Homogeneous Pd Nanoparticles Produced in Direct Reactions: Green Synthesis, Formation Mechanism and Catalysis Property

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1. Experiments

1) HPLC-MS spectrometry

The analyses were carried out using an Accela UPLC (Thermo Fisher Scientific, San Jose, CA, USA). The mobile phase consisted of 0.1% (v/v) formic acid in water (eluent A) and ACN (eluent B). The analysis was held with 5% of eluent A during 2 min. The flow rate was 0.40 $mL \cdot min^{-1}$ and the column temperature was set at 20 ºC.

The UHPLC system was coupled to a single stage Orbitrap mass spectrometer (Exactive TM, Thermo Fisher Scientific, Bremen, Germany) operating with a heated electrospray interface (HESIII, Thermo Fisher Scientific, San Jose, CA, USA), in negative ionization mode (ESI−) using the following operational parameters: spray voltage, -2.5 kV; skimmer voltage, -20 V; capillary voltage, -60 V; tube lens voltage, -120 V; sheath gas (N_2, >95%), 40 (adimensional); auxiliary gas (N_2, >95%), 10 (adimensional); heater temperature, 150 ºC; and capillary temperature, 350 ºC.

The mass spectra were acquired using an acquisition function: full MS, ESI−, mass resolving power is 25,000 FWHM; mass range is 100-2000; scan time is 0.25 s.

2) GC-MS spectrometry

Gas chromatography-mass spectrometry (GC–MS) analyses were conducted using a GC mass spectrometer (Agilent 6890-5975c mass selective detector). The desorption time was 5 min in the injection port at 250 °C and using a column, HP-5 ms (60 m×0.25 mm i.d., 0.25 μm film thickness; J&W Scientific). The temperature was programmed to be held at 40 °C for 5 min, then increased to 50 °C at a rate of 2 $°C \cdot min^{-1}$, and finally increased to 250 °C at a rate of 5 °C/min. The carrier gas was He, which was delivered at a linear velocity of 2 $mL \cdot min^{-1}$. The mass

selective detector was operated in the electron impact ionization mode at 70 eV in the scan range of 10-80 m/z.

3) UV-vis spectrometry

The UV-vis spectra were acquired using a TU-1901 UV-vis spectrometer. The spectrum for each sample was collected between 500-200 nm using quartz cell with 1 cm optical path length.

2. The direct reaction between solid ascorbic acid and $Pd(NO_3)_2 \cdot 2H_2O$ by grinding

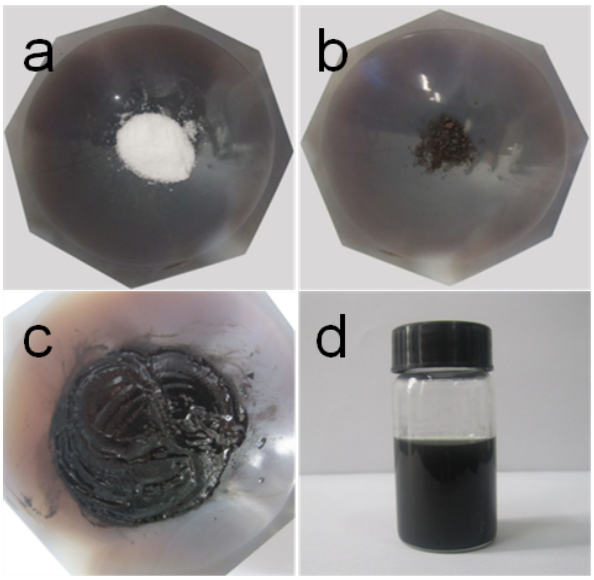


Fig. S1. Solid powders of reactants: (a) ascorbic acid and (b) $Pd(NO_3)_2 \cdot 2H_2O$. (c) The paste-like materials produced directly by grinding the mixture of ascorbic acid and $Pd(NO_3)_2 \cdot 2H_2O$, and (d) colloid solution of Pd nanoparticles in water.

3. **Direct reaction between solid ascorbic acid and $Pd(NO_3)_2 \cdot 2H_2O$ by shaking in a vial**.

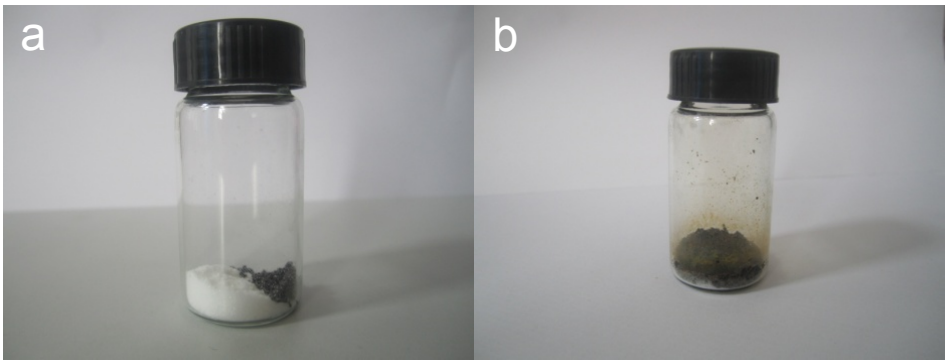


Fig. S2. A vial with (a) reactants - $Pd(NO_3)_2 \cdot 2H_2O$ and ascorbic acid, and (b) Pd nanoparticles after shaking for *ca*. 8 minutes.

4. **HRTEM images of Pd nanoparticles produced by grinding the mixture of solid ascorbic acid and $Pd(NO_3)_2 \cdot 2H_2O$ directly**.

