Supporting information for

Hollow Bimetallic Nanoparticles Generated *in situ* Inside a Polymer Thin Film: Fabrication and Catalytic Application of Silver-Palladium-Poly(vinyl alcohol)

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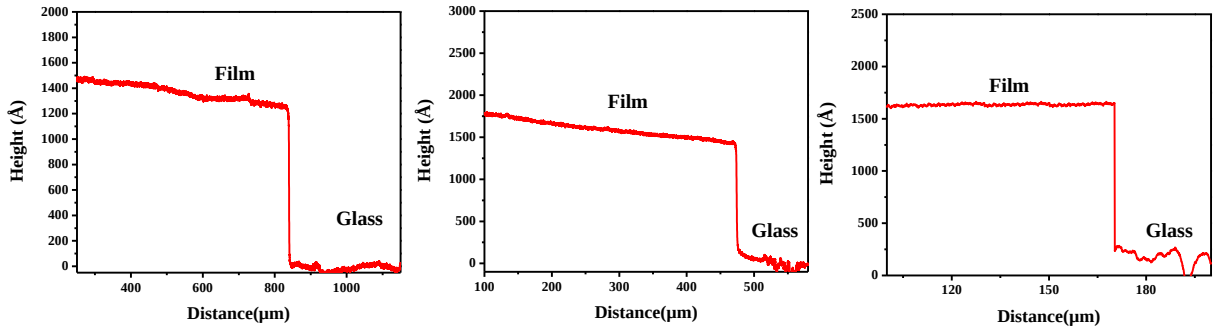
Characterization of Ag-Pd-PVA and Ag-Pd-PVA thin films

Thickness

Films were prepared on glass plates partially covered with a Teflon tape, by spin-coating at 500 rpm for 10 s followed by 6000 rpm for 10 s, and following the procedure described in the main text. The tape was removed to expose the substrate and the thickness of the layer was measured using an Ambios Technology XP-1 Profilometer. Thickness of the film is found to be ~ 150 nm (profiles at three different points are shown below).



ICP analysis of the metal content

Ag-PVA thin film (fabricated with Cu^{2+})

The Ag-PVA film coated on a 3.5 × 1.5 cm^2 glass plate was dissolved in 69% nitric acid. The solution was diluted to 100 ml and ICP-OES analysis was carried out. The metal content found are provided below.

Metal	Concentration of the solution analyzed (ppm)	Total weight in the film (μg)	Atom content in the film (μmol)
Cu	0.0174	1.74	0.027
Ag	0.632	63.2	0.59

The Cu/Ag weight (atom) ratio from the ICP analysis is: 0.028 (0.046). This is consistent with the Cu/Ag weight (atom) ratio obtained from the EDX analysis: 0.023 (0.039) (based on the spectra shown on page S11).

Weight of the PVA matrix in the sample analyzed works out to be 86.4 μg (assuming a film thickness of 150 nm, density of PVA to be 1.20 g cm^{-3}, and correcting for the very small volume occupied by the Ag nanoparticles). This implies an Ag/PVA weight ratio of ~0.73 and Cu/PVA weight ratio of 0.02. The Ag/PVA ratio is smaller than the weight ratio of 0.8 taken for the synthesis, since the film is heated only for 30 min, leaving some of the Ag^+ unreduced that is subsequently washed away during the last step of the Ag-PVA fabrication.

Ag-Pd-PVA thin film

The Ag-Pd-PVA film (concentration of K_2PdCl_4 solution spread = 0.25 mM) coated on a 3.5 × 1.5 cm^2 glass plate was dissolved in 69% nitric acid. The solution was diluted to 100 ml and ICP-OES analysis was carried out. The metal content found are provided below.

