

*Electronic Supplementary Information (ESI) for*

**Multidentate polyoxometalate modification of metal nanoparticles with tunable electronic states**

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## 1. Experimental Section

### Instruments

Transmission electron microscope (TEM) observations were conducted by JEM-2000EX and JEM-2010F at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were measured on ULVAC-PHI PHI5000 VersaProbeIII at the Advanced Characterization Nanotechnology Platform of The University of Tokyo, and analyzed with a Multipak software (version 9.9.0.8, by Ulvac-phi, inc.) in which the Shirley method was used for the background and a Gauss–Lorentz type function was performed for fitting through calibrating the binding energies by using the C 1s core-level at 284.5 eV. Solution-state ultraviolet-visible (UV-vis) spectra were measured on JASCO V-770 spectrometer with 1 cm quartz cells. Dynamic light scattering (DLS) characterizations were performed on Malvern Zetasizer NanoZS at the backscatter mode. Zeta-potential measurements were performed on Malvern Zetasizer NanoZS with a working voltage of 40 V for the later. Infrared (IR) spectra were measured on JASCO FT/IR-4100 using the attenuated total reflection method. Raman spectra were measured on JASCO NRS-5100.

### Materials

Silver nitrate ( $\text{AgNO}_3$ ), hydrogen hexachloroplatinate hexahydrate ( $\text{K}_2\text{PtCl}_6$ ), palladium chloride ( $\text{PdCl}_2$ ), sodium chloride ( $\text{NaCl}$ ), and trisodium citrate dihydrate (citrate) were obtained from Kanto Chemical. Potassium pentachlororuthenate hydrate ( $\text{K}_2\text{RuCl}_5$ ) and charcoal (carbon support) were obtained from FUJIFILM Wako Chemical. Polyvinylpyrrolidone (PVP) was obtained from Sigma Aldrich. PVP-protected silver nanoparticles (Ag-PVP) were obtained from Tanaka Precious Metals Inc. (Lot No. 160803-1). PVP-protected platinum nanoparticles (Pt-PVP) were obtained from NanoComposix, Inc. (Lot No. JDR004). Pd/C was obtained from N. E. CHEMCAT Co Ltd (E-type, Lot No. 217-183621) and used as received. All substrates for catalytic hydrogenation reactions were obtained from Tokyo Chemical Industry Co., Ltd. These chemicals were directly used without pre-treatment.  $\text{Na}_2\text{PdCl}_4$  was synthesized by mixing  $\text{PdCl}_2$  and  $\text{NaCl}$  a molar ratio of 1:2.<sup>S1</sup>  $\text{Na}_{10}\text{SiW}_9\text{O}_{34}$  (sodium salt of **SiW9**) and  $\text{K}_4\text{SiW}_{12}\text{O}_{40}$  (potassium salt of **SiW12**) were prepared according to previous report.<sup>S2</sup>

### **Synthesis of metal nanoparticles with multidentate polyoxometalate modification (M-SiW9)**

Metal nanoparticles and their supported materials were prepared according to our previous method<sup>S3</sup> with slight modifications. A sodium salt of **SiW9** ( $\text{Na}_{10}\text{SiW}_9\text{O}_{34}$ , 150 mg, 50  $\mu\text{mol}$ ) was dissolved in water (145 mL) in ice-bath ( $\sim 3\text{ }^\circ\text{C}$ ), then to this solution was added 0.1 M metal precursor aqueous solution (500  $\mu\text{L}$ , 50  $\mu\text{mol}$ ). After stirring the solution for 30 min, a freshly made ice cold aqueous solution of 0.1 M  $\text{NaBH}_4$  (5 mL, 500  $\mu\text{mol}$ ) was added dropwise in 10 min. For unsupported/colloidal metal nanoparticles (M-POM), the solution was stirred for another 15 min and stored in refrigerator or freeze-dried by liquid nitrogen to obtain solid samples for characterization. Metal nanoparticles modified with other protecting ligands ( $\text{K}_4\text{SiW}_{12}\text{O}_{40}$ , PVP, and citrate) were prepared using similar procedures as that for M-**SiW9**, except for using different protecting ligands.

