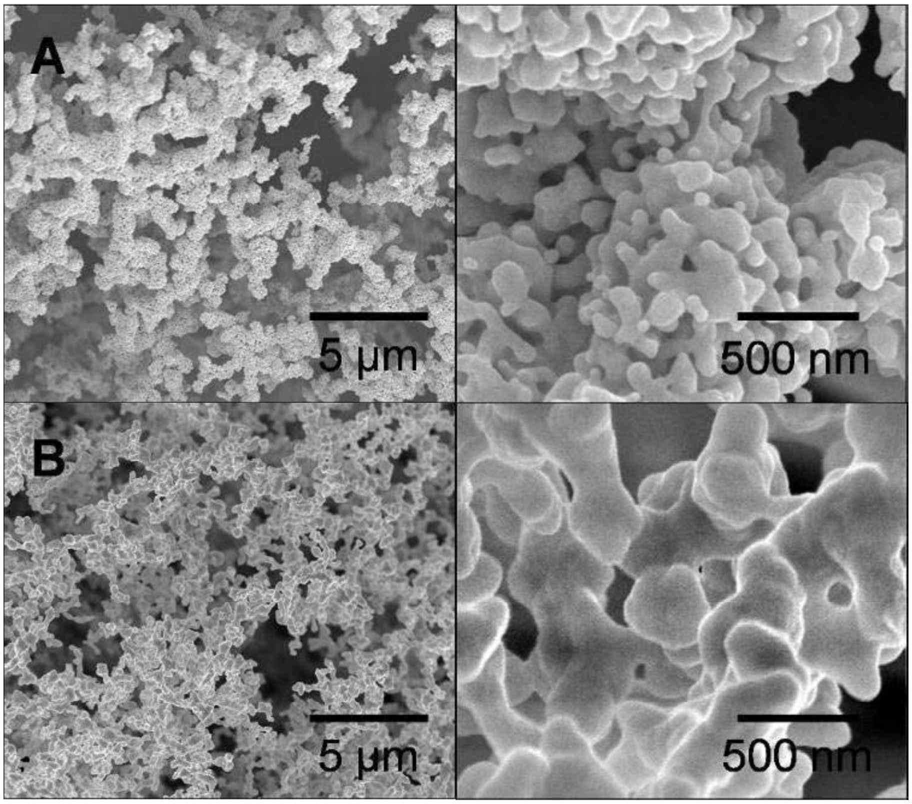

FIGURE S2. SEM images of aerogels from gold nanoparticles de-stabilized from solution by the addition of H_2O_2. The morphologies from two gels on the top (A) and on the bottom (B) differ only on the amount of H_2O_2 added. Reprinted with permission from ref. 2, copyright 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

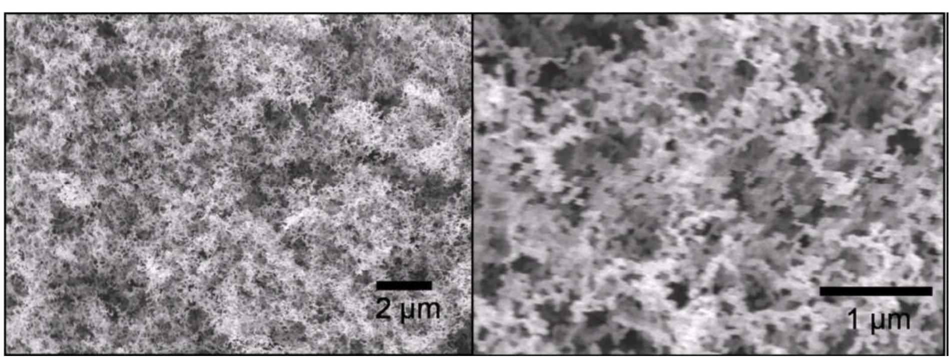

FIGURE S3. SEM images of an aerogel from silver nanoparticles de-stabilized from solution by the addition of H_2O_2. The gel consists of grains with diameters of 50 – 100 nm being homogeneously distributed over large areas. Reprinted with permission from ref. 2, copyright 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