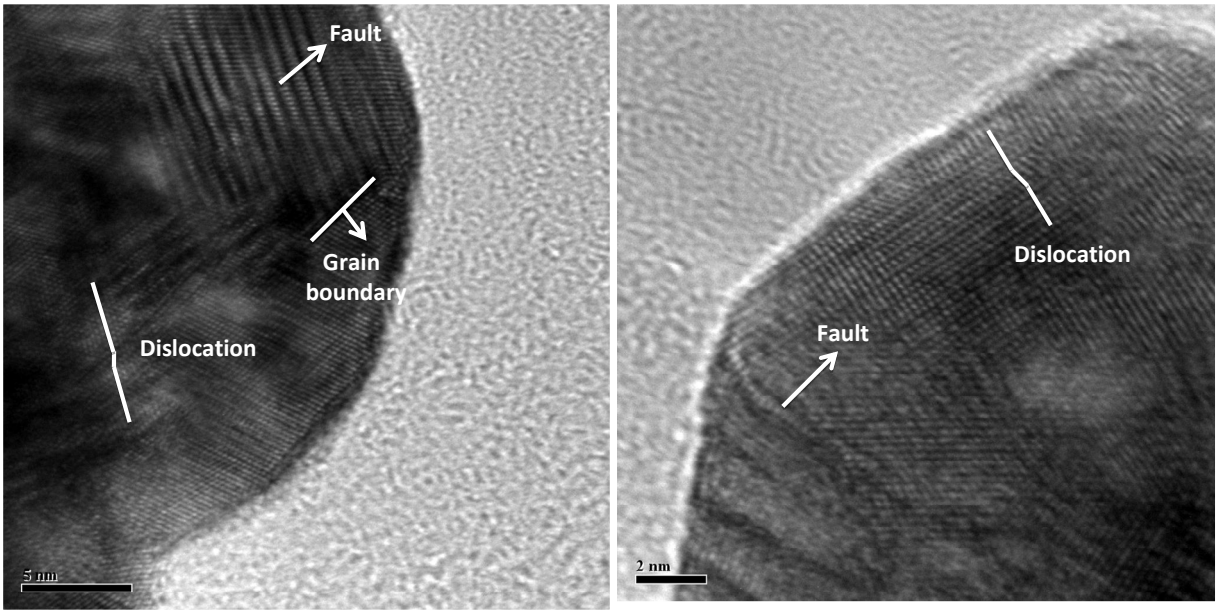


Fig. S3. The HRTEM images of Pd nanoparticles with defects of high concentration.

5. **TEM and HRTEM images of Pd nanoparticles produced by shaking solid ascorbic acid and $Pd(NO_3)_2 \cdot 2H_2O$ in a vial**.

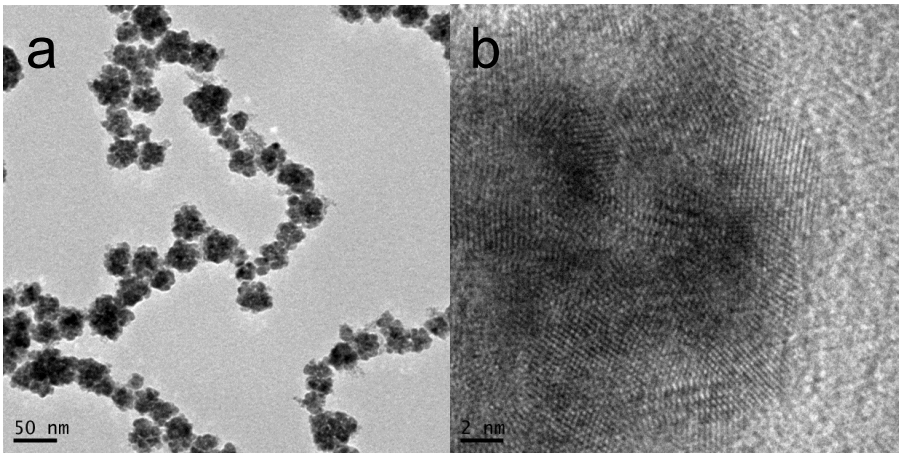


Fig. S4. (a) TEM and (b) HRTEM images of Pd nanoparticles produced by shaking the two reactants - $Pd(NO_3)_2 \cdot 2H_2O$ and ascorbic acid powders in a vial directly.

6. **Direct reaction between solid ascorbic acid and $Pd(NO_3)_2 \cdot 2H_2O$ in water**.

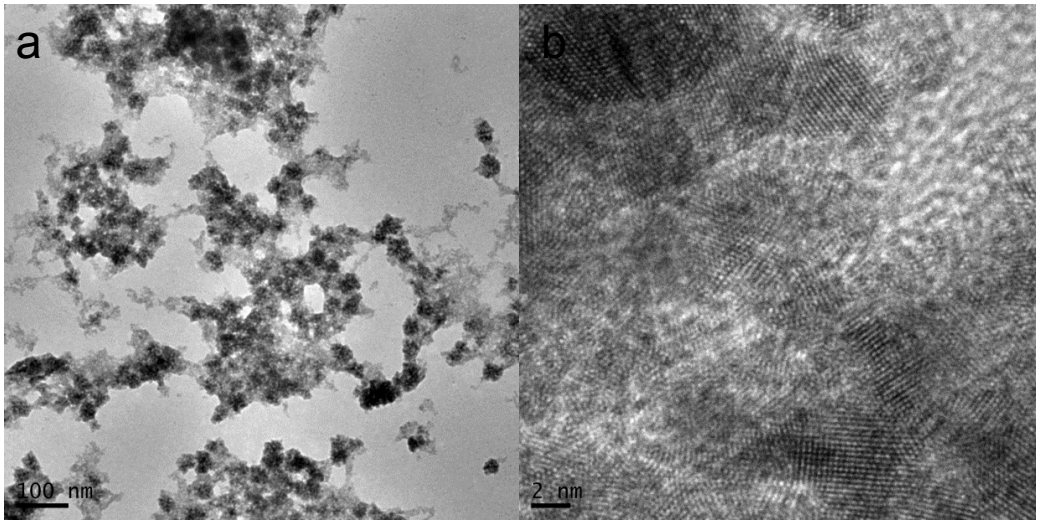


Fig. S5. (a) TEM and (b) HRTEM images of Pd nanoparticles produced by directly adding ascorbic acid into $Pd(NO_3)_2 \cdot 2H_2O$ water solution and stirring the solution for 3 hours.

