

Supporting Information:

## A Facile Approach for Morphosynthesis of Pd Nanoelectrocatalysts

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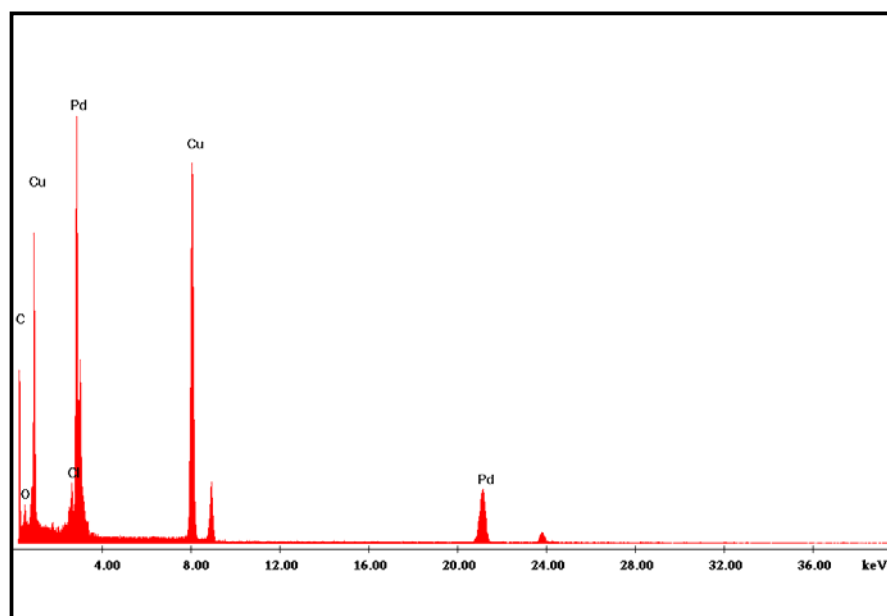
### EXPERIMENTAL SECTION

**Characterization.** TEM images were obtained from FEI, TECHNAI G2 transmission electron microscope operating at 200 kV. The specimens were prepared by dropping 2  $\mu$ l of colloidal solution onto carbon coated copper grids. X-ray diffraction analysis was carried out with X'pert PRO (Pan Analytica) X-ray diffraction unit using Ni filtered CuK $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation.

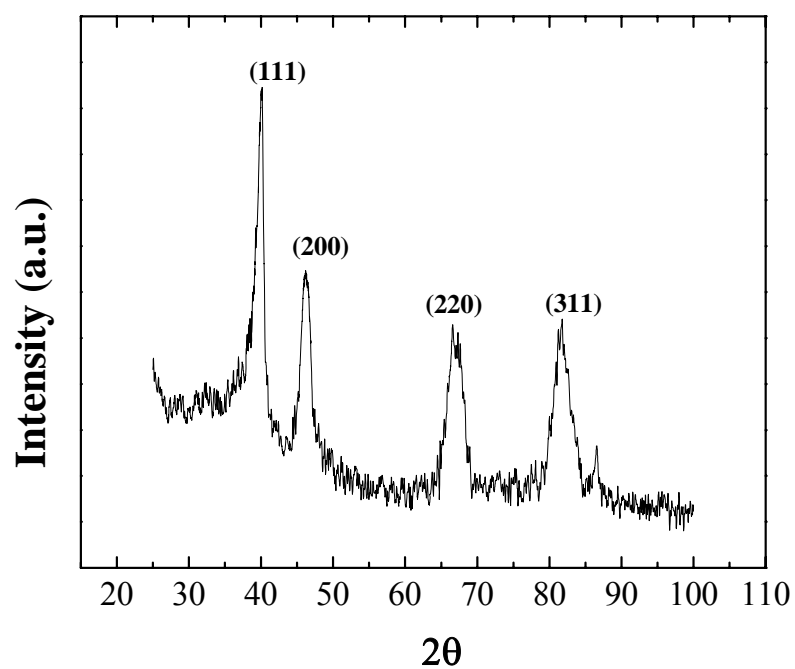
**Materials.** PdCl<sub>2</sub>, Rutin hydrate, were obtained from Himedia, India. Other chemicals not mentioned here are of analytical grade and used as received from the suppliers. Carbon coated copper grids were obtained from SPI supplies, USA. All the solutions were prepared with deionised water (18  $\Omega$ m) obtained from Millipore system.

**Synthesis of Pd Nanostructures.** Glasswares used for synthesis were well cleaned with freshly prepared aqua regia, then rinsed thoroughly with water and dried prior to use (*Caution! aqua regia is a powerful oxidizing agent and it should be handled with extreme care*). In a typical synthesis, 10 ml aqueous solution of PdCl<sub>2</sub> (0.1 mM) was taken in round bottle flask (double mouth) fitted with a water condenser and heated up to 100 °C under stirring condition for 2-3 min. Then 0.2 ml of Rutin (15 mM) was injected into the solution and heating was continued for 30 min. The solution was cooled to room temperature for prior use of nanoparticles.

