Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information:

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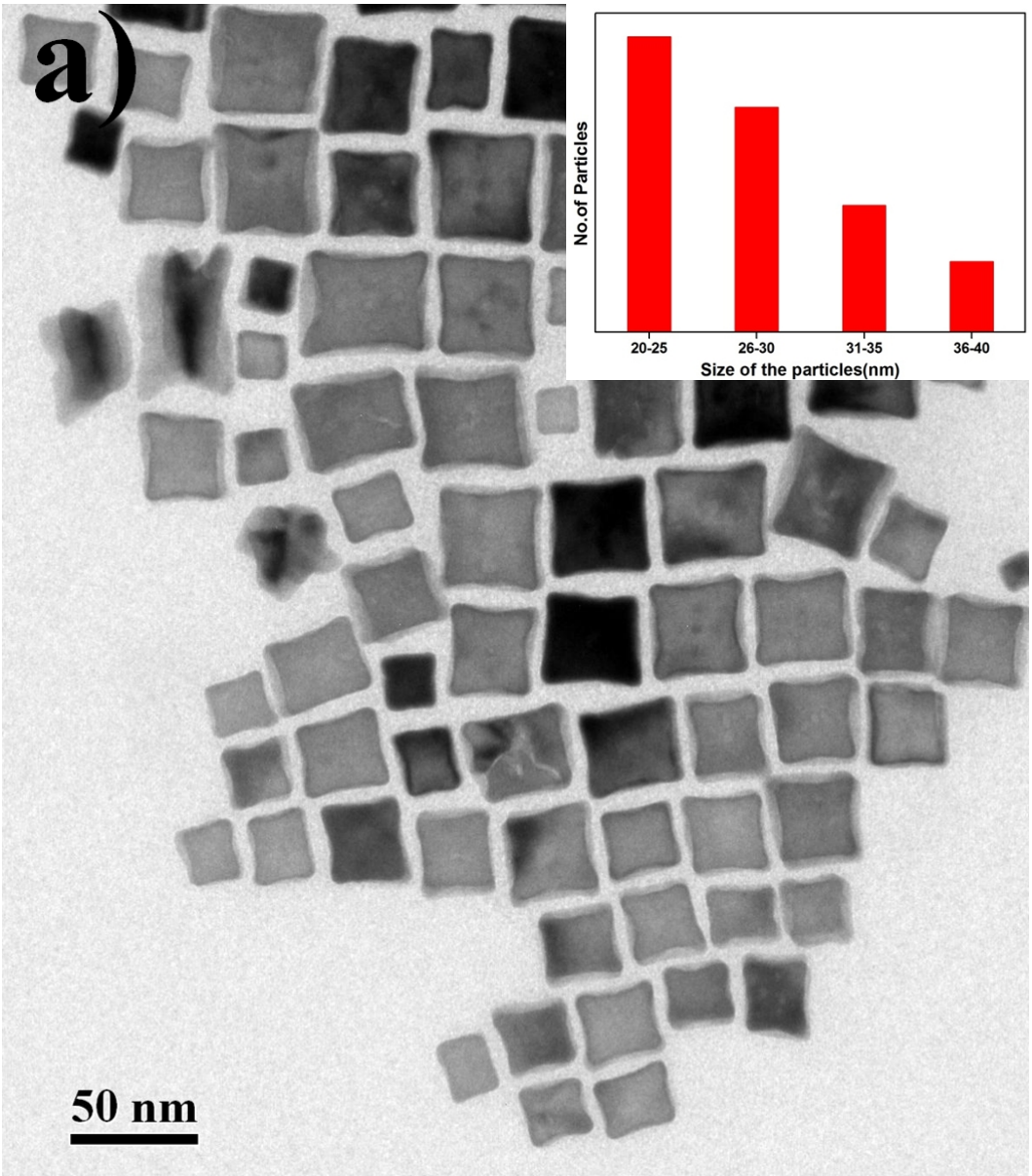