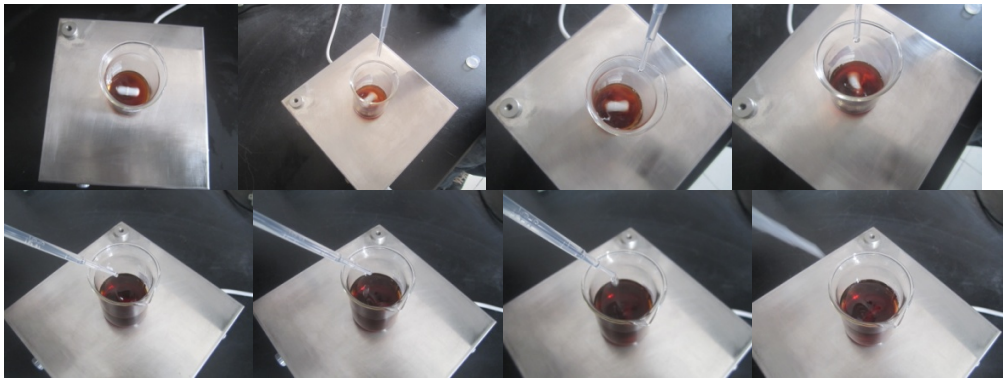


Fig. S6. The color changes of the reaction system in water, when adding water solution of ascorbic acid into the water solution of $Pd(NO_3)_2$.

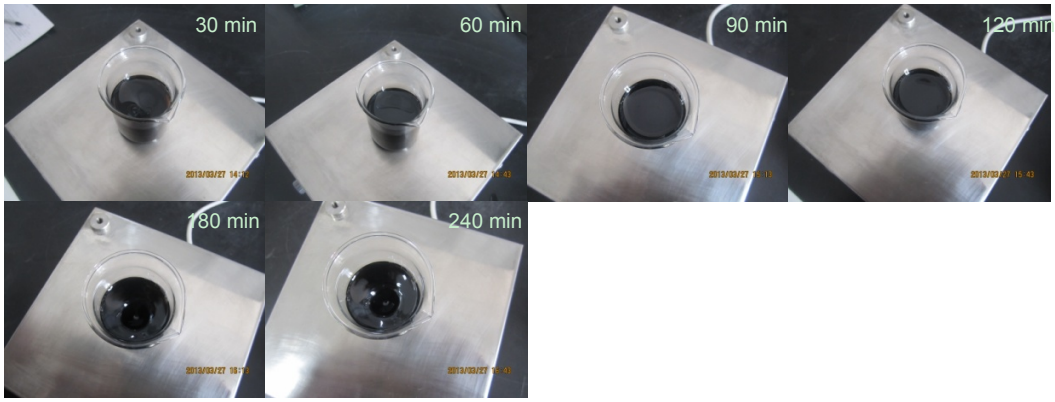


Fig. S7. Photos of the reaction solution taken every 30 min, after adding ascorbic acid into $Pd(NO_3)_2$ solution.

7. GC-MS spectrum of the gas produced by shaking the two reactants - $Pd(NO_3)_2 \cdot 2H_2O$ and ascorbic acid powders in a headspace sampler directly.

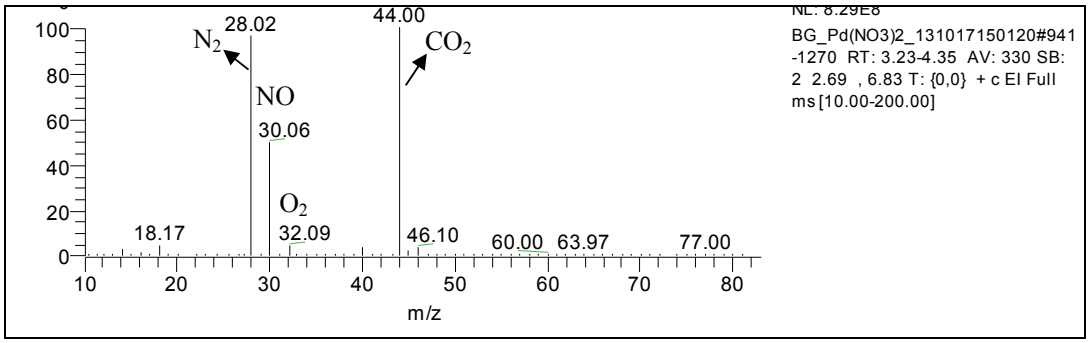


Fig.S8. GC-MS spectra of the gas produced by shaking the two reactants - $Pd(NO_3)_2 \cdot 2H_2O$ and ascorbic acid powders in a headspace sampler directly.