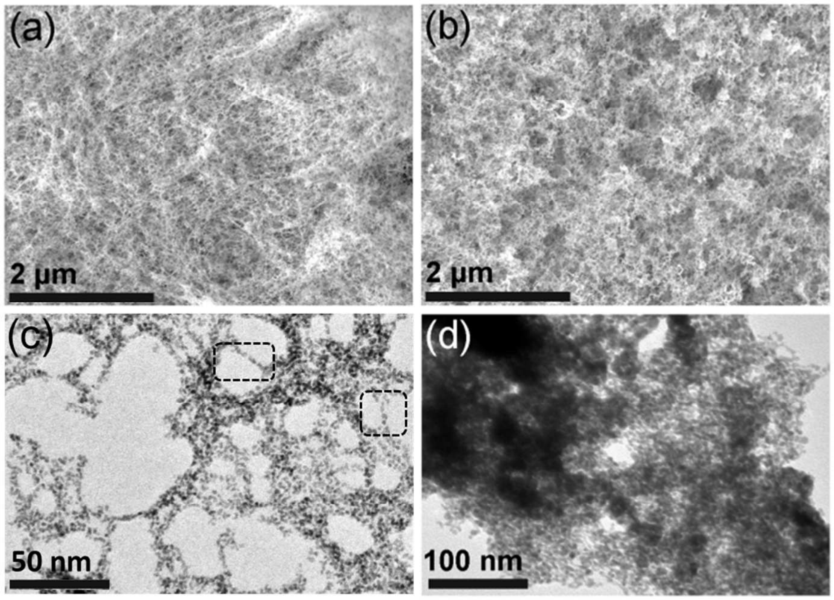

FIGURE S4. SEM (a, b) and TEM (c, d) images of Pt aerogel (a, c) and Pd aerogel (b, d) prepared via strategy (II). The dot squares in (c) show the necklace structure with interspace between particles in the Pt aerogel. Reprinted with permission from ref. 3, copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

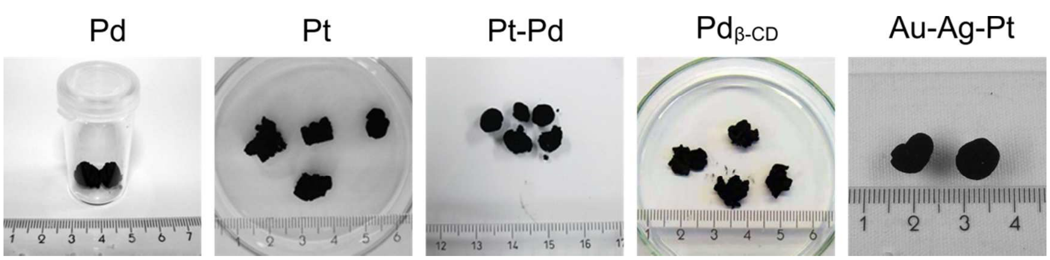

FIGURE S5. Photographs of some noble metal aerogel monoliths. The Pd, Pt, Pt-Pd and $Pd_{\beta\text{-CD}}$ aerogels were prepared by strategy (II), photographs reproduced with permission from ref. 3 and ref. 1, copyright 2013 and 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. The Au-Ag-Pt aerogel was prepared via strategy (I).