**Electrochemical measurements.** Electrochemical measurements were performed using two compartment three-electrode cell with a glassy carbon working electrode (area 0.07 cm<sup>2</sup>), a Pt wire auxiliary electrode and Ag/AgCl (3M KCl) as reference electrode. Cyclic voltammograms were recorded using a computer controlled CHI660C electrochemical analyzer. All the electrochemical experiments are carried out in an argon atmosphere. The as-synthesized nanoparticles are dispersed over glassy carbon electrode with nafion and dried prior to electrochemical experiments.

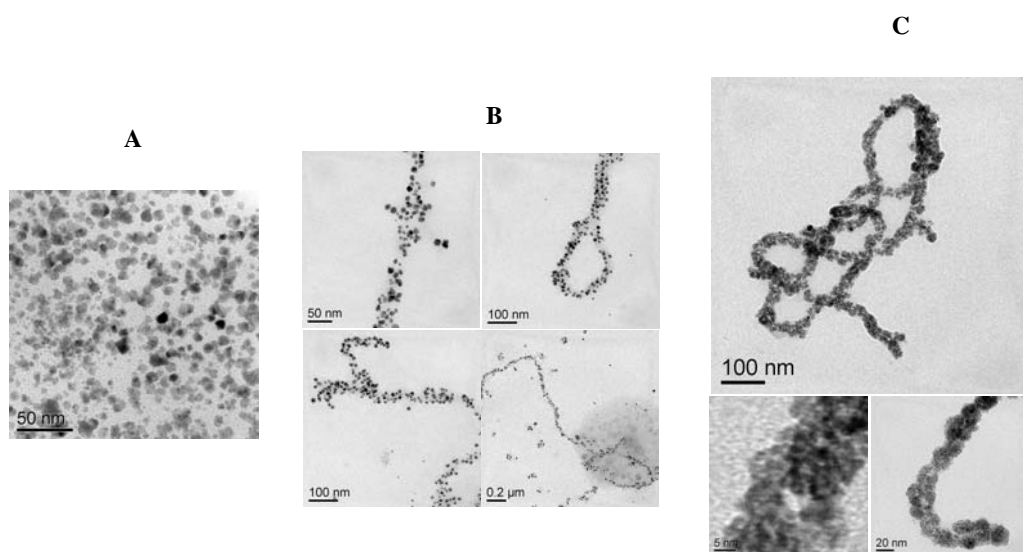


**Figure S1. EDAX of Pd dendritic nanowires.**



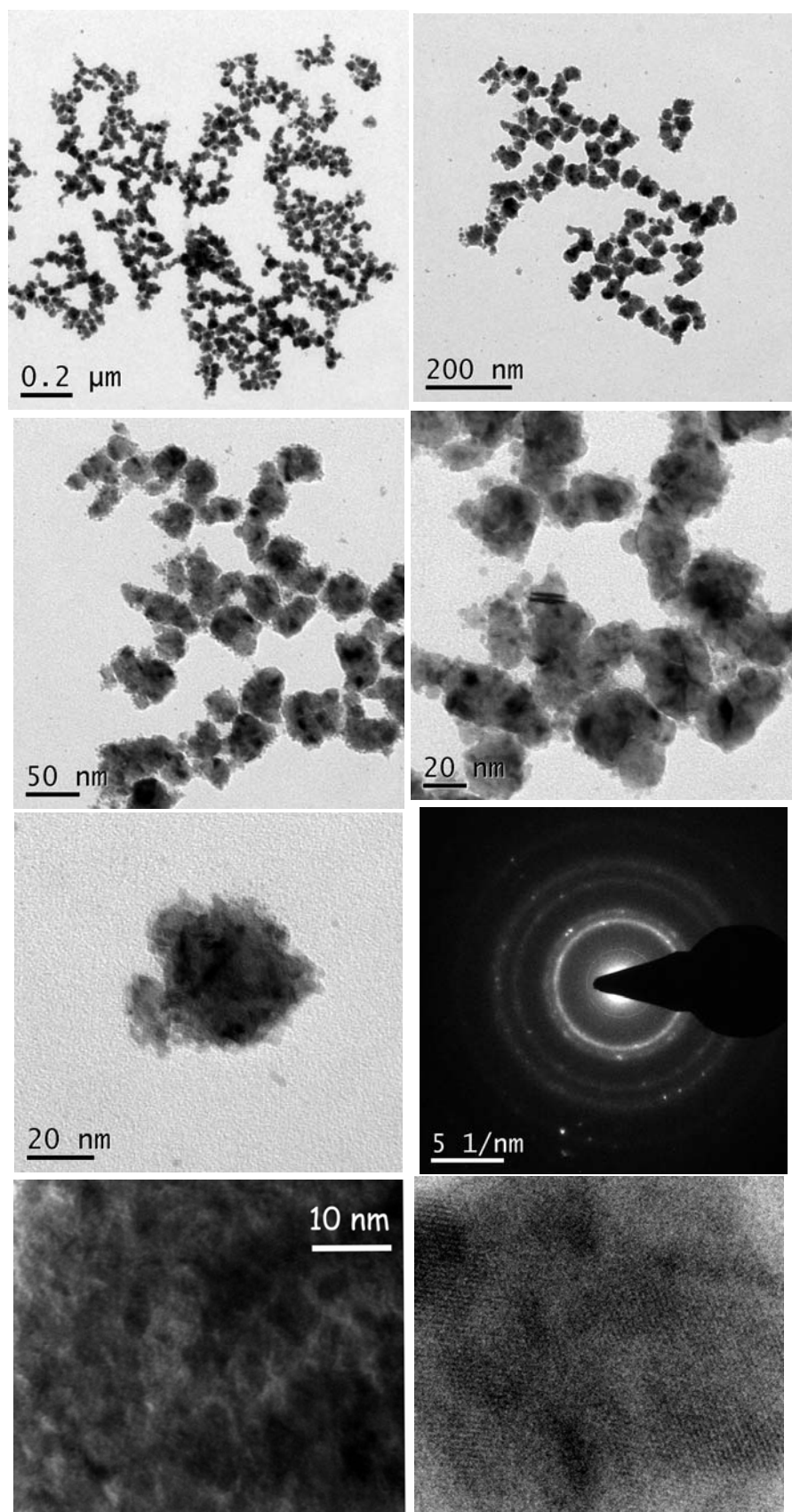
**Figure S2. XRD of Pd dendritic nanowires.**

