

## Highly active small Pd nanocatalyst obtained by visible-light-induced photo-reduction with citrate and oxalate salts under batch and flow approaches

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## 1. General materials and methods

All chemicals were reagent grade and were used as received from the manufacturer. Palladium (II) chloride ( $\text{PdCl}_2$ , Anhedra<sup>®</sup>); hydrochloric acid (HCl 37 % w/w); trisodium citrate dihydrate (Sigma Aldrich<sup>®</sup>); disodium oxalate (Sigma Aldrich<sup>®</sup>), poly(*N*-vinylpyrrolidone) polymer (Mw PVP = 10000 Da), 4-chloronitrobenzene,  $\text{NaBH}_4$ , 4-bromoacetophenone, phenylboronic acid,  $\text{K}_3\text{PO}_4$ , ethanol 98 % (Porta <sup>®</sup>) and anhydrous  $\text{Na}_2\text{SO}_4$  were used as received. All solvents were analytical grade and distilled before use.  $\text{H}_2\text{PdCl}_4$  was prepared from analytical grade chemicals and Milli-Q-Millipore water. All reactions were carried out under atmosphere of nitrogen. Silica gel (0.063–0.200 mm) was used in column chromatography.

Photochemical reactions in batch were carried out in scintillation vials equipped with a magnetic bar and sealed with teflon plugs. The mixtures were irradiated with a purple 3 W LED lamp (395 nm) or with a blue 3W LED (462 nm) and stirred under nitrogen or argon atmosphere.

Photochemical reactions in flow were carried out in a mesoscale photochemical flow reactor (6.56 mL with 0.75 mm ID FEP-tubing) equipped with a blue-LED reactor (15 x 3W at 462 nm). The PdNPs were characterized by Transmission Electron Microscopy (TEM) using a JEM-Jeol 1120 microscope operating at 80 kV, available at the Research Institute IPAVE- INTA-CIAP in Córdoba, Argentina. The hydrodynamic apparent diameter ( $d_H$ ) of the samples were determined by Photon Correlation Spectroscopy (Dynamic Light Scattering, DLS) using a Delsa Nano C instrument (Beckman Coulter, Osaka, Jp.).

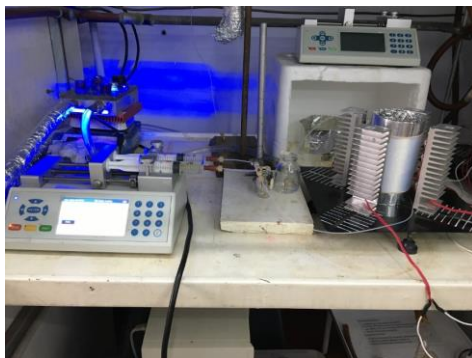
Gas chromatographic analysis were performed on a gas chromatograph with a flame ionization detector, and equipped with the following columns: HP-5 25 m x 0.20 mm x 0.25  $\mu\text{m}$  column.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were conducted on a High-Resolution Spectrometer Bruker Advance 400, in  $\text{CDCl}_3$  or  $\text{D}_2\text{O}$  as solvent. Gas Chromatographic/Mass Spectrometer analyses were carried out on a GC/MS QP 5050 spectrometer equipped with a VF-5ms, 30 m x 0.25 mm x 0.25  $\mu\text{m}$  column. UV-Vis determinations were performed using a SHIMATZU UV-Vis UV- 1800

series. FTIR spectra were recorded on a Nicolet iN10 IR Microscope (Thermo Scientific). Samples contained in KBr discs were scanned from 400 and 4000  $\text{cm}^{-1}$ , and the recording conditions were: normal resolution, sample scan, 64  $\text{s}^{-1}$ .