Metal	Concentration of the solution analyzed (ppm)	Total weight in the film (µg)	Atom content in the film (µmol)
Pd	0.0881	8.81	0.0828
Ag	0.386	38.6	0.358

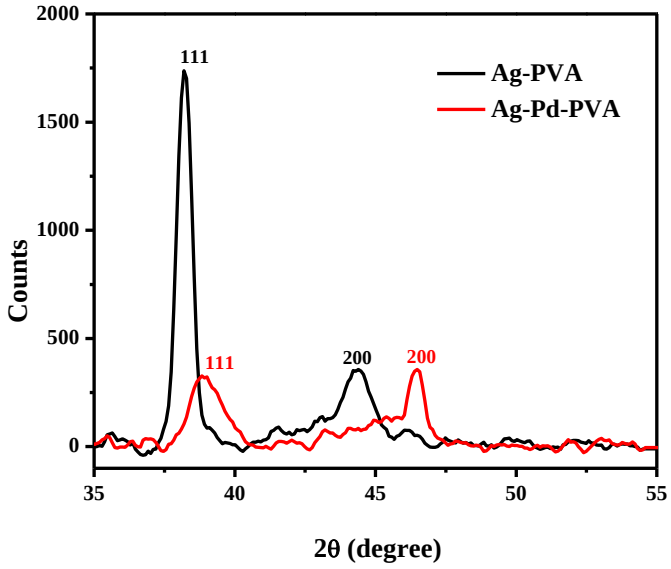
The Ag/Pd weight (atom) ratio from the ICP analysis is: 4.38 (4.32). This is consistent with the Ag/Pd weight (atom) ratio obtained from the EDX analysis: 4.09 (4.04) (based on the spectra shown on page S8).

Weight of the PVA matrix in the sample analyzed works out to be 94.2 µg (assuming a film thickness of 150 nm, density of PVA to be 1.20 g cm^{-3}, and correcting for the very small volume occupied by the Ag nanoparticles). This implies an Ag/PVA weight ratio of ~0.41. This ratio is less than that in the Ag-PVA film as the Ag is partly replaced by Pd and the biproduct Ag^+ is washed away during the second stage of fabrication.

The catalysis (Suzuki-Miyaura reaction) study employed two Ag-Pd-PVA films (total surface area = 2 × 3.5 × 1.5 = 10.5 cm^2). Therefore the amount of Pd used = 0.165 µmol *ie.* 17.6 µg.

X-ray diffraction

Samples were prepared as thick films maintaining the initial Ag/PVA ratio as 0.8, following the same procedure as described in the main text, and spreading 0.25 mM solution of K_2PdCl_4. X-ray used: Cu-K_α (λ = 1.5418 Å). The diffractograms obtained and the indexing of the peaks are shown below.

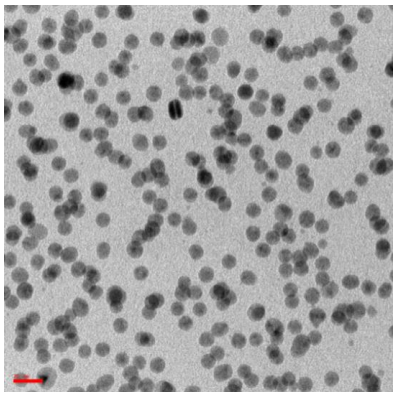


Film	2θ (deg.)	d (Å)
Ag-PVA	38.2	2.356
	44.4	2.040
Ag-Pd-PVA	38.9	2.315
	46.5	1.953

The lattice spacing estimated above are in good agreement with the values deduced from the electron diffraction patterns (page S6) and HRTEM images (page S7).

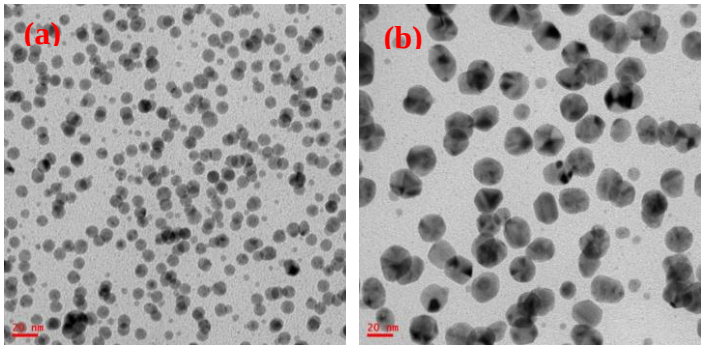
Transmission Electron Microscopy

Ag-PVA film fabricated using high Ag/PVA weight ratio and short thermal annealing