8. HPLC-MS spectrum of as-prepared materials

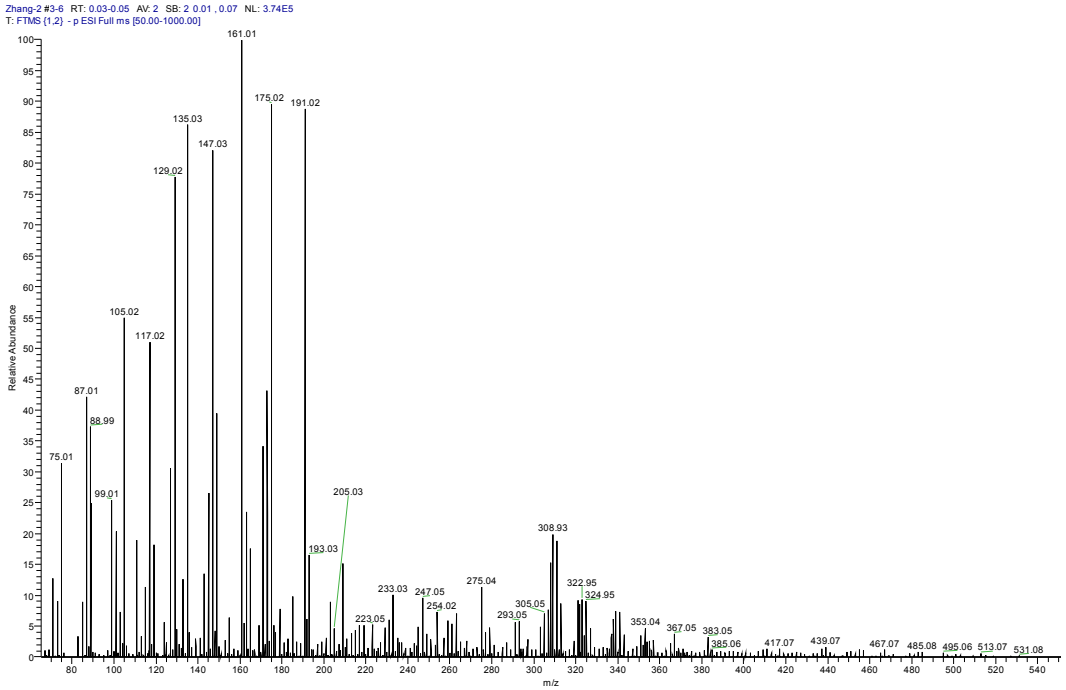
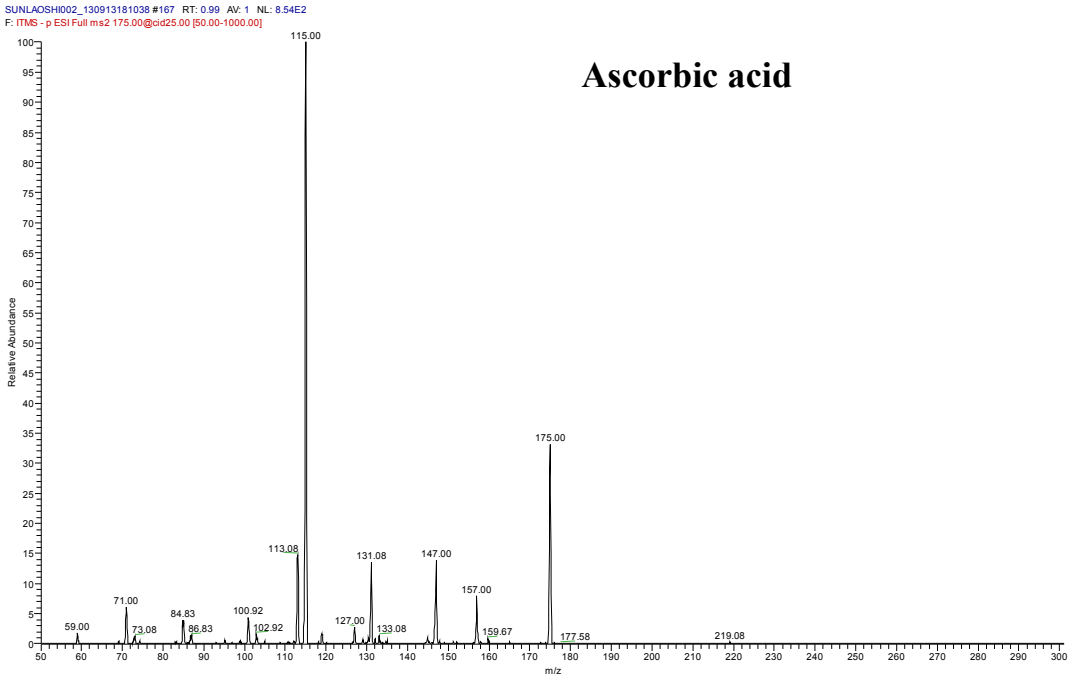