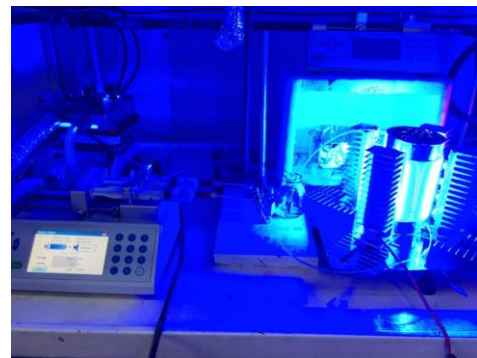
## 2. Photochemical reactors



Batch reactor- Blue LED 3 W



Continuous photo-flow device



**Figure SI1:** photochemical reactors used in the batch and photo-flow synthesis of Pd-PVP NPs.

## 3. Synthesis of Pd-PVP NPs dispersion in batch conditions

In a 5 mL scintillation vial equipped with a magnetic stir, were placed 44.0 mg PVP (2 % w/v); 11.0 mg of sodium citrate (molar ratio  $\text{Pd}^{2+}:\text{PI}$  1:10) and 2 mL of a feedstock aqueous solution of  $\text{H}_2\text{PdCl}_4$  2 mM. The vial was sealed and high purity  $\text{N}_2$  (or Ar) bubbled for 5 min to saturate the solution. Next, the vial was placed into the photochemical reactor, and was irradiated under vigorous magnetic stirring until the mixture colour change to dark brown solution. Finally, the vial was opened to the air, and the Pd-PVP NPs dispersion was stored in a falcon tube to be used as catalyst solution without further purification.

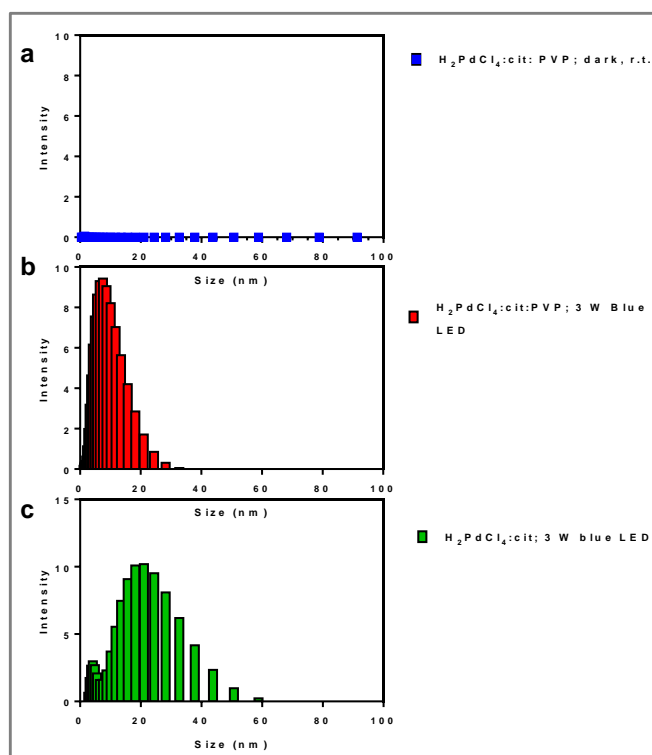
## 4. Characterization of Pd nanoparticles

Average dimensions and shape of Pd-PVP NPs were determined by Transmission Electron Microscope (TEM) images. Samples for morphological characterization were prepared by depositing a drop of the colloidal suspension on a 300 mesh formvar-carbon coated copper grid