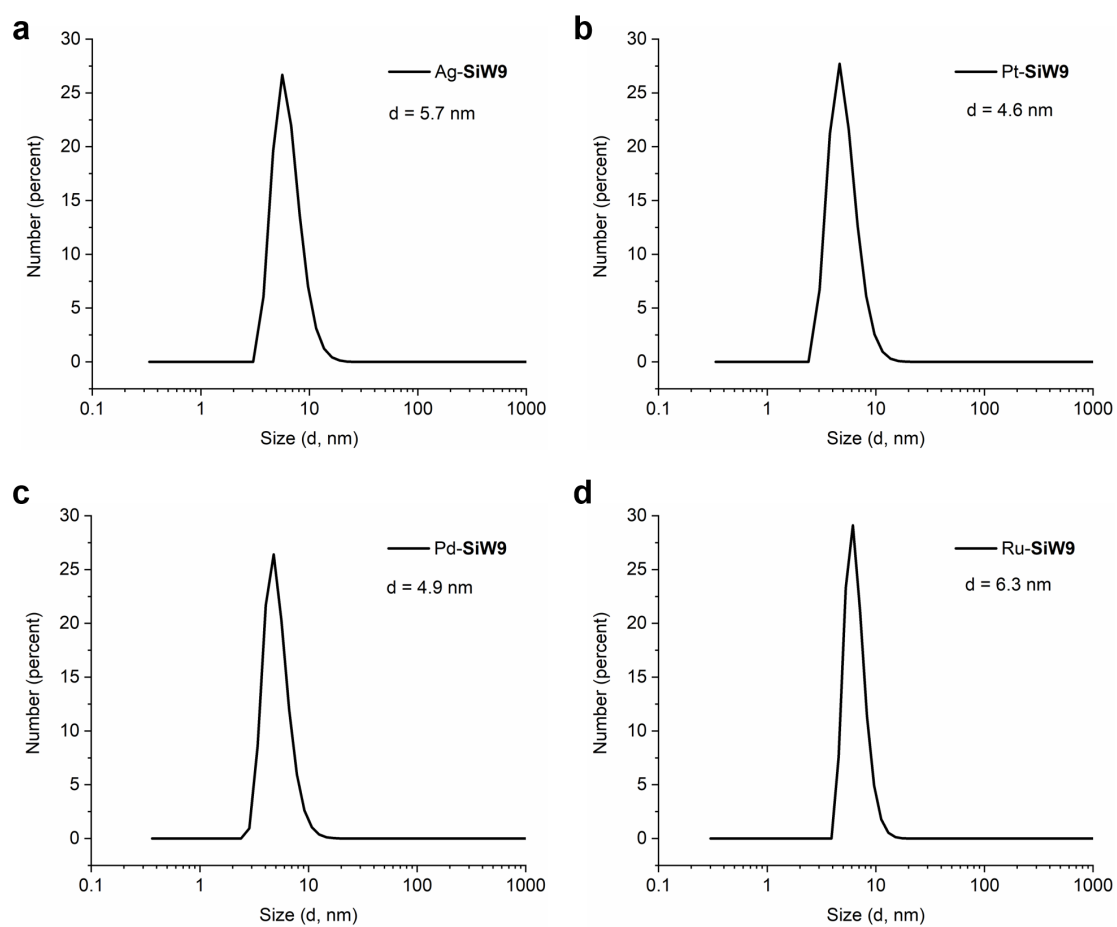
### **Immobilisation of metal nanoparticles modified with multi-dentate polyoxometalates on carbon supports (M-SiW9/C)**

To the freshly made synthesis aqueous solution (ca. 150 mL) of M-**SiW9** without any pre-treatment, carbon supports (300 mg) were added, and the resulting suspension was stirred for 20 min for dispersion and immobilization of M-**SiW9** on the support. Then, the suspension was transferred into a 300 mL-sized round-bottom flask, and the solvent was completely removed by using a rotary evaporator under reduced pressure at  $40\text{ }^\circ\text{C}$  for 60 min to obtain the supported metal nanoparticles with multi-dentate polyoxometalate modifications (M-**SiW9/C**). For hydrogenation reactions, as-prepared Pd-**SiW9/C** was directly used.