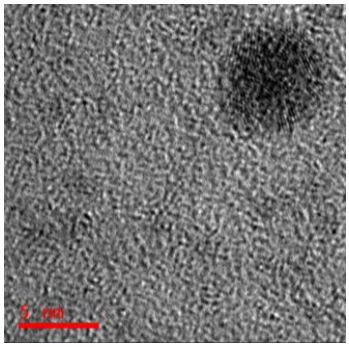
The Ag/PVA was increased from the low ratios used in earlier studies (Ref. 35, 36 in main text) to the high value of 0.8, and the thermal annealing was restricted to 30 min. The film was subsequently washed with water to remove the unreacted Ag^{+} ions and dried. TEM image of this film showed particles ~ 12 nm in diameter.

Ag-PVA films fabricated without and with Cu^{2+} under vacuum conditions



In order to explore the effect of oxygen present in the atmosphere on the size of the Ag nanoparticles, the thermal annealing was carried out with the samples kept under vacuum. Heating was carried out at 130^{o}C for 30 min. TEM images of Ag-PVA thin film fabricated (a) without and (b) with the addition of a small amount (1.4 weight % in terms of the total metal content) of Cu^{2+} show that the size of Ag nanoparticles obtained are very similar to those fabricated under ambient atmosphere (Fig. 3a and 3e of the main text).

High resolution image of the small particles present in the TEM image of Ag-PVA film prepared with 1.4 weight % Cu^{2+}.



The lattice spacing is found to be 2.34 Å, indicating that the particle is Ag.

Electron Diffraction

Ag-PVA and Ag-Pd-PVA thin films

Electron diffraction patterns recorded for the Ag-PVA thin film and the film treated with different concentrations of K_2PdCl_4 solutions are provided in Fig. 5 of the main text. Indexing of the spots in the pattern for each case based on the fcc structures of Ag, Pd and the Ag-Pd alloy (see references on page S6) are shown in the table below.

Image label in Fig. 5	Conc. of K_2PdCl_4 solution (mM)	d (Å)	h k l
a	0.00	2.34 2.04 1.44 1.18	1 1 1 (Ag) 2 0 0 (Ag) 2 2 0 (Ag) 2 2 2 (Ag)
b	0.05	2.34 2.03 1.23 2.24	1 1 1 (Ag) 2 0 0 (Ag) 3 1 1 (Ag) 1 1 1 (Pd)
c	0.10	2.33 2.29 2.23 1.99 1.39	1 1 1 (Ag) 1 1 1 (Ag-Pd) 1 1 1 (Pd) 2 0 0 (Ag-Pd) 2 2 0 (Ag-Pd)
d	0.15	2.29 1.97 1.14	1 1 1 (Ag-Pd) 2 0 0 (Ag-Pd) 2 2 2 (Ag-Pd)
e	0.20	2.28 2.00 1.39	1 1 1 (Ag-Pd) 2 0 0 (Ag-Pd) 2 2 0 (Ag-Pd)
f	0.25	2.30 1.98 1.14	1 1 1 (Ag-Pd) 2 0 0 (Ag-Pd) 2 2 2 (Ag-Pd)

Lattice Images

Ag-PVA and Ag-Pd-PVA thin films

High resolution TEM images of the nanoparticles in Ag-PVA thin film and the film treated with different concentrations of K_2PdCl_4 solutions are provided in Fig. 6 of the main text. The images along with the FFT of different regions in each image are shown below. The lattice spacing inferred from the FFT and the assignment of the lattice planes based on the fcc structures of Ag, Pd and the Ag-Pd alloy (see references on page S6) are provided in the table.