Fig. S9. MS spectrum of as-prepared materials



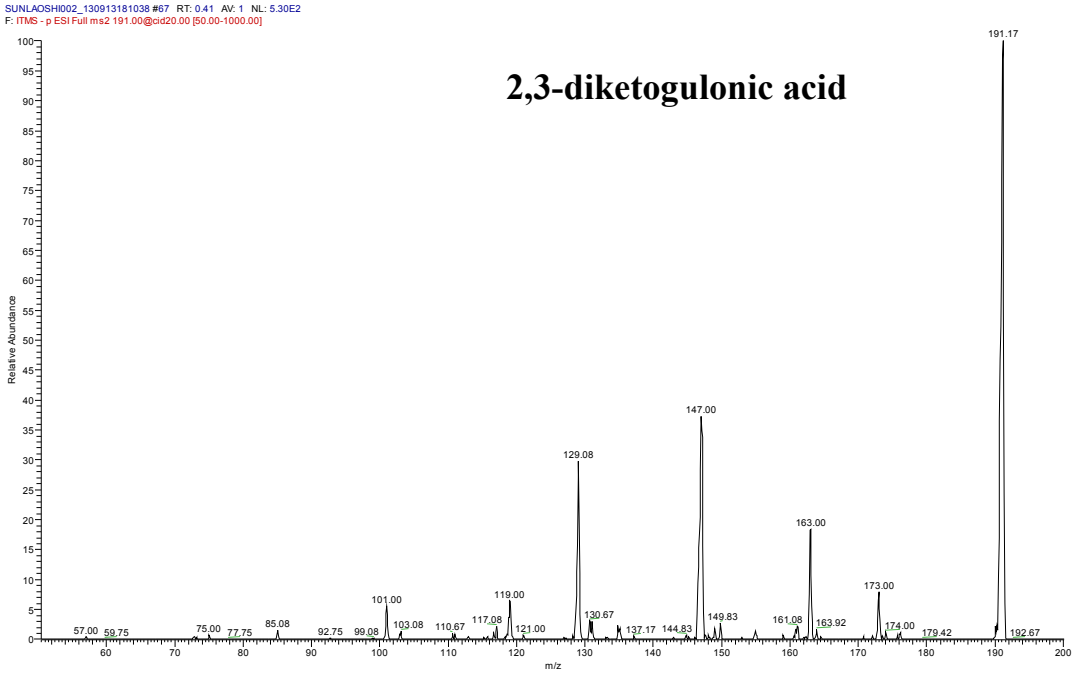


Fig. S10. MS/MS spectrum of ascorbic acid and 2,3-diketogulonic acid.

9. TEM images of Pd nanoparticles produced in direct reaction between solid ascorbic acid and $Pd(Ac)_2$.

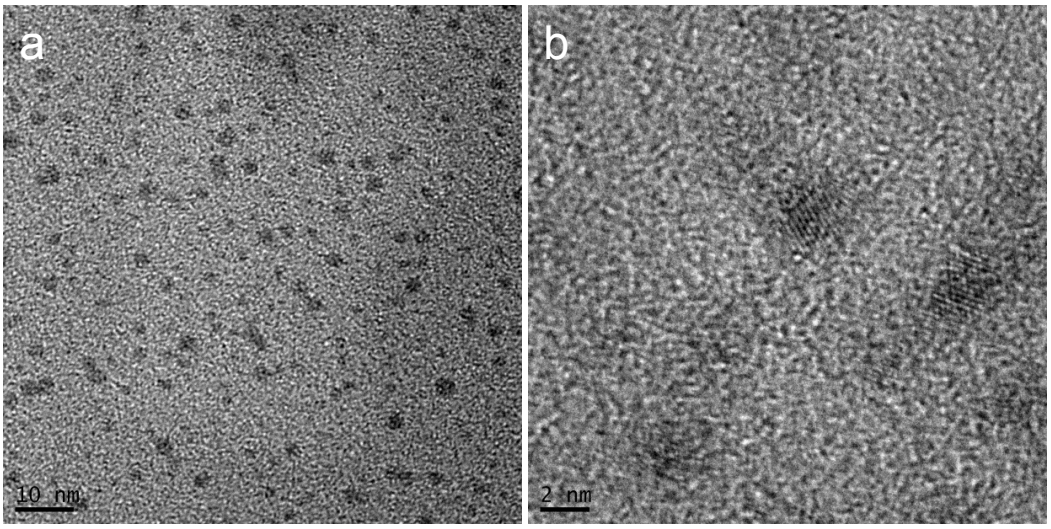


Fig. S11. (a) TEM and (b) HRTEM images of Pd nanoparticles of 2.6 nm produced by directly grinding $Pd(Ac)_2$ and ascorbic acid for 20 min.

10. Direct reaction between ascorbic acid and anhydrous palladium nitrate

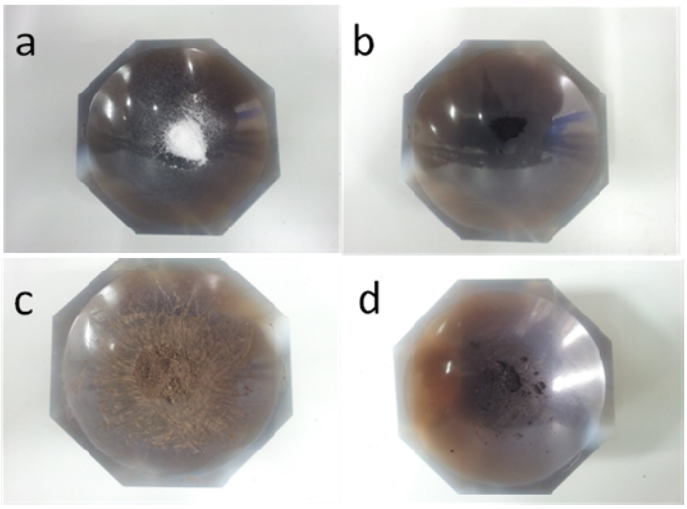


Fig.S12. Photos of solid powders of (a) ascorbic acid, (b) $Pd(NO_3)_2$, (c) The mixture of ascorbic acid and $Pd(NO_3)_2$ produced by grinding for 30 minutes, and (d) the mixture of the reactants after kept at room temperature in air for one week.