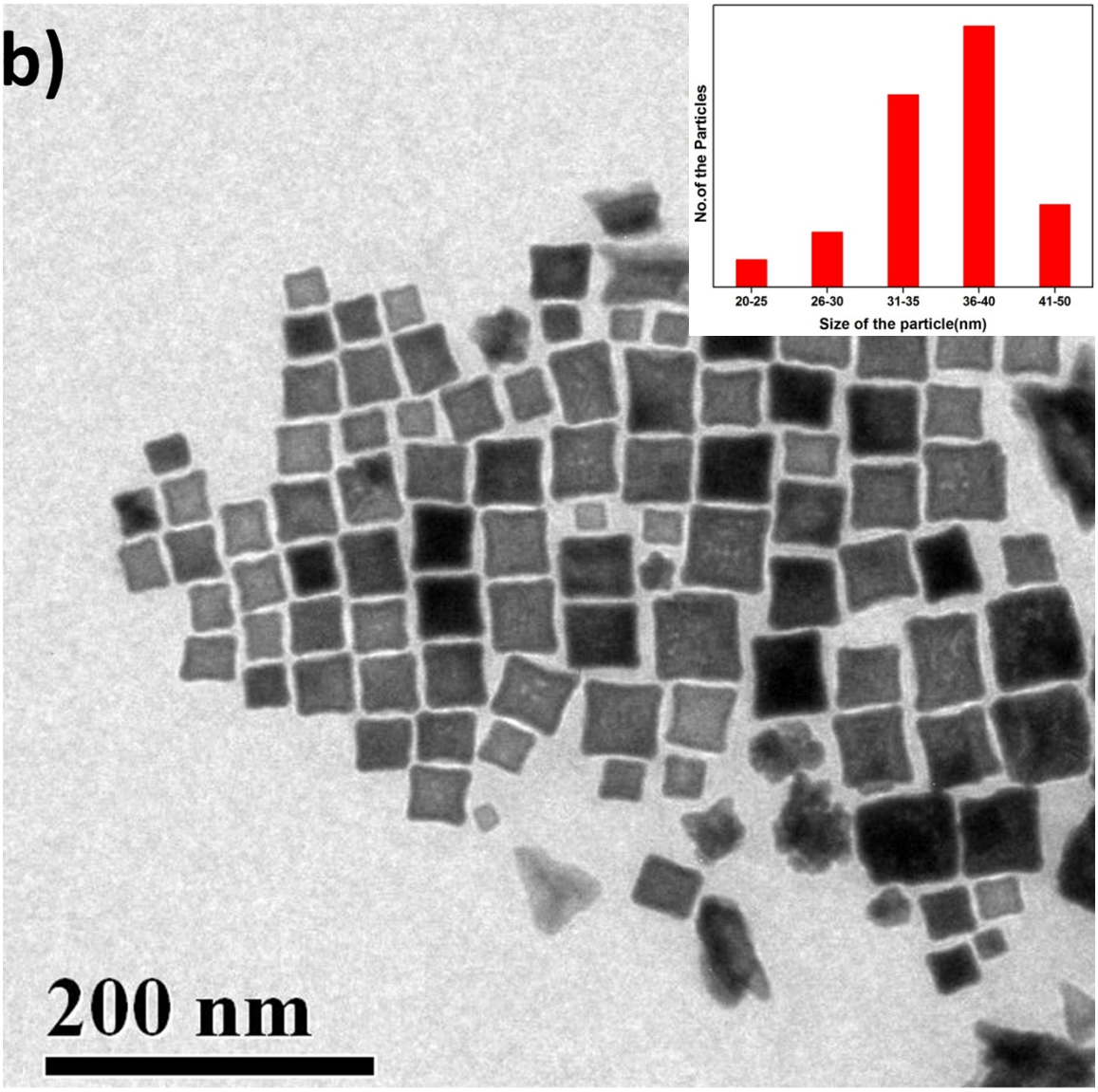
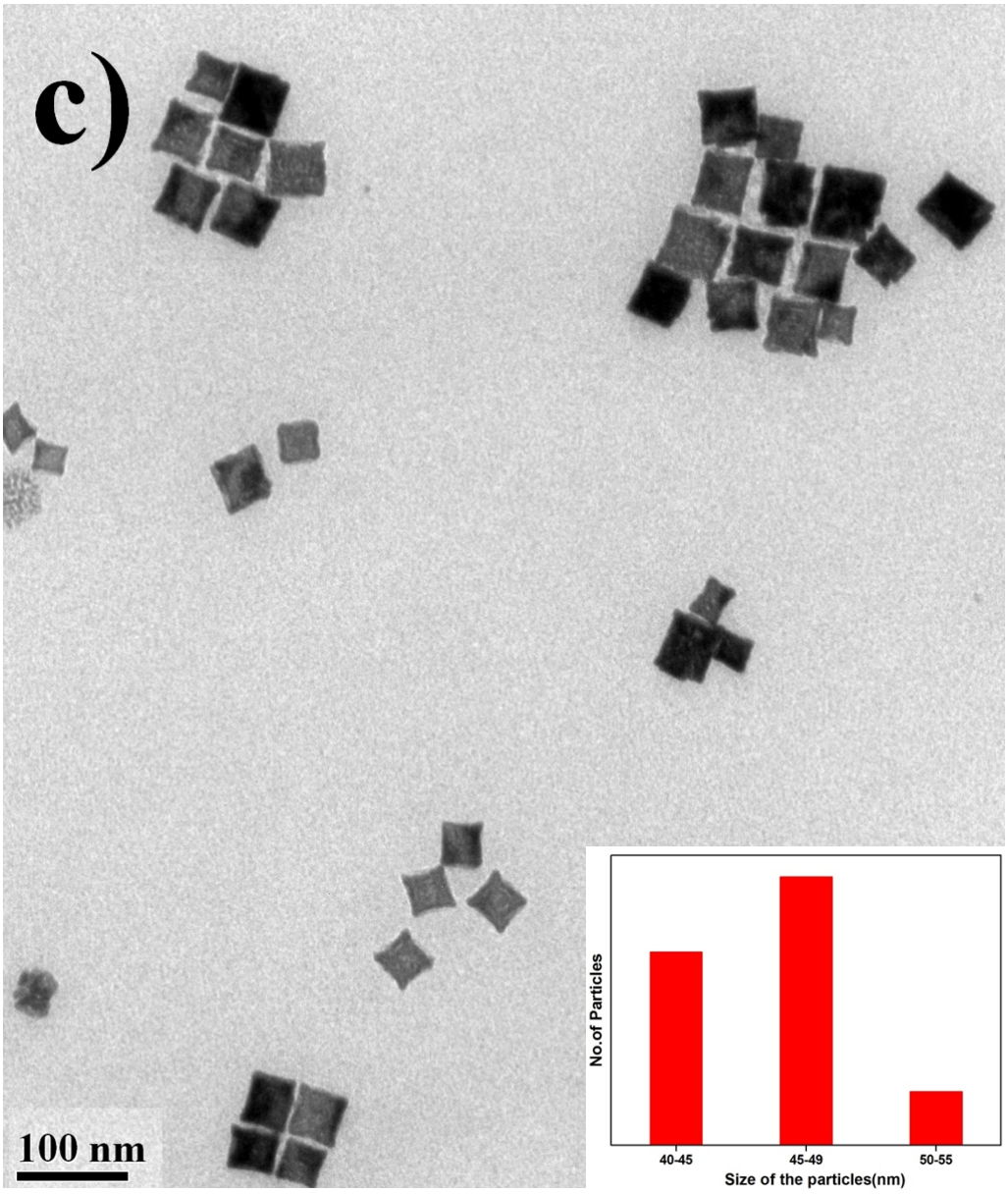