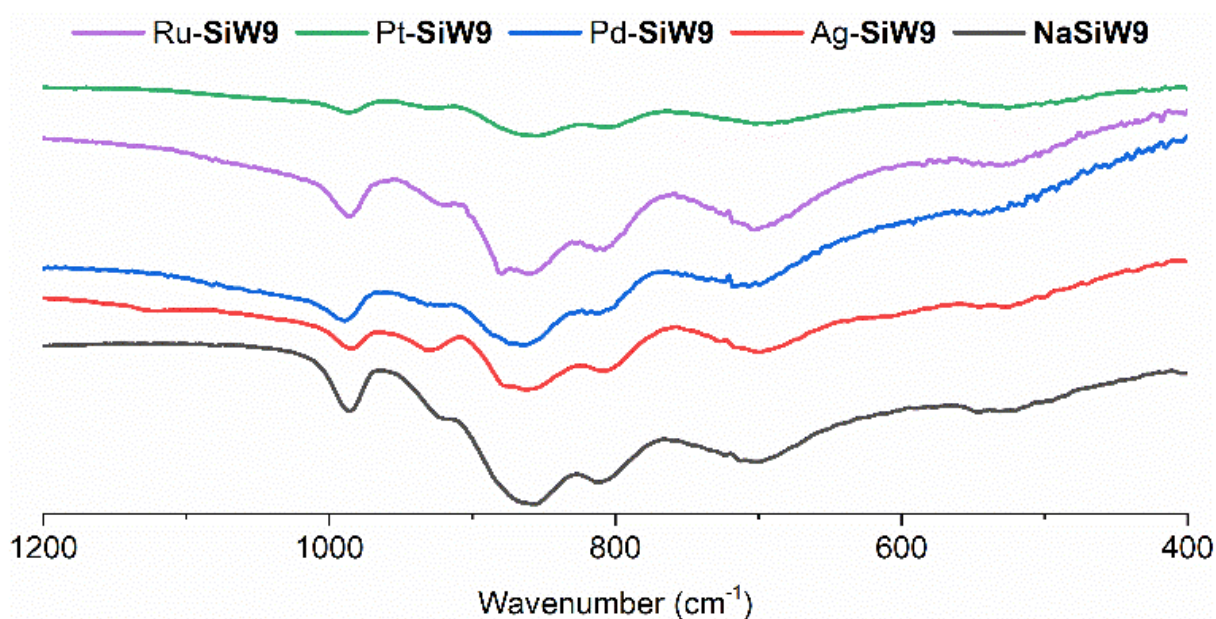
### **A typical procedure for catalytic hydrogenation reactions using Pd nanoparticle catalysts**

Ethynylbenzene **1a** (0.5 mmol), an internal standard substance biphenyl (0.1 mmol), Pd-**SiW9/C** (25 mg, Pd: 0.5 mol% with respect to **1a**), diglyme (2 mL) and a magnetic stirrer bar were added to a 20 mL Schlenk tube. After removing air in the Schlenk tube by freezing and degassing, a balloon filled with  $\text{H}_2$  gas was attached to maintain a constant gas atmosphere in the Schlenk tube during the reaction. The reaction solution was stirred at room temperature ( $\sim 25\text{ }^\circ\text{C}$ ) in a thermostat reactor and started the reaction. Sampling was performed using a syringe at predetermined time intervals with removal of the catalyst by filtration, and then the conversion of **1a** and the yields of products were determined by GC analysis.