For a complete understanding of the dendritic nanowires formation process and mechanism, a morphology evolution study was carried out over total reaction time. Products were collected from the reaction solution at different time and cast over the carbon coated copper grid for TEM measurement.

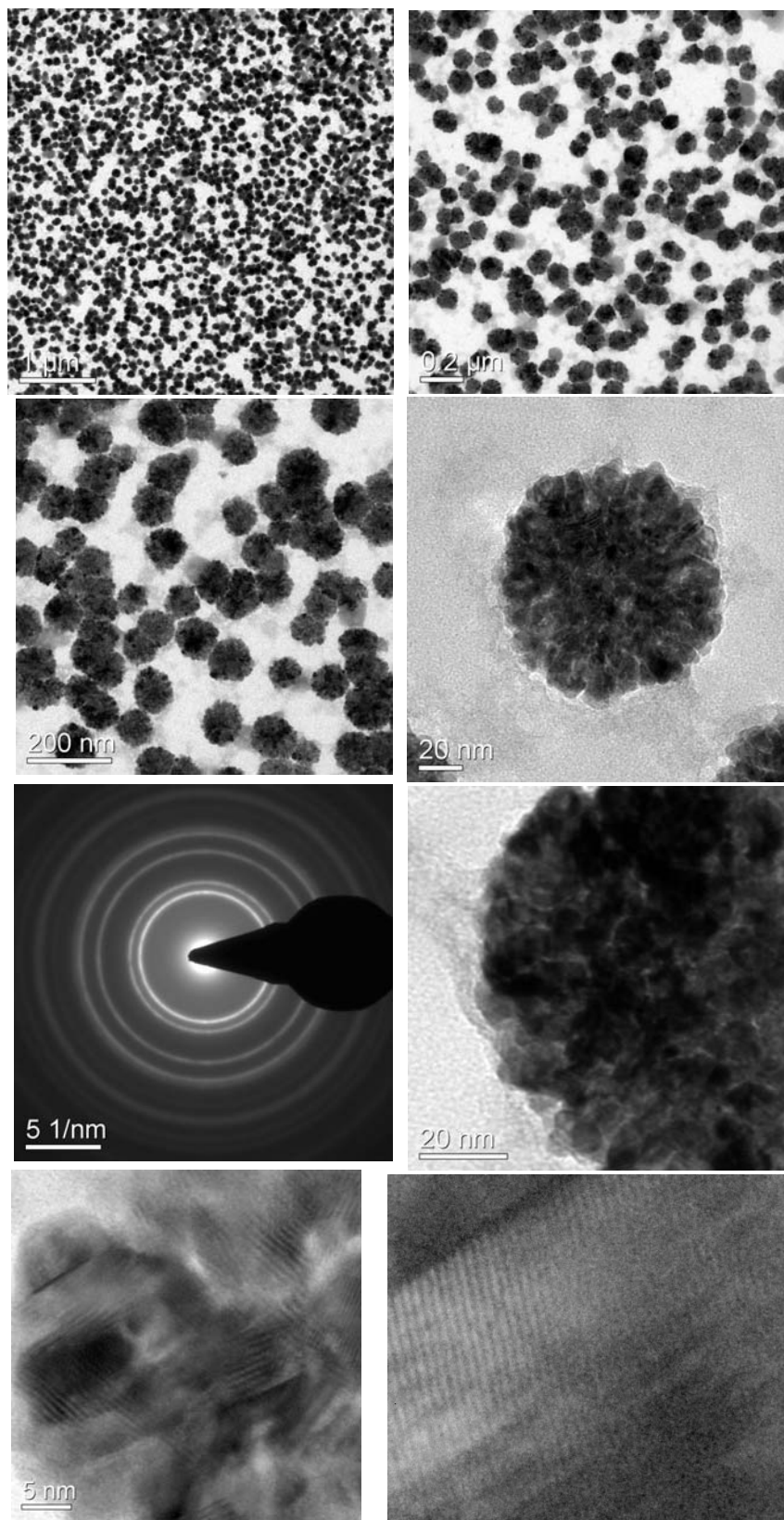


**Figure S3. TEM measurements at different intervals of reaction time; A: 4 min, B: 12 min and C: 30 min.**

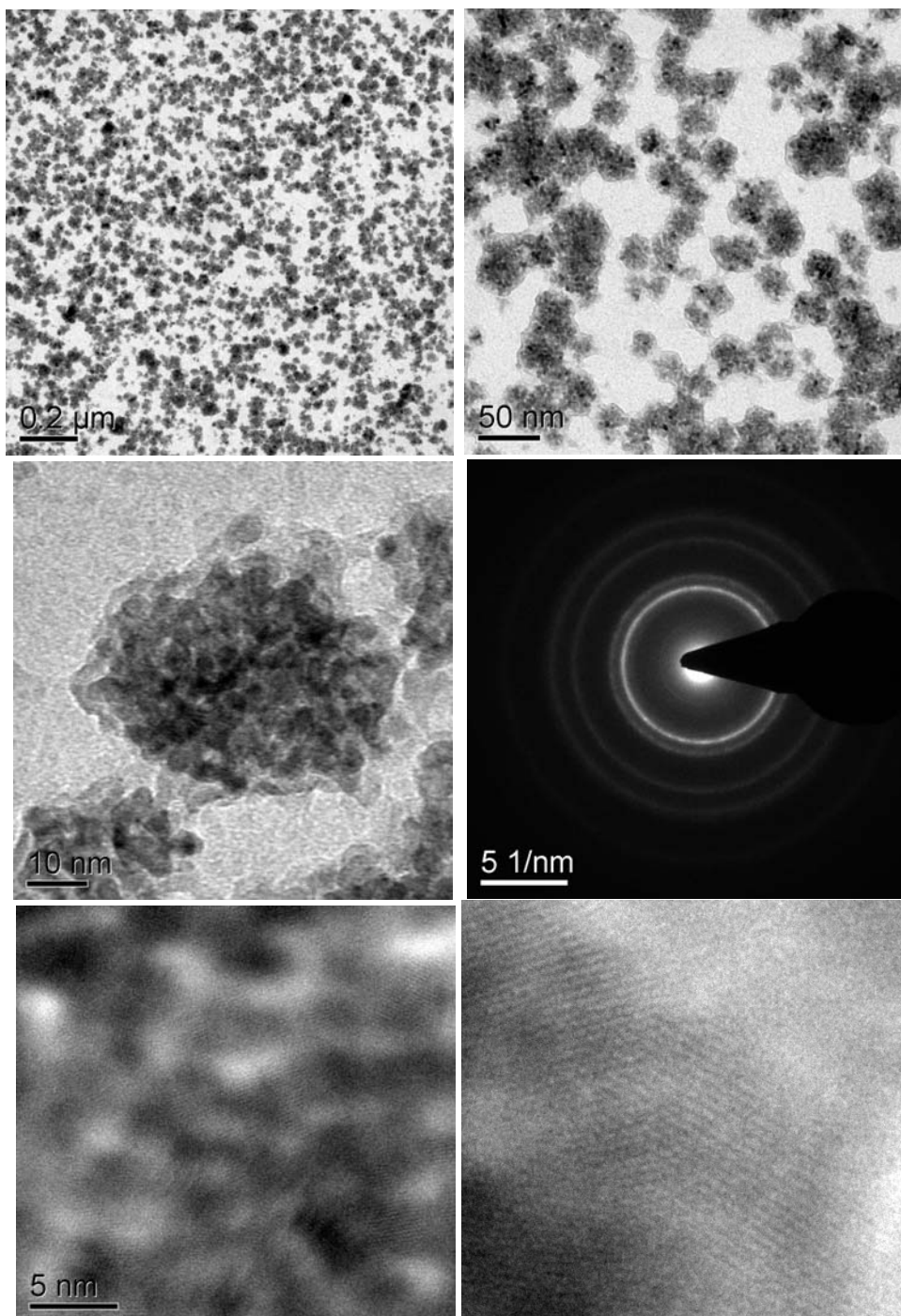




**Figure S5. TEM measurements of Pd nanoparticles at different concentrations of Pd (II). [Rutin]: 0.3 mM; [Pd(II)]: 3 mM.**