b)
No.of the Particles
20-25
26-30
31-35
36-40
41-50
Size of the particle(nm)
200 nm



FigS1:TEM images of Pd conacve nanocube of three different sizes synthesised by varying the amount of seed solution, and the corresponding histograms of the formed nanoparticles

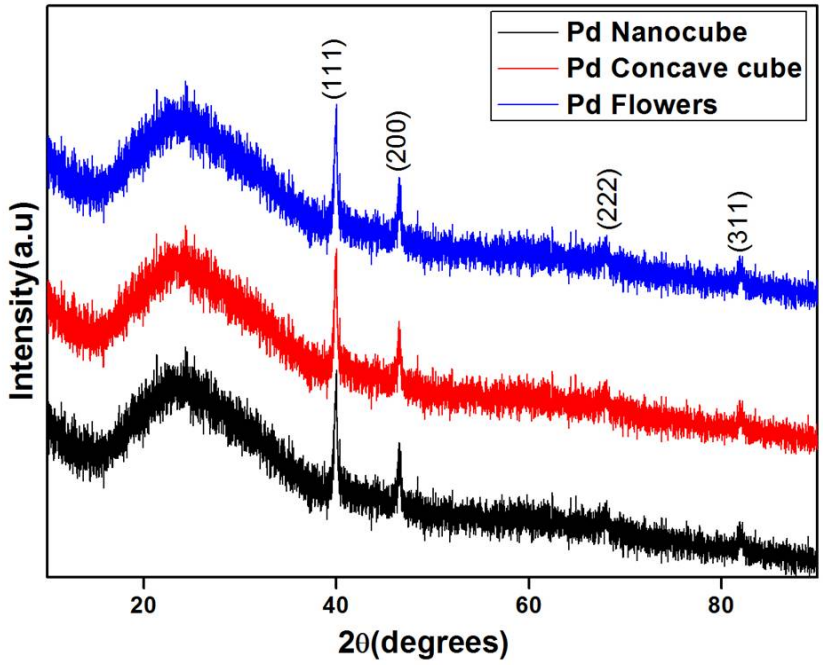


Fig S2: The X-ray Diffraction pattern for the as synthesised Pd nanoparticles. The reflections match with that of FCC Pd crystal lattice.

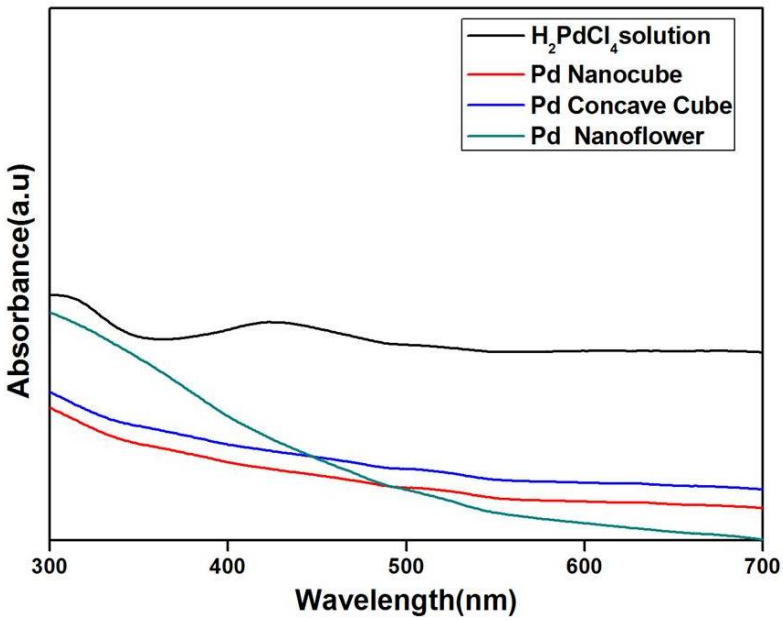


Fig S3: UV-visible spectrum of the as synthesised Palladium nanoparticles.