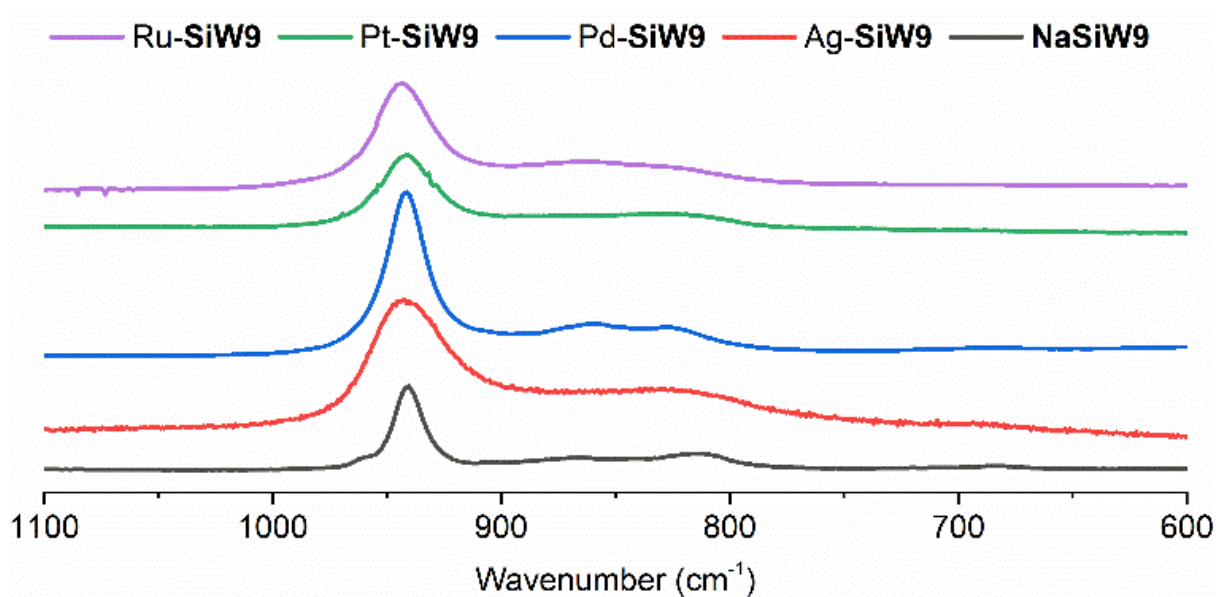
## 2. Supplementary Figures



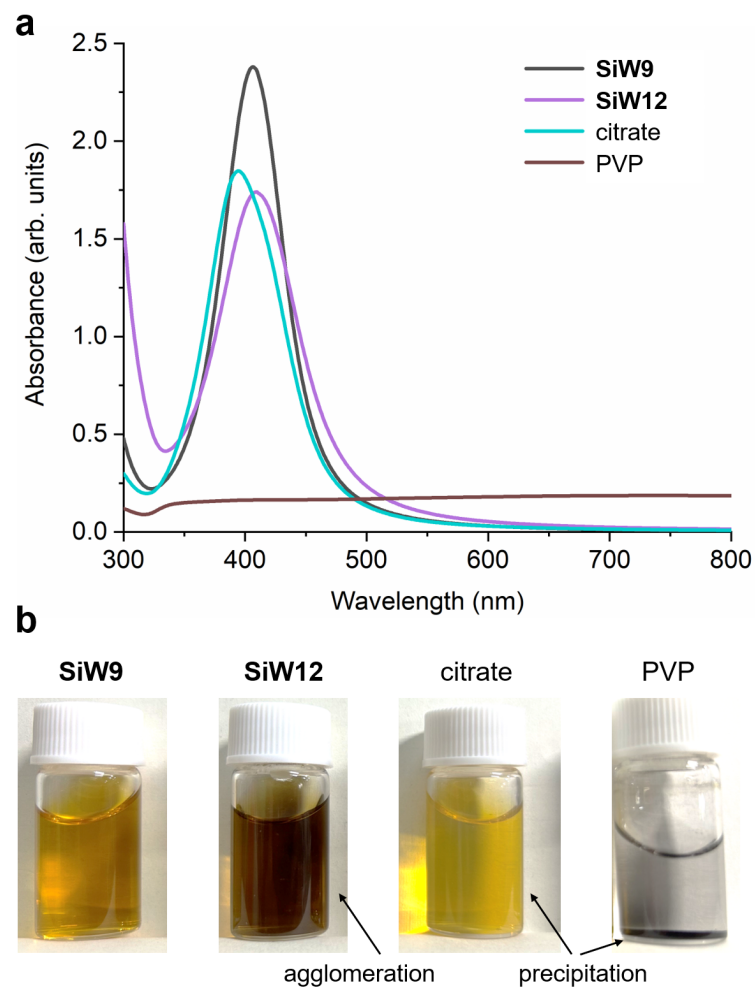
**Fig. S1** DLS analysis of metal nanoparticles with multidentate POM modification. (a) Ag-SiW9, (b) Pt-SiW9, (c) Pd-SiW9, and (d) Ru-SiW9.