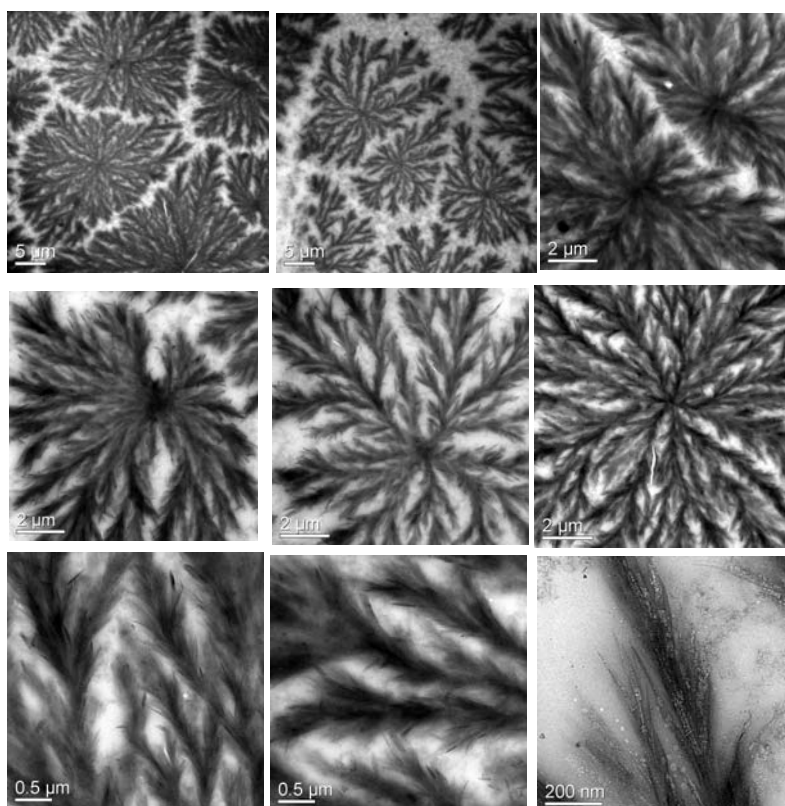


**Figure S6. TEM measurements of Pd nanoparticles at different concentrations of Pd (II). [Rutin]: 0.3 mM; [Pd(II)]: 1 mM.**

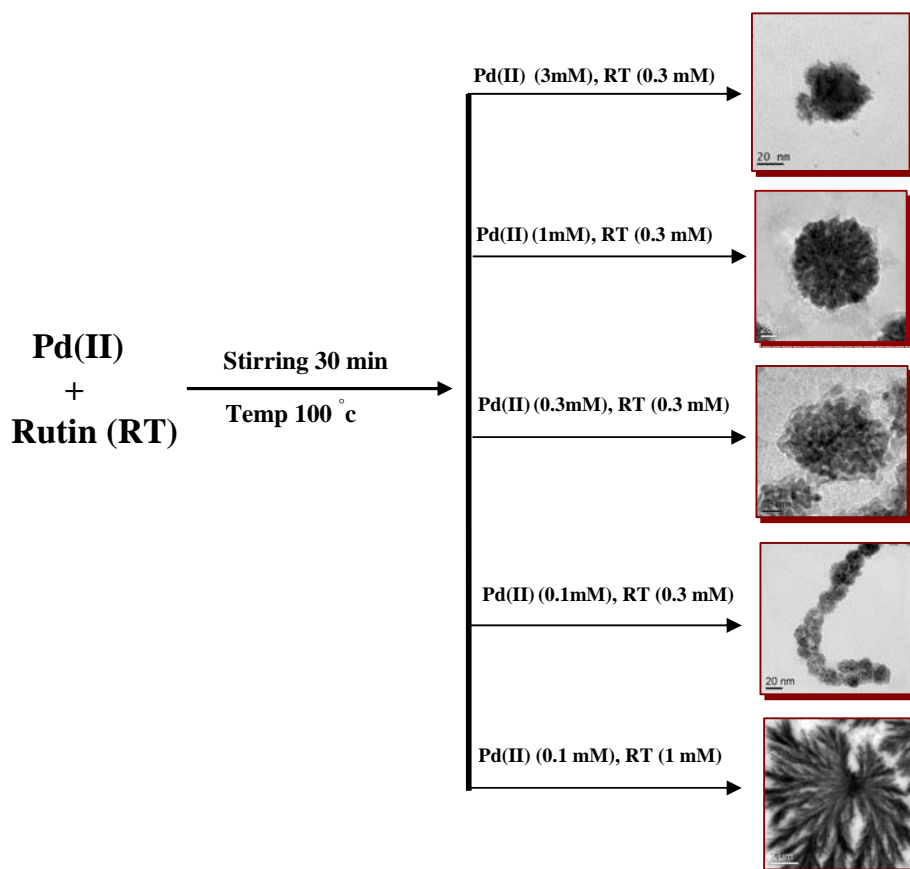


**Figure S7. TEM measurements of Pd nanoparticles at different concentrations of Pd (II). [Rutin]: 0.3 mM; [Pd(II)]: 0.3 mM.**





**Figure S8. TEM measurements of Pd nanoparticles at different concentrations of Pd (II). [Rutin]: 1 mM; [Pd(II)]: 0.1 mM.**