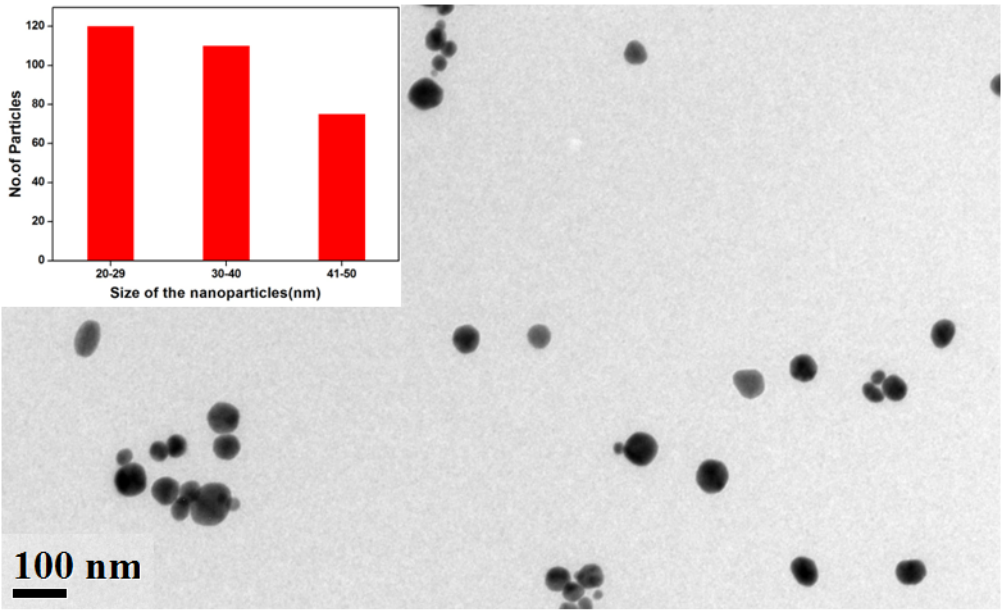
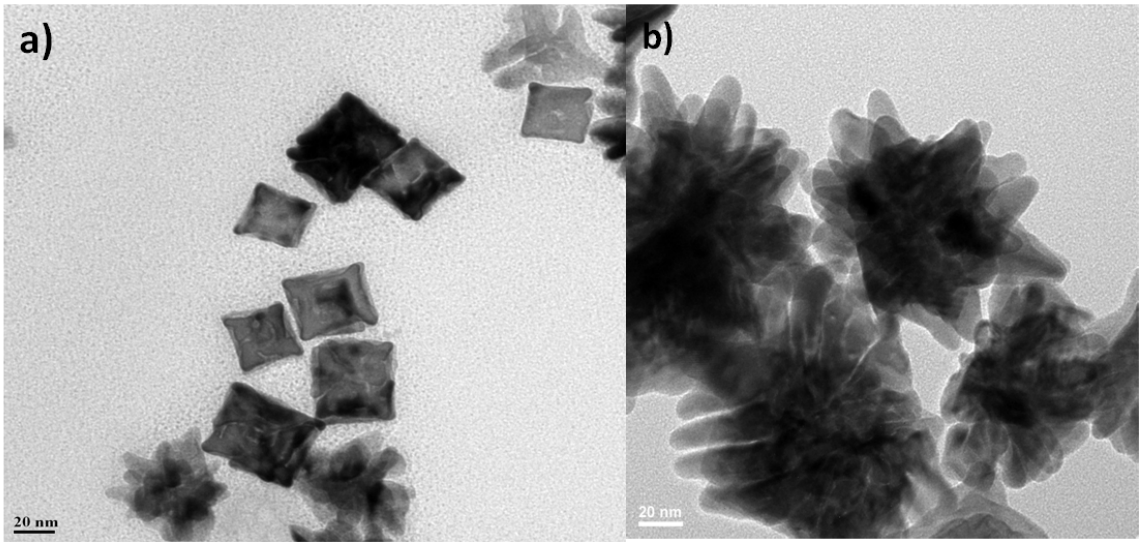


Fig S4: TEM image showing spherical Palladium nanoparticles which was used in control experiments



FigS5: The TEM image of the catalyst (a) concave nanocube and (b) nanoflowers after Heck coupling which shows that morphology is retained.