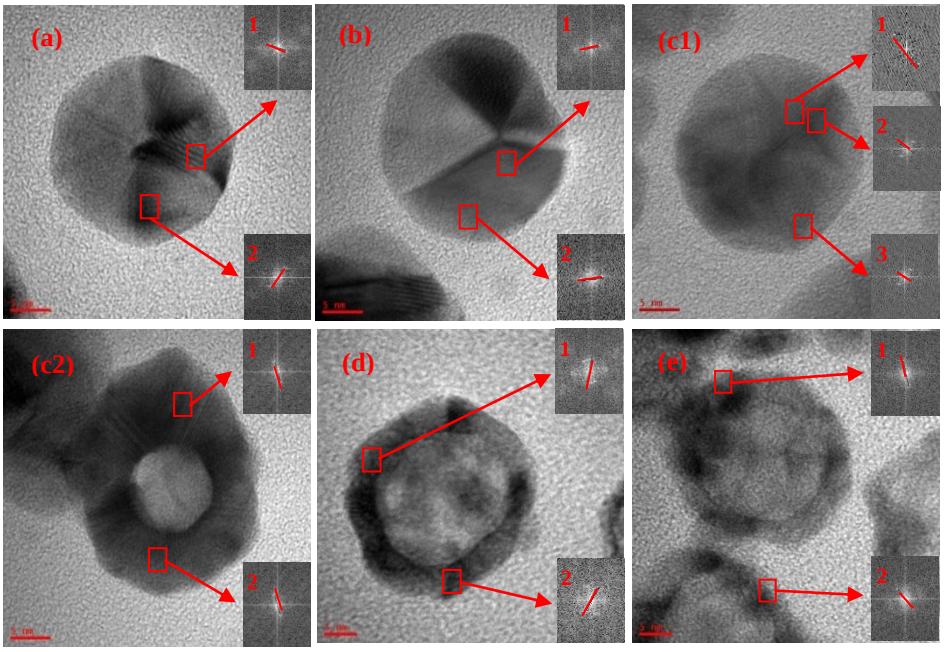


Image label in figure	Conc. of K_2PdCl_4 solution (mM)	Region selected	d (Å)	h k l
a	0.00	1	2.34	1 1 1 (Ag)
		2	2.05	2 0 0 (Ag)
b	0.05	1	2.34	1 1 1 (Ag)
		2	2.23	1 1 1 (Pd)
c1	0.10	1	2.23	1 1 1 (Pd)
		2	2.34	1 1 1 (Ag)
		3	2.29	1 1 1 (Ag-Pd)
c2	0.10	1	2.23	1 1 1 (Pd)
		2	2.30	1 1 1 (Ag-Pd)
d	0.15	1	2.30	1 1 1 (Ag-Pd)
		2	2.29	1 1 1 (Ag-Pd)
e	0.25	1	2.29	1 1 1 (Ag-Pd)
		2	2.29	1 1 1 (Ag-Pd)

References for the lattice spacing values

Metal/Alloy	h k l	d (Å)	Ref.
Ag	1 1 1	2.40	S1
		2.35	S2 – S6
		2.32	S7
	2 0 0	2.03	S4
		2.07	S5
		2.04	S8
	2 2 0	1.44	S8
	3 1 1	1.23	S8
	2 2 2	1.18	S8
Pd	1 1 1	2.20	S1
		2.22	S9
		2.24	S4
	2 0 0	1.93	S9
Ag-Pd	1 1 1	2.30	S1
		2.28	S3
		2.27	S10
	2 0 0	2.00	S10

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S5. S. Sun, D. Deng, C. Kong, Y. Zhang, X. Song, B. Ding and Z. Yang, *CrystEngComm*., 2011, **13**, 4827.