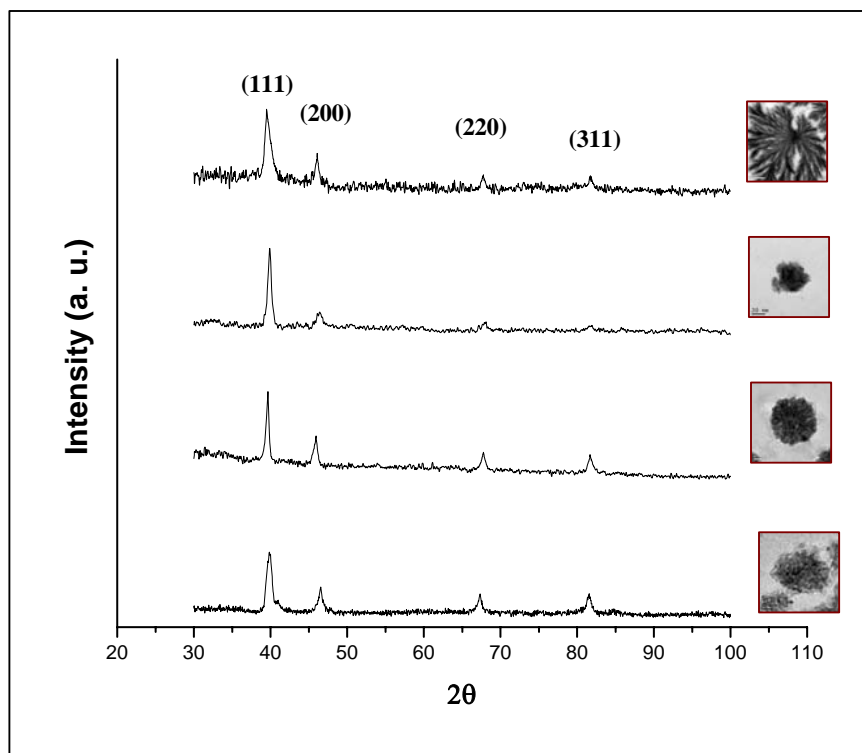


**Figure S9. TEM measurements of different morphology of Pd nanoparticles induced at different concentration of rutin and Pd(II). \***

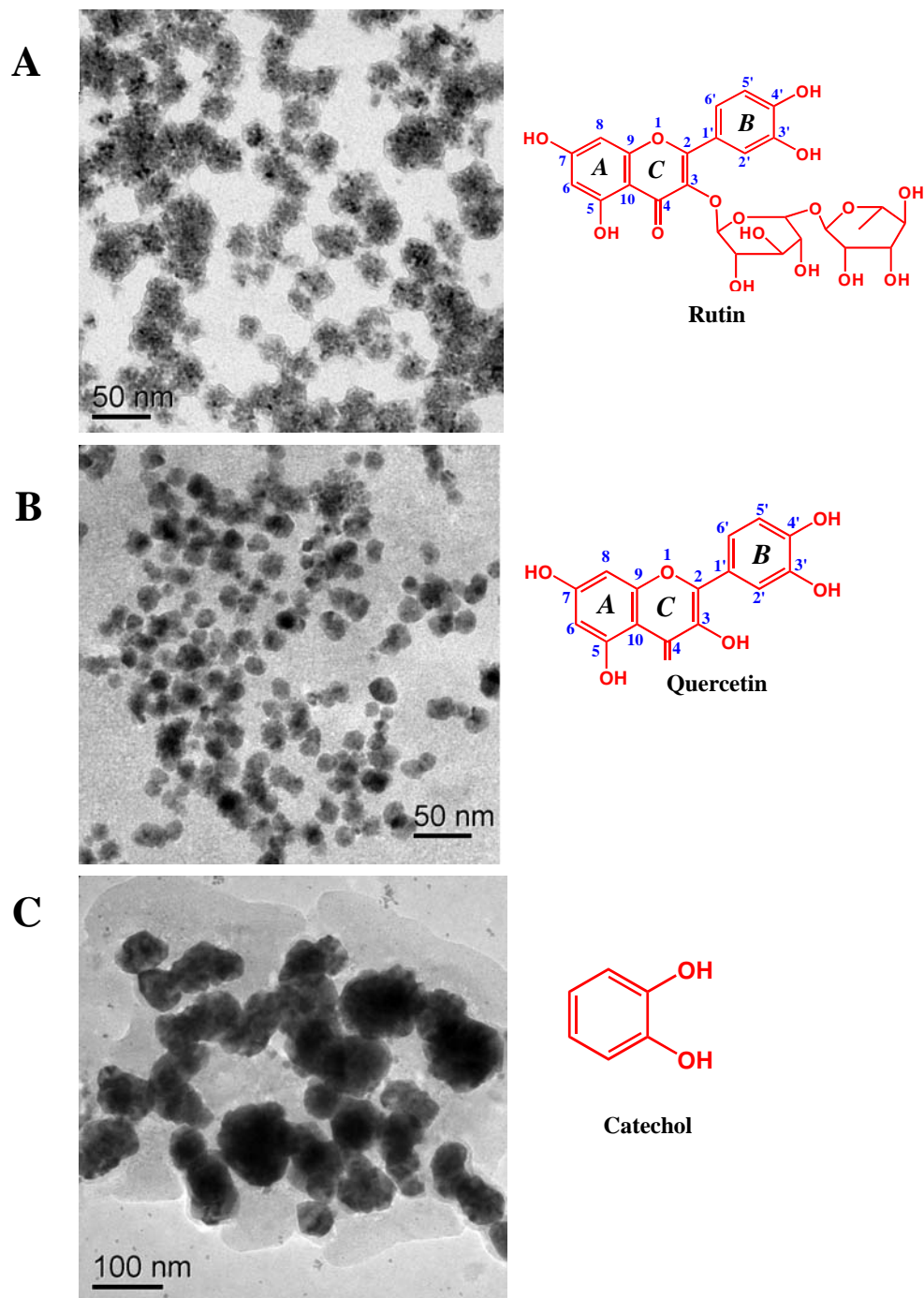
\* We propose that the balancing act between the concentration of precursor and stabiliser determine their shape evolution process. The effect of Pd<sup>2+</sup> concentration can be speculated as at high concentration, Pd<sup>2+</sup> ions are floating around to seed the growth of the Pd nanoparticles and speed up the nucleation to form compact large nanoparticles. On the other hand at lower concentration the Pd<sup>2+</sup> ions are diluted enough to decrease the seeding and small nanoparticles were formed. Those small nanoparticles undergo controlled nucleation to form the dendritic morphology. When the concentration of rutin is increased, Pd nanostructures with a dendritic nanowire and fractal morphology were obtained. This may be due to the high concentration of rutin (reducing /stabilising agents) not only expedites the reduction of Pd<sup>2+</sup> to Pd<sup>0</sup>, but control the nucleation process. The sufficient numbers of rutin molecules present around the reaction direct the nucleation/assembly of the reduced primary Pd particles