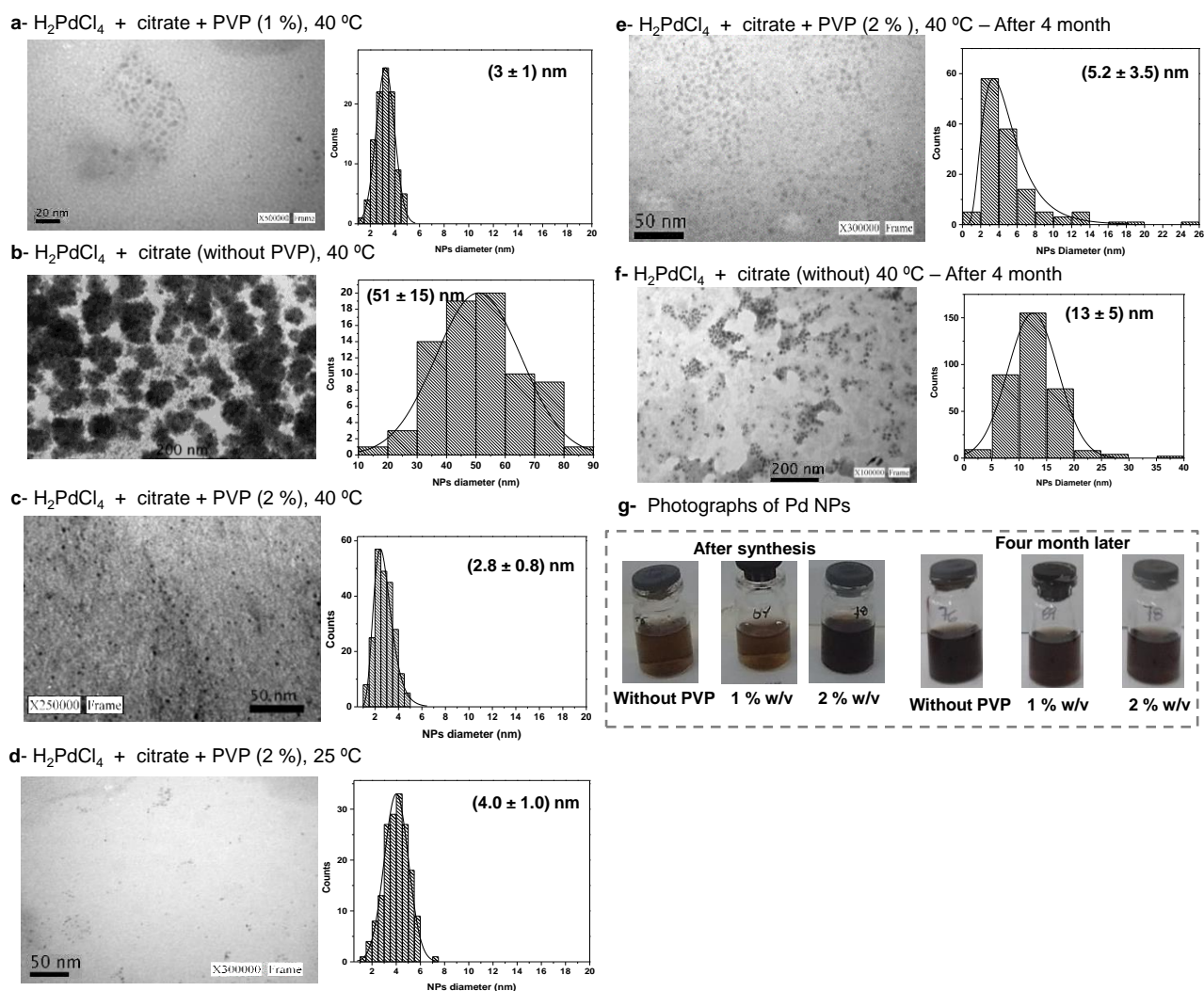
and dried at room temperature. Size distribution of Pd-PVP NPs was established by the average over 100 NPs from different places at each image of all samples. Distribution plots of the size were resolved by fitting data with a Gaussian behavior.

After synthesis, the colloidal dispersion was examined by Dynamic Light Scattering technique (DLS) to determine the hydrodynamic apparent diameter ( $d_H$ ) of the samples by photon correlation spectroscopy.

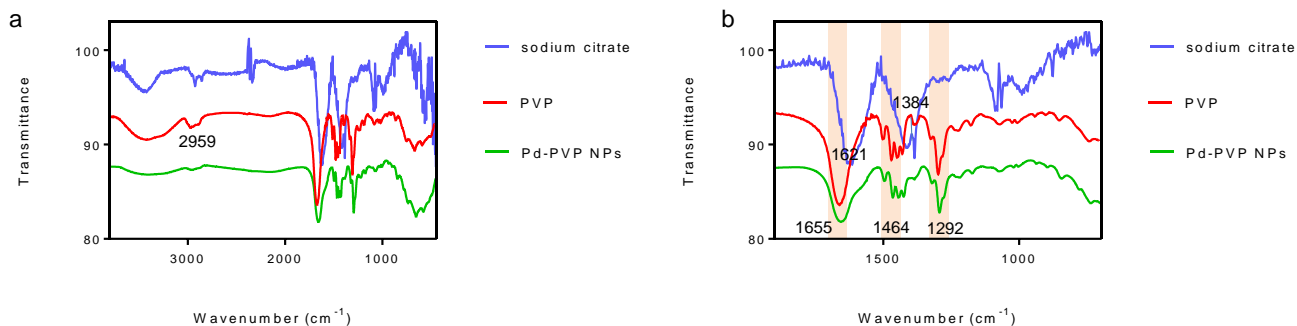
## 5. Characterization by DLS, TEM and FT-IR analysis of Pd-PVP NPs obtained by photoreduction with sodium citrate.