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S7. M. A. M. Khan, S. Kumar, M. Ahamed, S. A. Alrokayan and M. S. AlSalhi, *Nanoscale Res. Lett.*, 2011, **6**, 434

S8. JCPDS file no: 89-3722

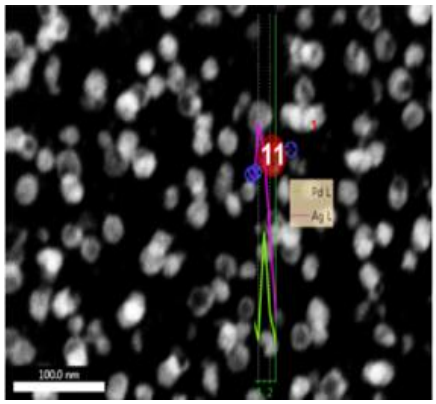
S9. Y. T. Chu, K. Chanda, P. H. Lin and M. H. Huang, *Langmuir*, 2012, **28**, 11258.

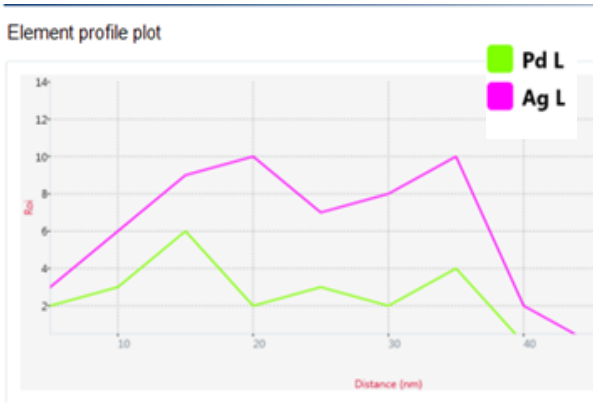
S10. S. Y. Jeon, H. N. Im, J. S. Lim, E. D. Wachsman and S. J. Song, *Ionics*, 2013**, 19**, 171.

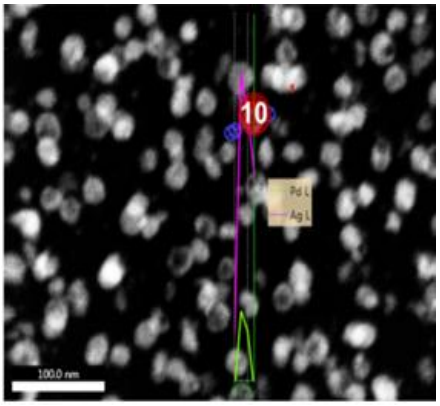
HAADF Images and Energy Dispersive X-ray Spectroscopy

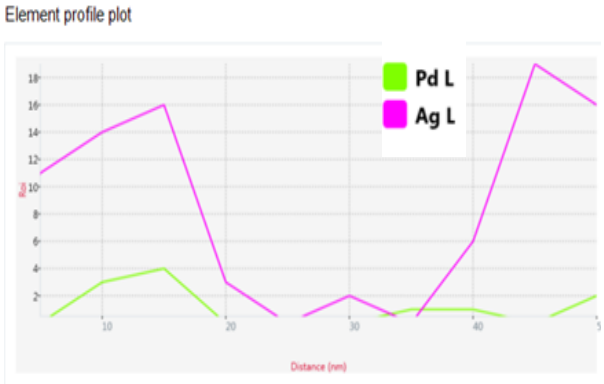
Ag-Pd-PVA thin film

HAADF image of the Ag-Pd-PVA thin film fabricated by treating with 0.15 mM K_2PdCl_4 solution along with EDX line spectra recorded along different directions. These spectra confirm the hollow interior of the particle and provide information on the local Ag/Pd ratio.