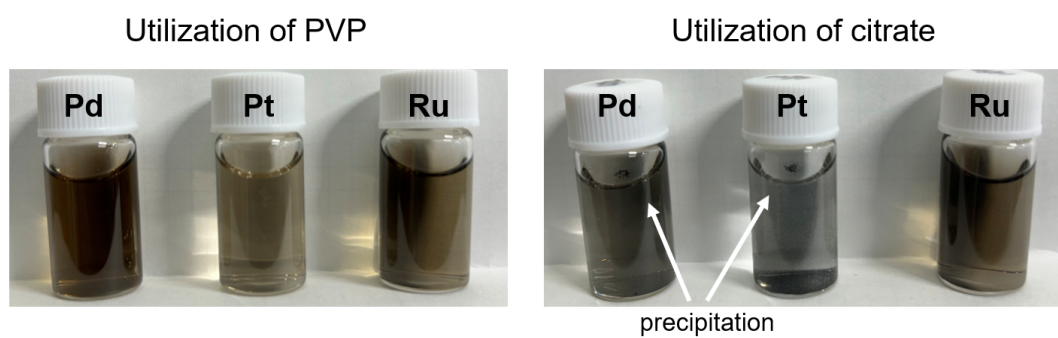
**Fig. S2** IR spectra of metal nanoparticles with multidentate POM modification (M-SiW9).



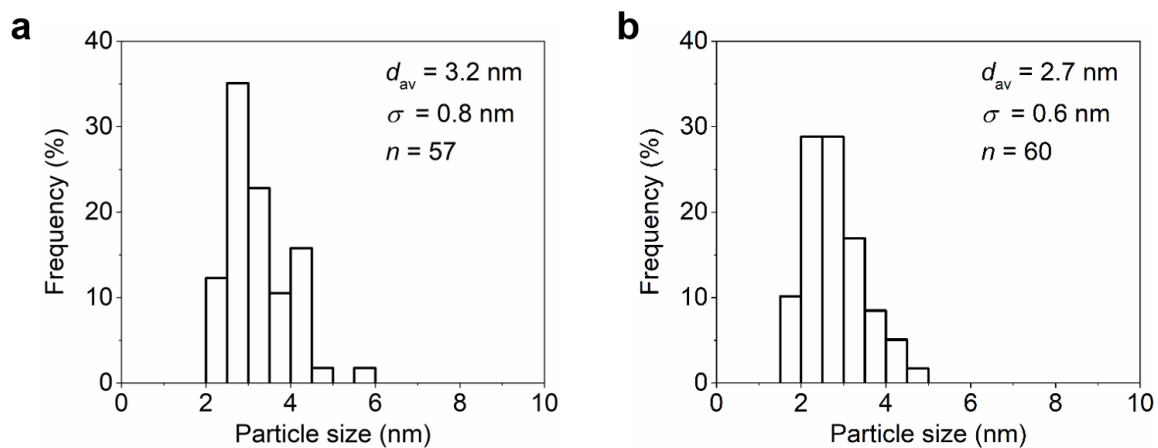
**Fig. S3** Raman spectra of metal nanoparticles with multidentate POM modification (M-SiW9).