Calculation of Turn over Frequency:

The efficiency of the catalyst was evaluated by computing TOF, where TOF can be defined as the iodobenzene conversion per surface Pd atom per second as described in the literature[1]

Calculation of the total number of Pd atoms in a Pd nanocube enclosed by {100} facets, and the total number of Pd atoms on the surface

(1) Conventional nanocubes enclosed by {100} facets

(a) Number of Pd atoms contained in a nanocube

The edge length of a Pd nanocube is approximately 31 nm. Its volume is $(31\ nm)^3 = 2.97 \times 10^4\ nm^3$. Pd occupies a face-centered-cubic structure with a lattice constant of 0.389 nm. The volume of a unit cell is $(0.389\ nm)^3 = 0.059\ nm^3$. Each unit cell contains four Pd atoms. Therefore the total number of Pd atoms in a single Pd nanocube is $(2.97 \times 10^4 nm^3/0.059\ nm^3) \times 4 = 2.01 \times 10^6\ nm^3$

(b) Number of Pd atoms on the surface of a nanocube

A Pd nanocube is has 6 {100} facets. The total surface area is $(31\ nm)^2 \times 6 = 5.76 \times 10^3\ nm^2$. Each two-dimensional unit cell on the {100} facets contains two Pd atoms, and the area of this unit cell is $(0.39\ nm)^2 = 0.15\ nm^2$. The total number of Pd atoms on the surface of a single nanocube is$(5.76 \times 10^3 nm^2/0.15\ nm^2) \times 2 = 0.76 \times 10^5$.

(c) Total number of Pd atoms on the surface of nanocubes used in the reaction

The total number of Pd atoms in the catalyst is $(10^{-4}g) / (106.42\ g/mol) \times (6.02 \times 10^{23} g/mol) = 5.66 \times 10^{17}$. The number of Pd nanocubes involved in the catalytic reaction is $(5.66 \times 10^{17}) / (2.01 \times 10^6) = 2.78 \times 10^{11}$. The total number of Pd atoms on the surface of Pd nanocubes used in the catalytic reaction is $2.78 \times 10^{11} \times 0.76 \times 10^5 = 2.11 \times 10^{16}$ Pd atoms

2.11×10^{16} Pd atoms $= 0.35 \times 10^{-4}$m moles of Pd, TOF can be calculated using this value.
TOF= %. Conversion X mol (substrate)/ mol (catalyst) X time (sec), For example

For Palladium Nanocube

TOF=48 x 1m mol/0.35×10^{-4}m moles X 3600(sec)

$= 3.8 \times 10^2\ s^{-1}$

(2) Concave nanocubes enclosed by {310} facets

1) Volume of a single concave nanocube{PCN-1}

The Pd concave nanocube has an average edge length of 23 nm

The volume of a cube = $(23nm)^3 = 1.21x10^4\ nm^3$

The volume of a square pyramid is $1/3\ a^2\ h$, = $1/3 \times (23\ nm)^2 \times 1/3 \times 23/2 = 0.675\ x10^3\ nm^3$ (here h = edge length /2 and 1/3 term comes from {310} step atom density.

The volume of a concave nanocube is $(1.21x10^4\ nm^3 - 6x0.675\ x10^3\ nm^3) = 0.805x10^4 nm^3$.

The number of Pd atoms in a single Pd concave nanocube = $(0.805x10^4 nm^3/0.0589)\ x4 = 5.4x10^5$

2) Number of Pd atoms on the surface of a concave nanocube {PCN-1}

The atomic density of {310} planes is 1/3of that of {100} planes. Considering a cube of 23 nm in edge length, the total surface area of the cube is $6a^2 = (23nm)^2 \times 6 = 3.17x10^3 nm^2$.