**Figure S12:** DLS analysis of reaction samples: a)  $H_2PdCl_4:citrate$  1:10, 2% PVP, dark settings, room temperature (blue columns), b)  $H_2PdCl_4:citrate:PVP$ , Blue LED 3 W 60 min (red columns) and c)  $H_2PdCl_4:citrate$ , Blue LED 3 W without PVP 60 min (green columns).

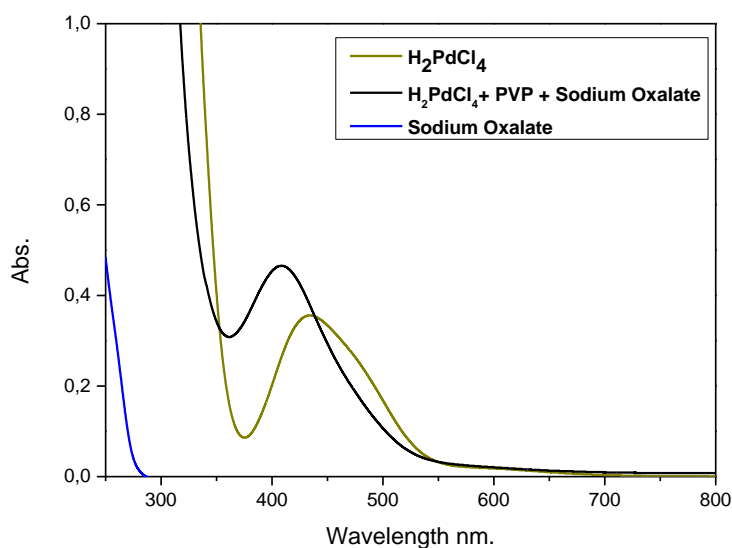


**Figure S13:** TEM micrograph and size distribution for Pd NPs synthesized by photoreduction of  $H_2PdCl_4$  aqueous solution with sodium citrate under batch experiments at 40 °C, irradiated with one 3 W Blue LED lamp (462 nm) for 60 min. PVP was employed under different proportion: a- 1 % w/v. b- without PVP. c- 2 % w/v. d- 2 % w/v at 25 °C e- Pd-PVP NPs, obtained with 2 % w/v PVP and sodium citrate (1:10 ratio Pd:PI) after 4 months. f- Photograph of Pd NPs obtained with different amounts of PVP after synthesis, and four months later.



**Figure SI4:** a- FT-IR spectra for Pd-PVP NPs, PVP and sodium citrate. b- Zoom-in view of the FT-IR spectra showing region between 700 and 1900  $\text{cm}^{-1}$ .