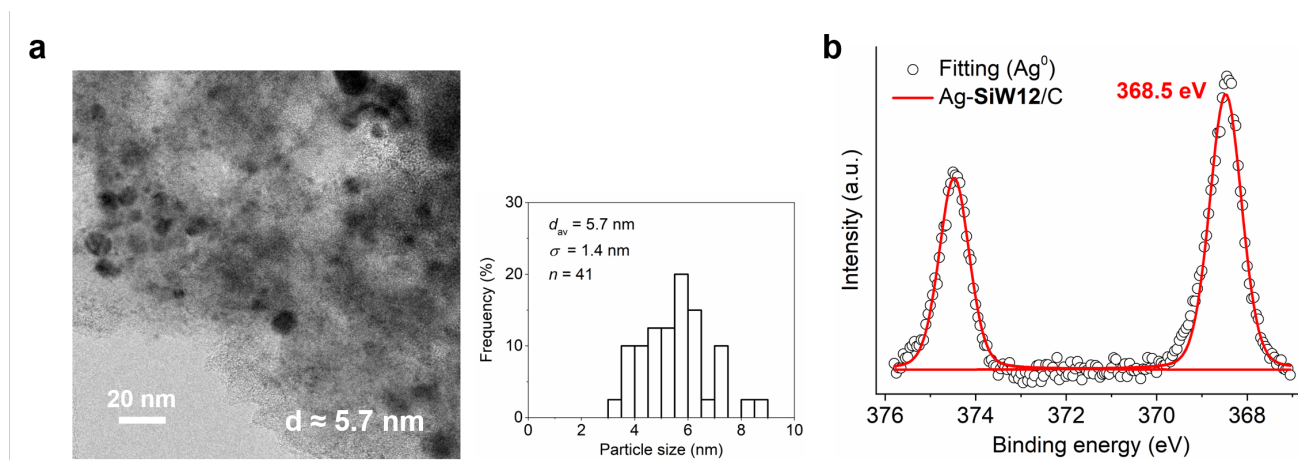
**Fig. S4** (a) UV-vis spectra and (b) photos of aqueous solution of silver nanoparticles modified with different protecting ligands (SiW9, SiW12, citrate, and PVP).



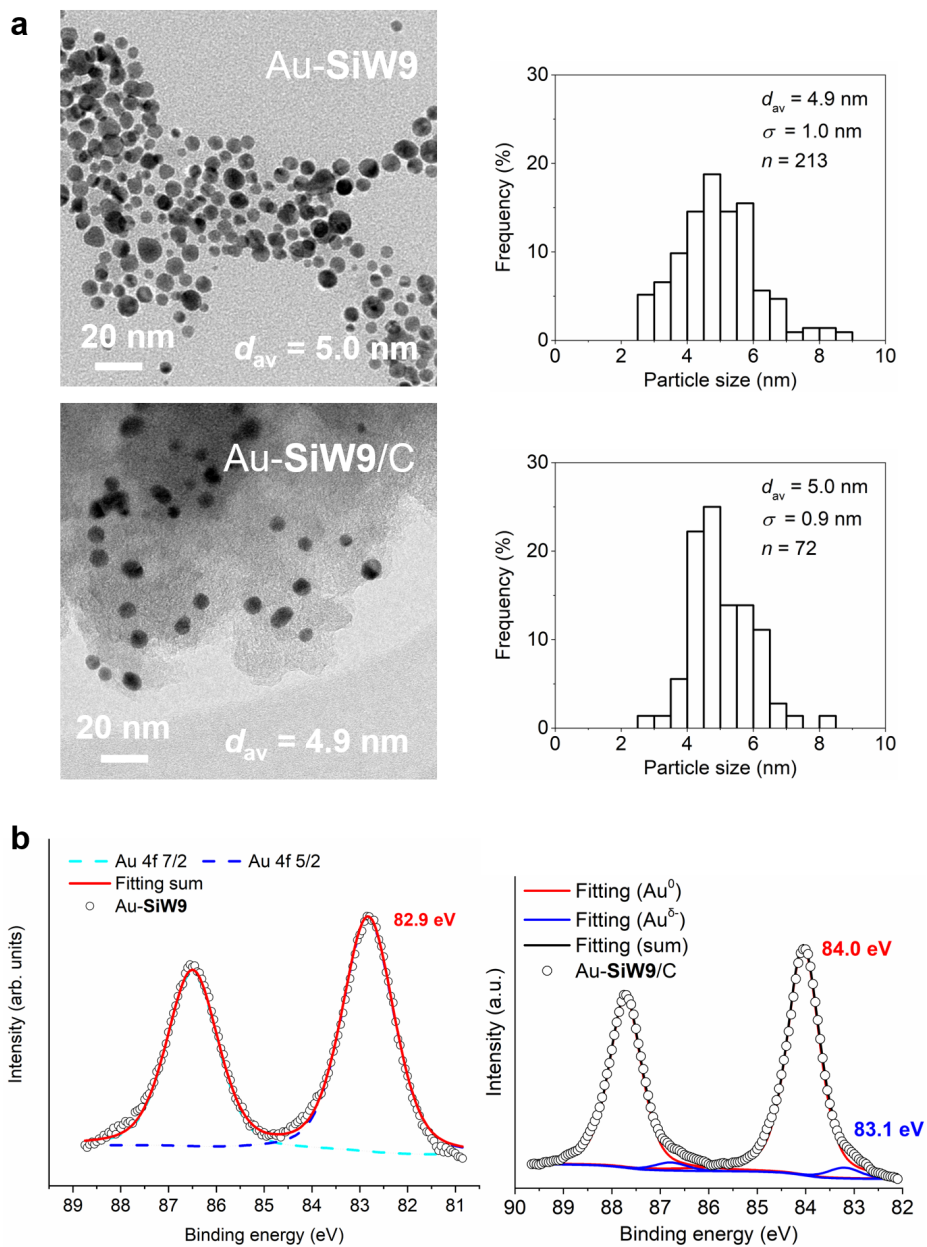
**Fig. S5** Photos of aqueous solution of Pd, Pt, and Ru nanoparticles modified with PVP and citrate.