in different arrays or unique direction to produce dendritic nanowires and multibranched fractal shapes. Limiting the no of molecules (lower concentration of rutin) only promote the formation of spherical patterns. So it can be speculated that the concentration of rutin not only stabilize the nanoparticles but its structure plays a vital role in controlling their nucleation or growth process in a universal pattern to produce Pd dendritic nanowires or fractal shapes. Hoewever it is well established that using surfactants or polymers with diiferent functional groups having different binding strategy such as acids and amines regulate the morphology of nanopararticles.<sup>1</sup> The formation of different shapes and morphology is controlled by the faceting tendency of the stabiliser and the growth kinetics to crystallographic planes.<sup>2-4</sup> The role of rutin molecule is still elusive at this point. Investigations are underway to explore the possible mechanism.

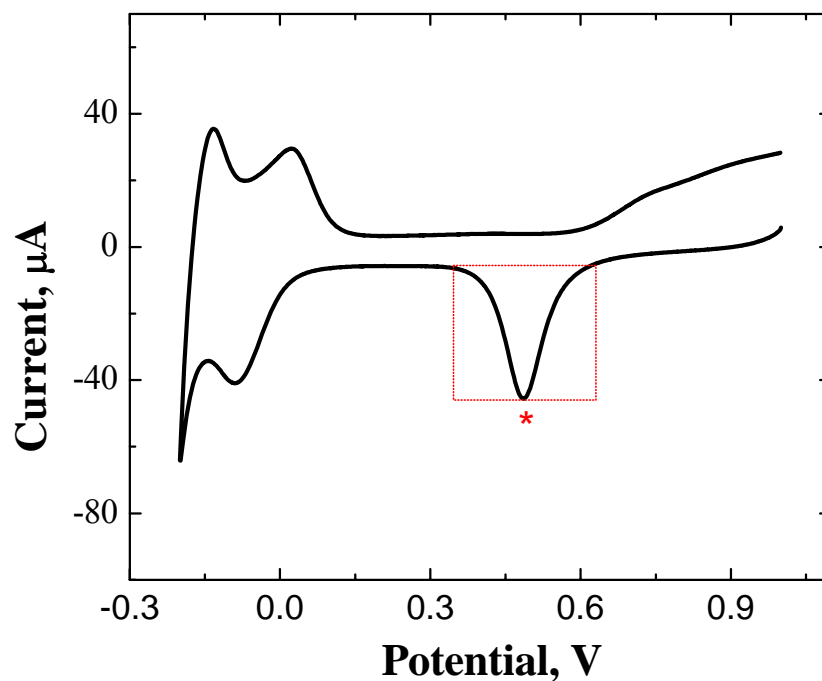
1. E. Ramirez, S. Jansat, K. Philippot, P. Lecante, M. Gomez, A. M Masdeu- Bulto and B. Chaudret *J. Organomet. Chem.* 2004, **689**, 4601.
2. C. J. Murphy, T. K. Sau, A. M. Gole, C. J. Orendorff, J. Gao, L. Gou, S. E. Hunyadi and T. Li, *J. Phys. Chem. B* 2005, **109**, 13857.
3. J. Watt, N. Young, S. Haigh, A. Kirkland and R. D. Tilley, *Adv. Mater.*, 2009, **21**, 2288.
4. Y. J. Xiong, Y. N. Xia, *Adv. Mat.* 2007, **19**, 3385.



**Figure S10. XRD patterns of different morphology of Pd nanostructures induced at different concentration of rutin and Pd(II).**

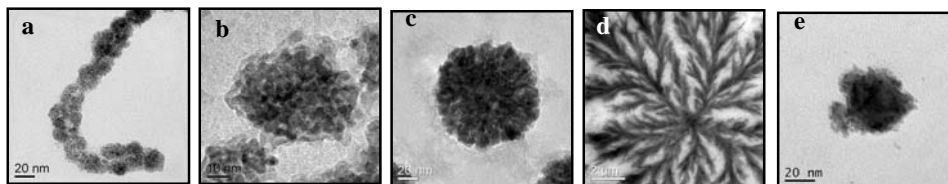


**Figure S11. TEM measurements of different morphology of Pd nanoparticles induced by 0.3 mM of (A) rutin, (B) quercetin and (c) catechol at a particular concentration of Pd<sup>2+</sup> (0.3mM).**



**Figure S12. Cyclic voltammogram of Pd dendritic NWs modified glassy carbon electrode in 0.5 M HClO<sub>4</sub> solution.**