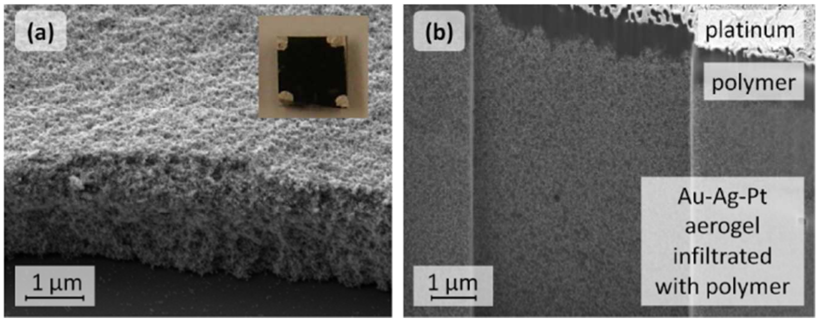

FIGURE S6. (a) SEM image of a Au–Pd xerogel film, the inset shows photograph of the corresponding sample. At the edges contact points made from silver paste are prepared for resistance measurements. (b) Focused ion beam (FIB) cut cross section of the Au-Ag-Pt trimetallic aerogel infiltrated with poly(ethyl cyanoacrylate). The platinum layer was sputtered on top of the sample before the FIB cut to protect the specimen surface from damage by the ion beam. The homogeneity of the appeal of the hybrid structure reveals that the network within the aerogel is retained during the infiltration process and the pores are mostly filled with the polymer. Images adapted with permission from ref. 4, copyright 2013 American Chemical Society.

TABLE S1. BET surface area values of porous noble metals prepared by different techniques. Adapted with permission from ref. 4, copyright 2013 American Chemical Society.

Material	**BET surface area** [$m^2\,g^{-1}$]
dextran templated Ag sponge[5]	0.5
hollow, hierarchical porous Au shells by use of templates and subsequent dealloying[6]	1.6
macroporous Ag framework by use of Triton X-114/silica sol as sacrificial template[7]	1.9
porous Ag made from 80-nm Ag superspheres[8]	8
nanoporous Au foam by electrochemical dealloying of $Ag_{75}Au_{25}$[9]	10–15
Pd nanowires synthesized in hexagonal mesophases[10]	12
mesoporous Au sponge by template-free assembly of glucose stabilized NPs[11]	12
noble metal (Au, Pd) foams by combustion synthesis with metal bistetrazolamine complexes[12]	11–37
interconnected hierarchical porous Pd nanostructures by controlled aggregation in organic media[13]	24
commercially available Pt black[14]	24–29
commercially available Pt black [from Sigma-Aldrich data sheet]	25
3D bimetallic alloy (Pd:Pt = 50:50) nanosponge by reduction in the absence of capping agents[15]	19
Au–Pd bimetallic foams via hydrothermal process[16]	20
noble metal (Au, Ag, Pt, Pd) nanosponges by kinetically controlled reduction process[17]	16–81
polycrystalline Pt nanowires synthesized in a 2-phase system[18]	53
mesoporous $Pd_{0.9}Rh_{0.1}$ alloy by partial consolidation of dendrimer-encapsulated NPs[19]	68
commercially available Pd black [from Sigma-Aldrich data sheet]	40–60
Ag–Pt aerogel via gelation of mixed preformed NPs[2]	**46**
Au–Ag aerogel via gelation of mixed preformed NPs[2]	**48**
$Pd_{\beta\text{-}CD}$ aerogel via *in situ* spontaneous gelation[1]	**92**
Pd aerogel via *in situ* spontaneous gelation[3]	**125**
$Pt_{80}Pd_{20}$ aerogel via *in situ* spontaneous gelation[3]	**73**
$Pt_{50}Pd_{50}$ aerogel via *in situ* spontaneous gelation[3]	**86**
$Pt_{20}Pd_{80}$ aerogel via *in situ* spontaneous gelation[3]	**75**
Pt aerogel via *in situ* spontaneous gelation[3]	**168**
Au/Ag, Pd/Ag and Pt/Ag aerogels via gelation of preformed bimetallic nanoshell particles[20]	**32-42**
Ag aerogels via gelation of preformed Ag nanoshell particles[21]	**43-160**
Au–Pd aerogel via gelation of mixed preformed NPs[4]	**57**
Pt–Pd aerogel via gelation of mixed preformed NPs[4]	**79**

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