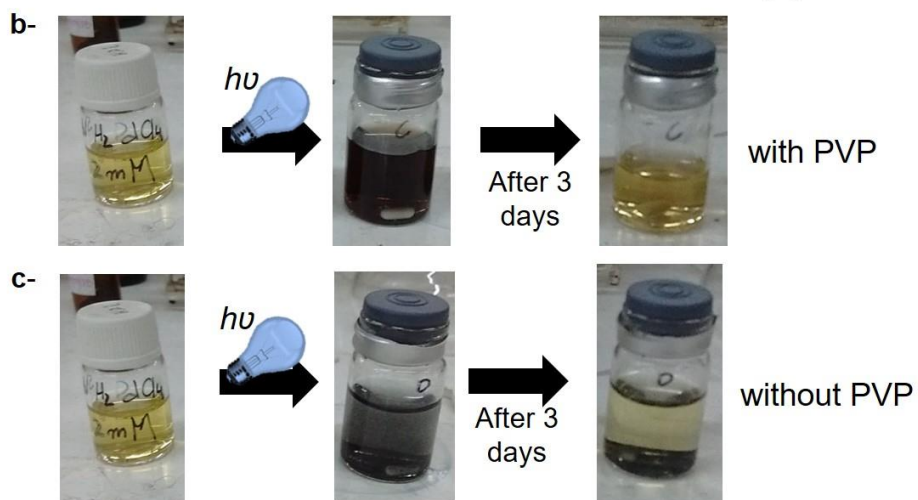
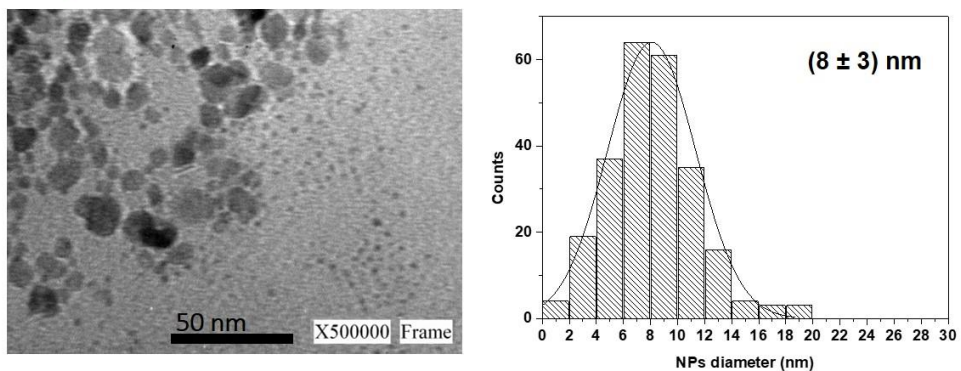
## 6. Characterization of Pd-PVP NPs obtained by photoreduction with sodium oxalate.



**Figure SI5:** Optical absorption spectra of a)  $\text{H}_2\text{PdCl}_4$  2 mM water solution (green line); sodium oxalate 20 mM water solution (blue line); reaction mixture of  $\text{H}_2\text{PdCl}_4$  + sodium oxalate (1:10 Pd:PI) + PVP (black line).



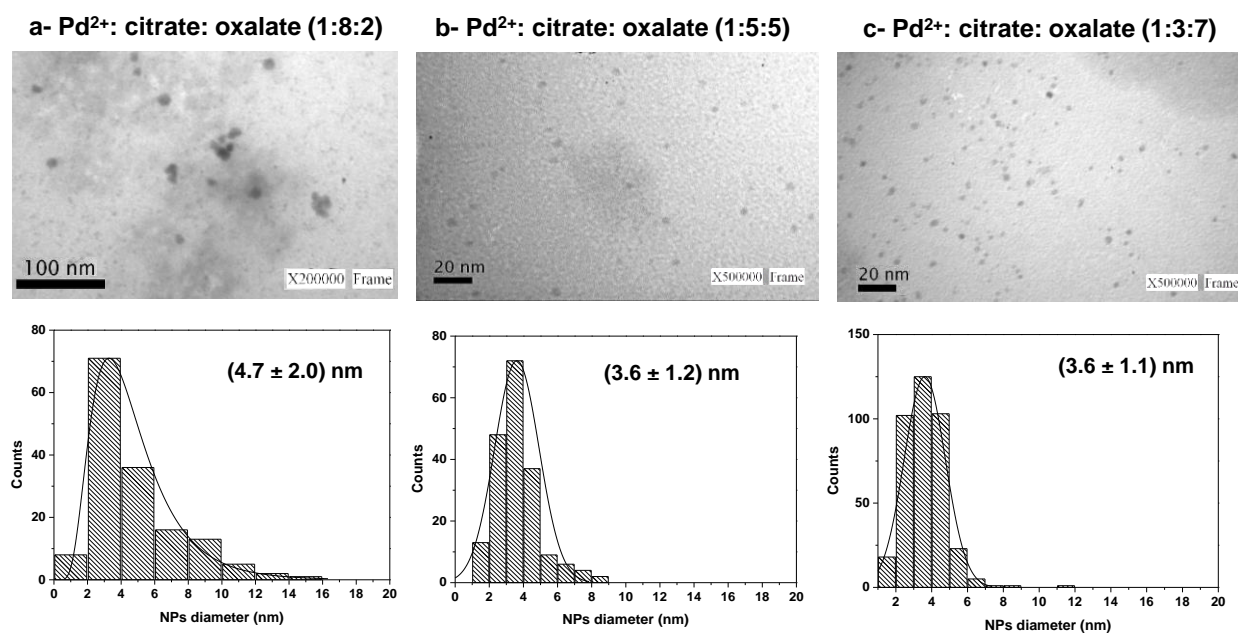
a-  $\text{H}_2\text{PdCl}_4$  + oxalate + PVP (2 % w/v), 20 min, 3 W Blue LED