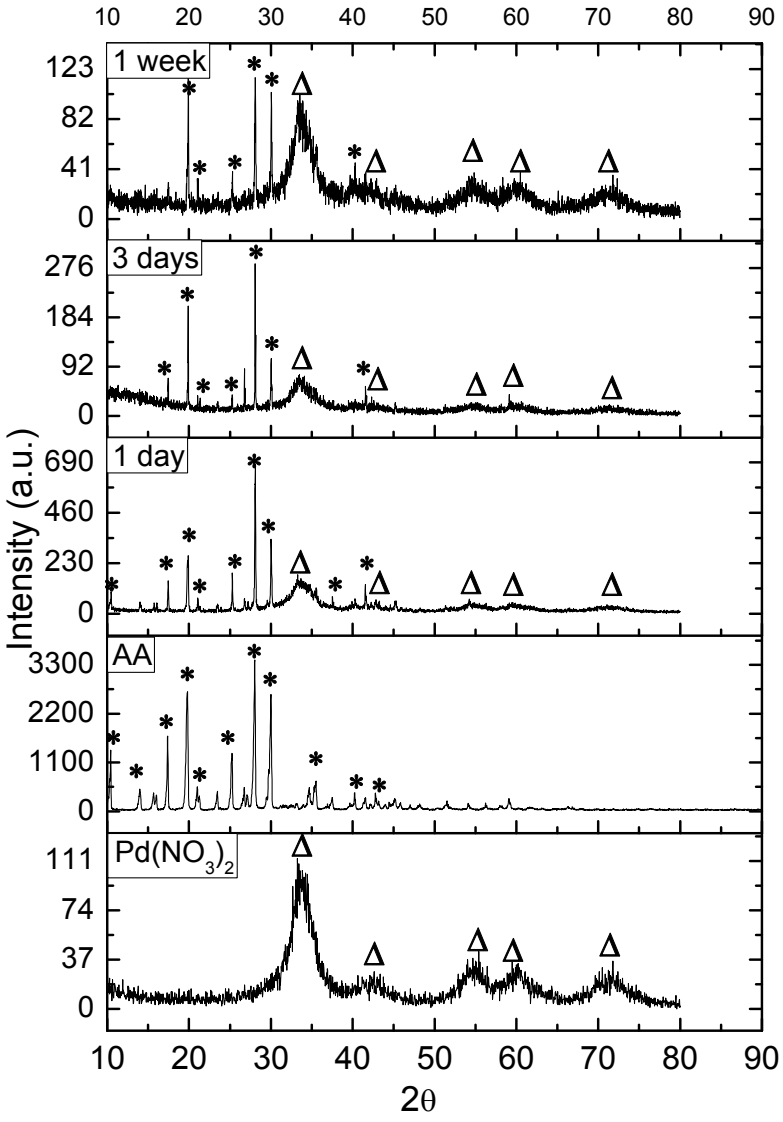


Fig.S13. The XRD profile of the mixture obtained by grinding $Pd(NO_3)_2$ and ascorbic acid directly and keeping in air at room temperature for 1day, 3 days and 1 week, respectively.

11. Direct reaction between ascorbic acid and $PdCl_2$

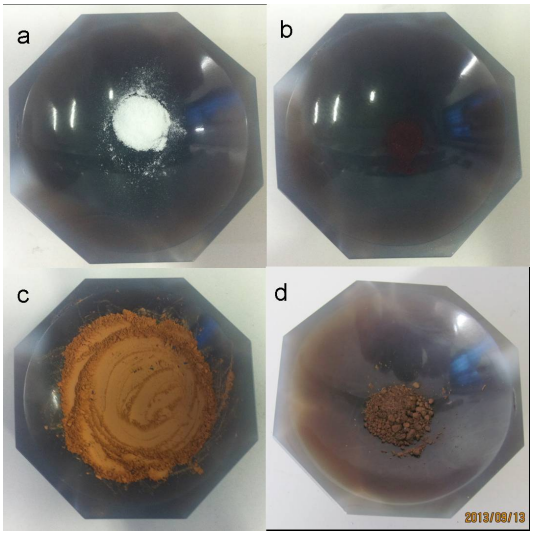


Fig.S14. Photos of solid powders of (a) ascorbic acid, (b) $PdCl_2$, (c) The mixture of ascorbic acid and $PdCl_2$ produced by grinding for 30 minutes, and (d) the mixture of the reactants after kept at room temperature in air for one week.