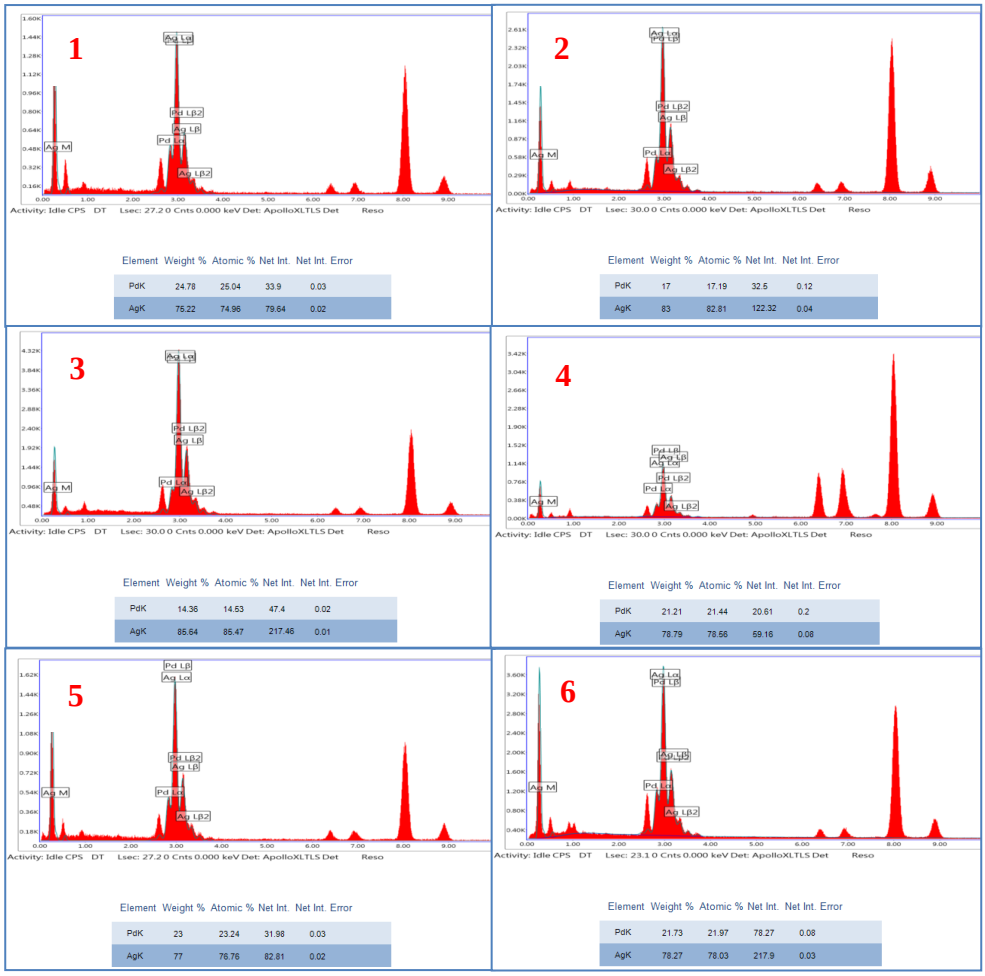








EDX spectra recorded at six different points in the image of the Ag-Pd-PVA thin film fabricated with 0.25 mM K_2PdCl_4 are provided below. The Ag/Pd weight ratios inferred from these spectra and the average value are collected in the table.



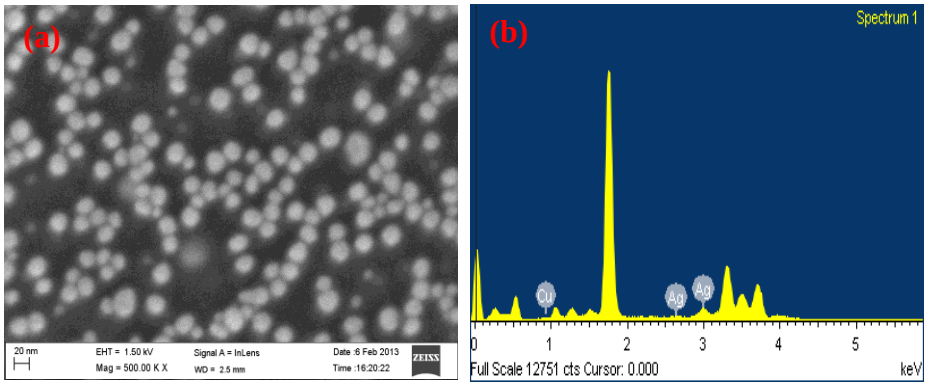
Position	Weight % of Pd	Weight % of Ag	Ag/Pd weight ratio
1	24.78	75.22	3.04
2	17.00	83.00	4.88
3	14.36	85.64	5.96
4	21.21	78.79	3.71
5	23.00	77.00	3.34
6	21.73	78.27	3.60
		Average	4.09*