**Fig. S6** Histograms of size distribution of (a) Ag-SiW9/C and (b) Pd-SiW9/C corresponding to the TEM images shown in Fig. 4.



**Fig. S7** (a) TEM image and the corresponding histograms of size distribution, and (b) XPS spectra of Ag-SiW12/C.

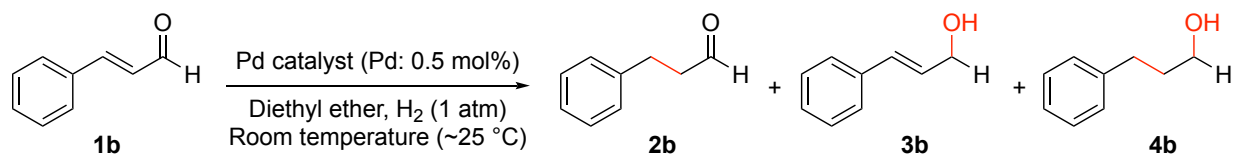


**Fig. S8** (a) TEM images and corresponding histograms of size distribution and (b) XPS spectra of Au-SiW9 and Au-SiW9/C.



### 3. Supplementary Table

**Table S1** Hydrogenation of cinnamaldehyde (**1b**) using Pd nanoparticle catalysts.<sup>a</sup>



Catalyst	Conversion of <b>1b</b> (%)	Yield (%)		
		<b>2b</b>	<b>3b</b>	<b>4b</b>
Pd-SiW9/C	82	71	n.d.	8
Pd/C	84	63	n.d.	18

<sup>a</sup> Reaction conditions: **1b** (0.5 mmol), catalyst (Pd: 0.5 mol%), diethyl ether (3 mL), room temperature (~ 25 °C), H<sub>2</sub> (1 atm), 18 h. Conversions and yields were determined by GC using biphenyl as an internal standard (n.d. = not detected).

### 4. Additional References

- S1 D. Choueiry and E. Negishi, "II.2.3 Pd(0) and Pd(II) Complexes Containing Phosphorus and Other Group 15 Atom Ligands" in E. Negishi (ed.). Handbook of Organopalladium Chemistry for Organic Synthesis. (John Wiley & Sons, Inc, 2002)
- S2 A. P. Ginsberg (Ed), *Inorg. Synth.* **27**, Ch. 3 (John Wiley & Sons, Inc, 1990).
- S3 K. Xia, T. Yatabe, K. Yonesato, T. Yabe, S. Kikkawa, S. Yamazoe, A. Nakata, K. Yamaguchi and K. Suzuki, *Angew. Chem. Int. Ed.* 2022, **61**, e202205873.