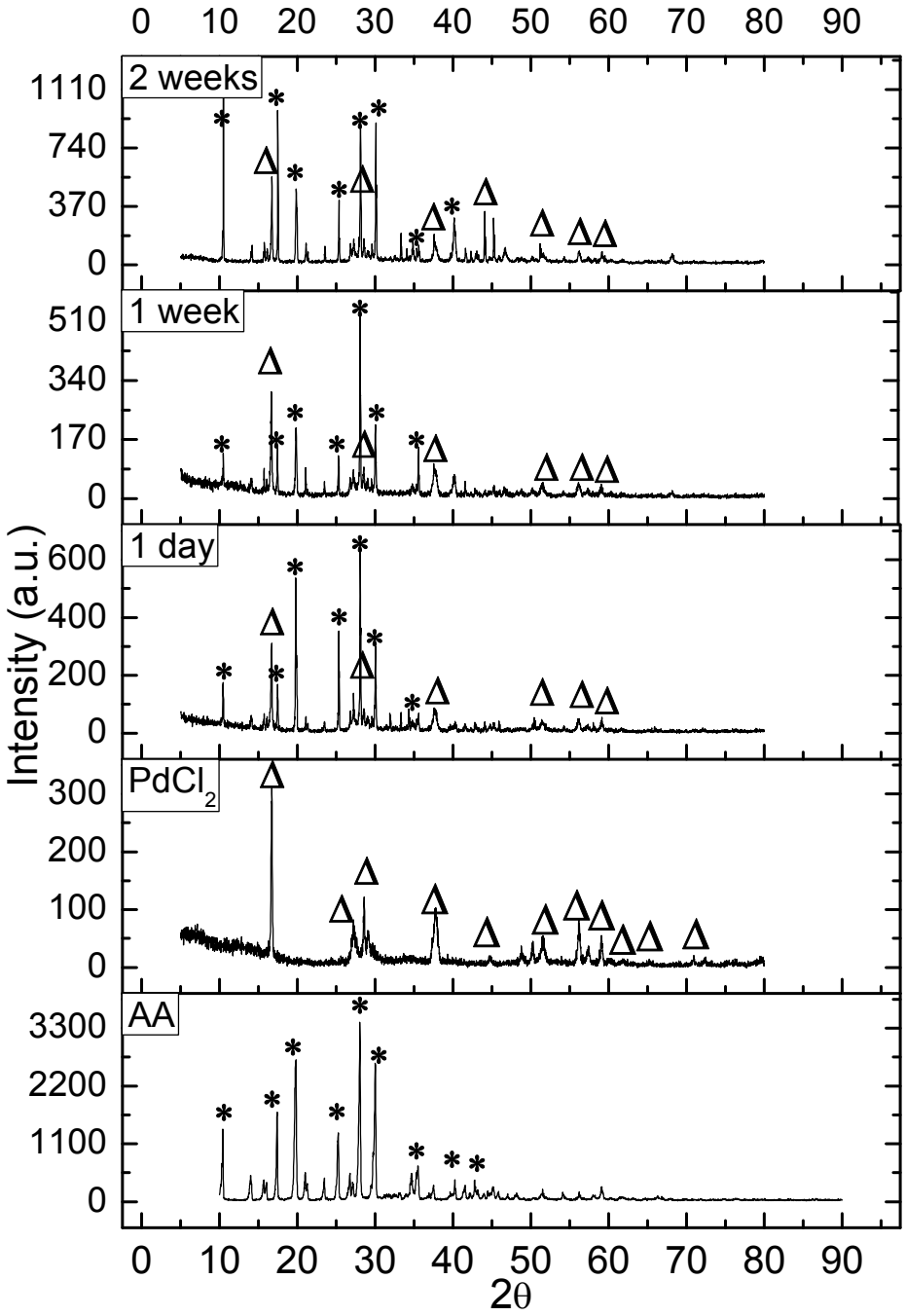


Fig.S15. The XRD profile of the mixture obtained by grinding $PdCl_2$ and ascorbic acid directly and keeping in air at room temperature for 1day, 1 week and 2 weeks, respectively.

12. TEM images of Pd nanoparticles after cycled for 6 times in Carbon-Carbon couple reaction

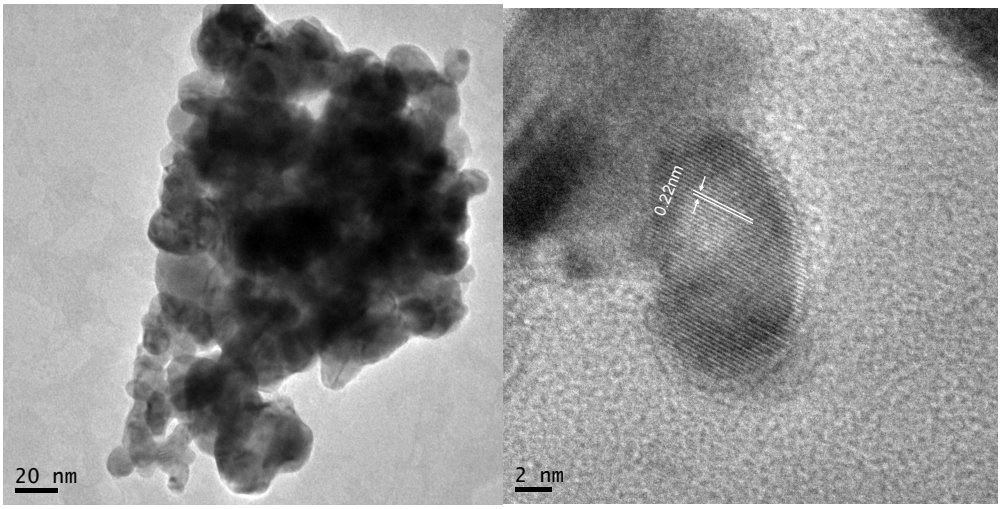


Fig.S16. TEM images of Pd nanoparticles after cycling in the catalysis reaction for six times.

13. UV-vis spectra of reactants and as-prepared materials in direct reaction of ascorbic acid and $Pd(NO_3)_2 \cdot H_2O$

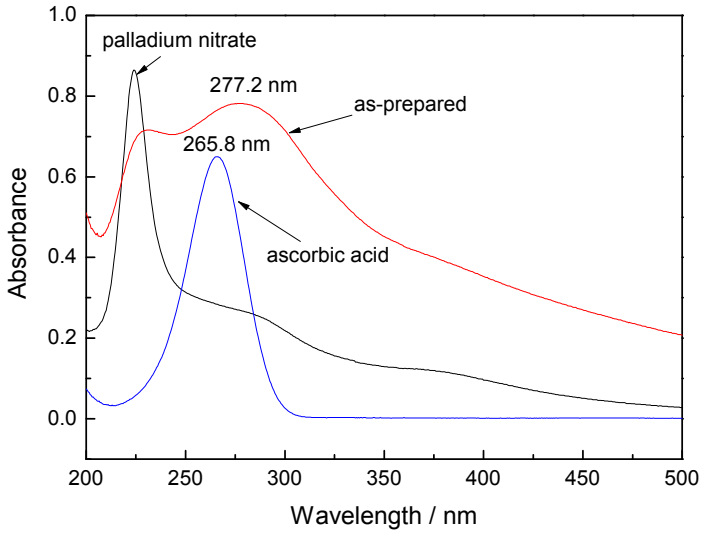


Fig.S17. Uv-vis spectra of palladium nitrate, ascorbic acid and as-prepared materials in water.