***Ag/Pd atom ratio = 4.03**

Field Emission Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Ag-PVA thin film fabricated with Cu^{2+}

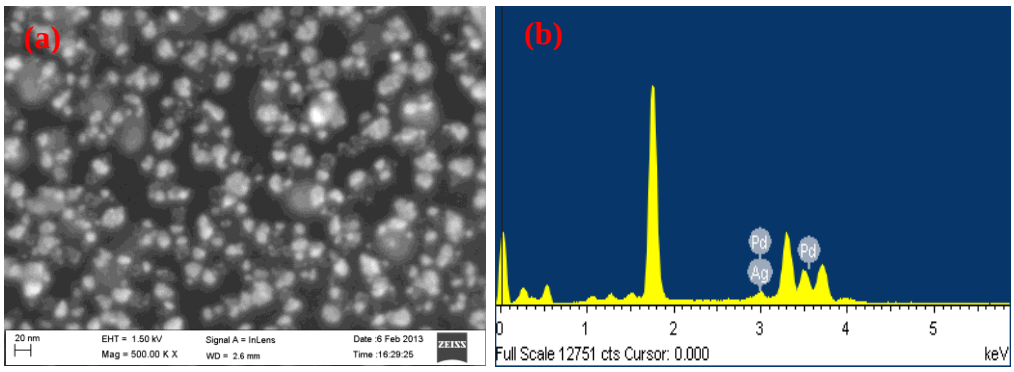
(a) FESEM image and (b) EDX spectrum of Ag-PVA thin film fabricated with 1.4 weight % Cu^{2+} (in terms of the total metal content) are provided below. TEM image of the sample is shown in Fig. 3e of the main text. The EDX data show the Cu weight % to be 2.22, consistent with the fabrication conditions.



Element	Weight %	Atomic %
Cu K	2.22	3.72
Ag L	97.78	96.28

Ag-Pd-PVA thin film

(a) FESEM image and (b) EDX spectrum of Ag-Pd-PVA thin film fabricated with using 0.15 mM solution of K_2PdCl_4 are provided below.

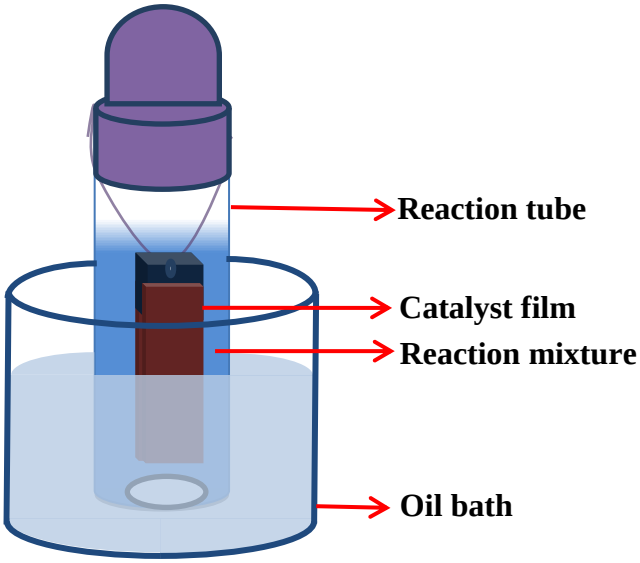


Element	Weight %	Atomic %
Ag L	83.99	83.80
Pd L	16.01	16.20

Catalysis using the Ag-Pd-PVA thin film

Reaction setup

A schematic diagram of the reaction setup described in the main text is provided below.



The catalytic application of Ag-Pd-PVA thin film was tested by using it to carry out the Suzuki-Miyaura reaction with the conditions shown in the following scheme.