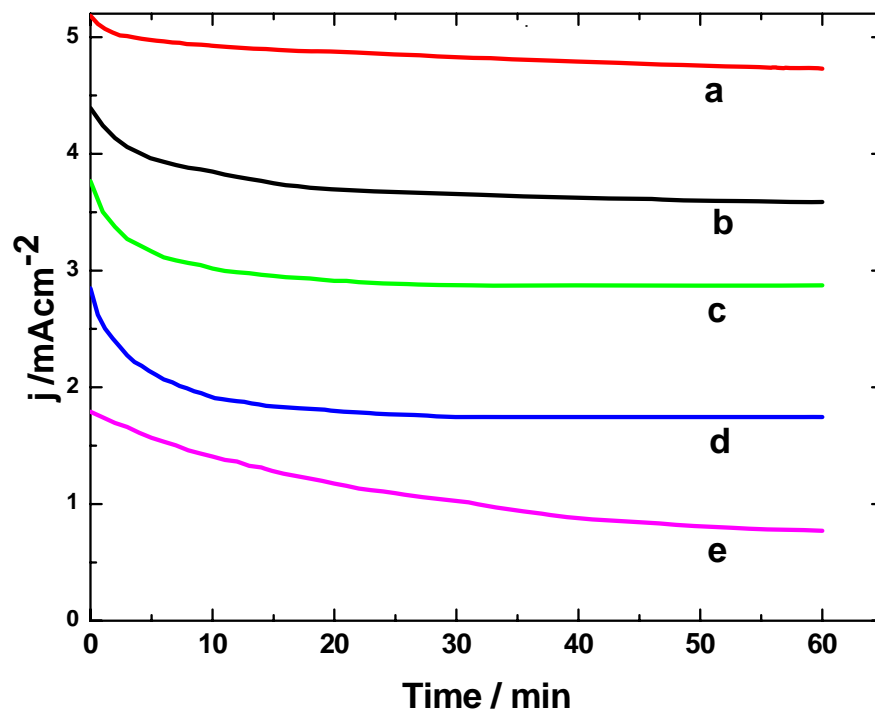
\*The charge consumed during the reduction of Pd oxides has been estimated by integration the area under the reduction wave. The electrochemically accessible area of Pd garlands was calculated to be 0.052 cm<sup>2</sup> using the reported value of 424 µC cm<sup>-2</sup>.



Structure	Current Density (mAcm <sup>-2</sup> ) <sup>[a]</sup>	Oxidation potential (mV) <sup>[a]</sup>	Current Density (mAcm <sup>-2</sup> ) <sup>[b]</sup>	Oxidation potential (mV) <sup>[b]</sup>
Dendritic NWs (a)	5.05±0.22	228±15	1.4±0.1	-206± 5
Structure (b)	4.25±0.30	252±11	1.21±0.11	-202±3
Structure (c)	3.78±0.19	311±17	0.91±0.13	-200±4
Structure (d)	2.85±0.37	343±13	0.65±0.12	-188±7
Structure (e)	1.81±0.25	390±14	0.47±0.1	-111±6

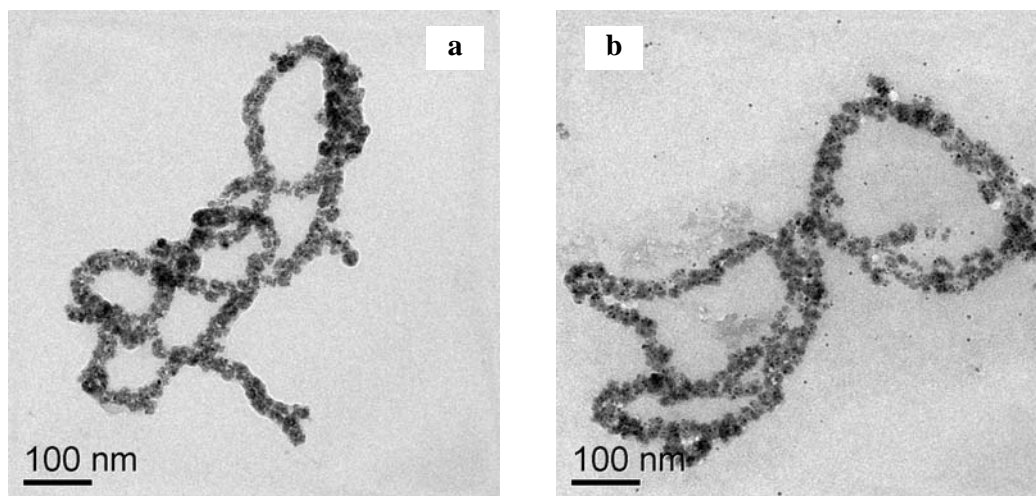
[a] Oxidation for formic acid and [b] Oxidation of methanol

**Figure S13.** Table summarized the electrocatalytic activity of different morphology Pd nanostructures towards oxidation of formic acid and methanol.



**Figure S14.** Chronoamperometric data obtained for (a-e of figure 3) Pd nanostructures modified GC electrode towards oxidation of formic acid (0.25M) in 0.5 M HClO<sub>4</sub> solution. Potentials are held at their oxidation potential.





**Figure S15. TEM measurements of (a) as-synthesized Pd dendritic nanowires and (b) after voltammetric measurements (50th cycles) towards oxidation of formic acid (0.25M) in 0.5 M HClO<sub>4</sub> solution).\***

\* After several cyclic voltammetric cycles (~ 50), the Pd nanostructures were removed from the electrode surface and dispersed in water with mild sonication. Few  $\mu$ l of colloidal solution was dropped onto carbon coated copper grids and dried prior to TEM measurements.