14. TEM image of Ag nanoparticles synthesized by direct reaction between ascorbic acid and silver nitrate.

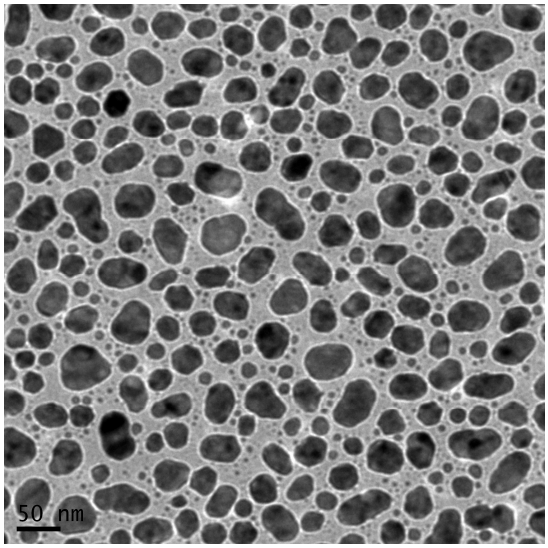


Fig.S18. TEM image of Ag nanoparticles synthesized by direct reaction between ascorbic acid and silver nitrate.

15. TEM image of Au nanoparticles synthesized by direct reaction between ascorbic acid and chloroauric acid.

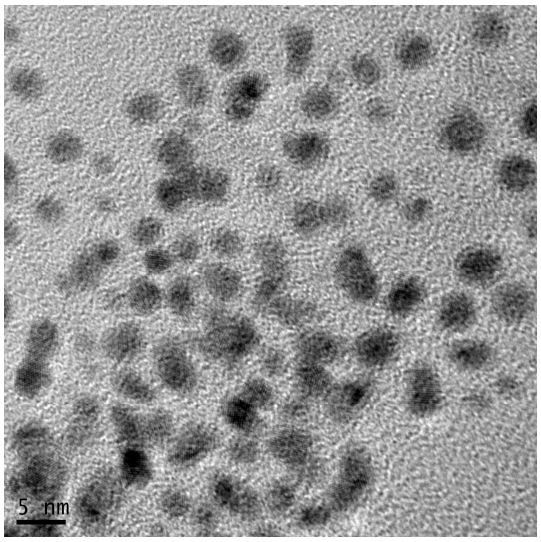


Fig.S19. TEM image of Au nanoparticles synthesized by direct reaction between ascorbic acid and chloroauric acid.

Table.S1. The main species tentatively verified with HPLC-MS as shown in **Fig. S8**.

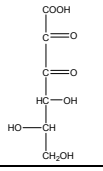
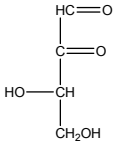
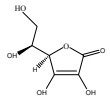
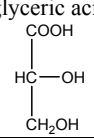
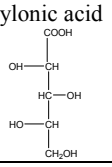
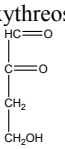
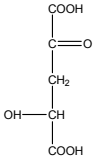
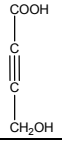
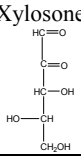
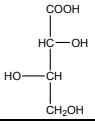
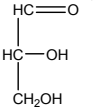
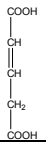
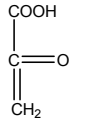
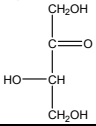
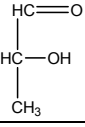
	m/z	Molecular formula	corresponding material[1]		m/z	Molecular formula	corresponding material[1]
1	191.01909	$C_6H_8O_7$	2,3-diketogulonic acid 	10	117.01850	$C_4H_6O_4$	Threosone 
2	175.02414	$C_6H_8O_6$	ascorbic acid 	11	105.01847	$C_3H_6O_4$	glyceric acid 
3	165.01898	$C_5H_{10}O_6$	xylonic acid 	12	101.01291	$C_4H_6O_3$	Deoxythreosone 
4	161.00844	$C_5H_6O_6$	*Pentanedioic acid* 	13	99.00789	$C_4H_4O_3$	*4-Hydroxybut-2-ynoic acid* 
5	147.02915	$C_5H_8O_5$	Xylosone 	14	88.98717	$C_2H_2O_4$	oxalic acid 
6	135.02910	$C_4H_8O_5$	threonic acid 	15	89.02935	$C_3H_6O_3$	glyceric aldehyde 
7	129.01853	$C_5H_6O_4$	*2-Pentenedi1oic acid* 	16	87.00788	$C_3H_4O_3$	*Pyruvic acid* 
8	118.98880	$C_3H_4O_5$	tartronic acid 	17	75.00787	$C_2H_4O_3$	glycolic acid 
9	119.09887	$C_4H_8O_4$	Erythrulose 	18	71.01296	$C_3H_4O_2$	Methylglyoxal 

Table. S2. Proposed structure of Pd clusters as shown in Fig. S8

m/z	308.93406	322.94961	338.90827	353.03630
structure	$(C_4H_6O_3)_2Pd$	$(C_4H_4O_3)(C_4H_6O_4)$ Pd	$(C_5H_6O_6)(C_3H_4O_2)$ Pd	$(C_5H_8O_5)(C_4H_4O_3)$ Pd