The total number of Pd atoms on the {310} facets of a single concave nanocube = total surface area of the nanocube/surface area of single fcc Pd lattice x 2 x 1/3

$(3.17x10^3 nm^2/0.151)\ x2x1/3 = 1.39\ x10^4$Pd atoms

3) Number of surface Pd atoms/particle/volume of the concave nanocube

For a 23 nm concave nanocube the number of surface Pd atoms/particle/volume of the concave nanocube = $1.39\ x10^4/0.805x10^4 nm^3 = 1.72$ Pd atoms $/nm^3$

3) Total number of Pd atoms on the surface of concave nanocubes in the reaction

The total number of Pd atoms in the catalytic reaction is 5.66×10^{17}. The number of Pd Concave nanocubes in the catalytic reaction is calculated as follows:

The total number of Pd atoms in 0.1 mg of the catalyst = (10^{-4} g /106.42 g/mol (molar mass of Pd)) x $6.02x\ 10^{23}$ g/mol = 5.66×10^{17} Pd atoms.

Total number of Pd concave nanocubes involved in the catalytic reaction = 5.66×10^{17} Pd atoms $/5.4x10^5 = 1.04x10^{12}$

The total number of Pd atoms on the surface of concave nanocubes in the catalytic reaction = Total number of Pd concave nanocubes x No of surface Pd atoms in a single concave nanocube = $1.04x10^{12}\ x\ 1.39\ x10^4 = 1.44x10^{16}$ Pd atoms = $0.239\ x10^{-4}$ mmoles.

By this value TOF can be calculated as mentioned above.

95 x 1 mmol $/0.239\ x10^{-4}$mmoles x 3600 s = $11\ x\ 10^2\ s^{-1}$

Calculation for the Number of step atoms for Palladium concave Nanocube of edge length 23nm

Edge length=23nm

Pd-Pd bond distance=0.27nm

No. of Palladium atoms along the edge=23/0.27nm=85 atoms

{310} facets consist of 3 atom wide {100} terrace followed by monoatomic {111} step.

So no. of step atoms along a edge of length 23nm=21step atoms

Each face of the concave cube has 4 edges and there are total of 6 faces

So the number of step atoms along the edges on the face of the concave nanocube per particle= 21x4x6=504

Calculation of TOF value taking the whole Pd catalyst into account:

Catalyst	Conversion[a] (%)	TOF (s^{-1})	Conversion[b] (%)	TOF (s^{-1})
Pd CNC1 (23nm)	**95**	**22.5**	**76**	**18**
Pd CNC2 (37nm)	**96**	**22.7**	**80**	**18.9**
Pd CNC3 (45nm)	**97**	**23**	**84**	**19.9**
Pd Flower (100nm)	**99**	**23.5**	**85**	**20.1**
a – Suzuki Coupling b – Heck Coupling				

TOF=%Conversion X mol(substrate)/mol(catalyst) X time(sec)

The amount of Pd in 10 mM H_2PdCl_4 solution is 0.106g of Pd in 100mL,The amount added for synthesising nanoflowers and Concave nanocubes is about 125µL which contains around 0.125mg of Pd if complete seperation can be achieved.

The calculated amount of Pd after the final growth step in our catalyst is around 0.125mg, if complete separation is achieved.This was then dispersed in ethanol to make it reactant miscible to 100µL and was added to reactant mixture.

So amount of Pd is 0.125mg which is used for reaction

1mole of Pd=106g

0.125mg of Palladium=1 X0.125/106 x1000

$=11.7x10^{-7}$moles$=11.7x10^{-4}$mmoles.

So in case of Pd nanoflowers, for Suzuki reaction, TOF=99x1mmol/$11.7x10^{-4}$mmolx3600(sec)=$23.5s^{-1}$.

References:

1. M. Jin, H. Zhang, Z. Xie and Y. Xia, *Angewandte Chemie International Edition*, 2011, 50, 7850-7854.