**Figure SI6:** TEM micrograph and size distribution for Pd-PVP NPs synthesized by photoreduction of  $\text{H}_2\text{PdCl}_4$  aqueous solution with sodium oxalate, 2 % w/v PVP, under batch experiment, irradiated with one 3 W Blue LED lamp (462 nm) for 60 min. b- Photograph of Pd-PVP NPs obtained by photoreduction with sodium oxalate after synthesis and 3 days later. c - Photograph of Pd NPs obtained by photoreduction with sodium oxalate, and without PVP, after synthesis and 3 days later.



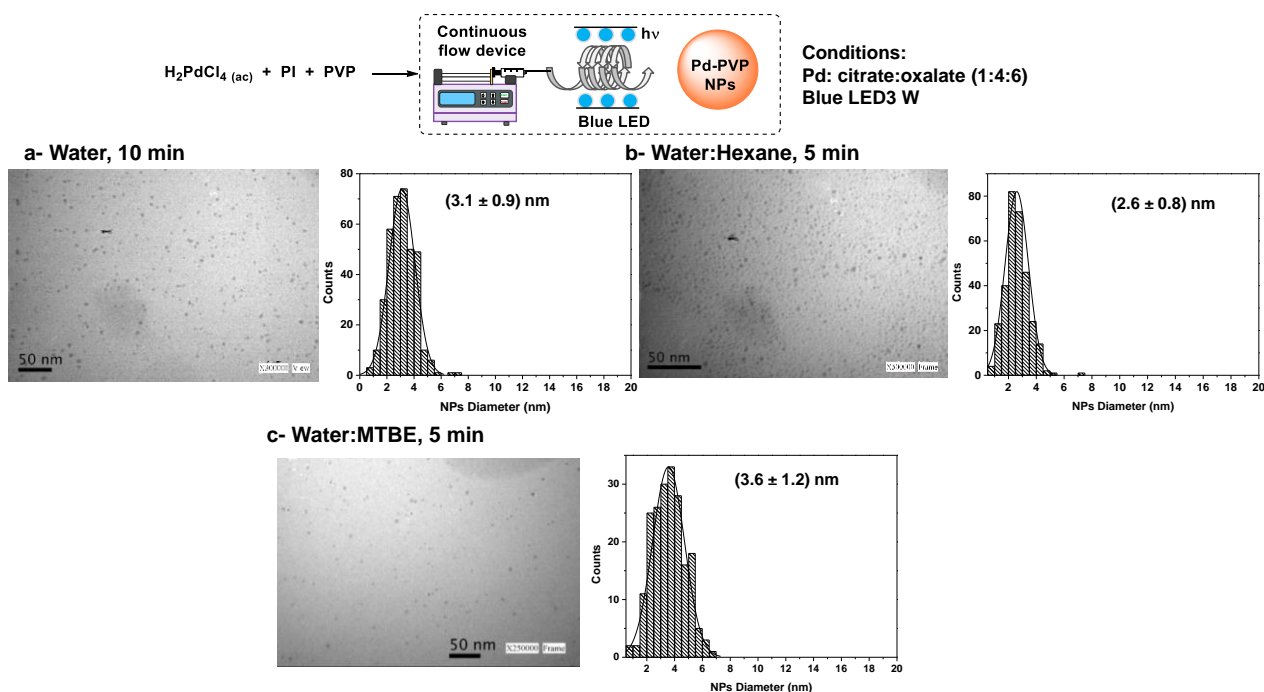
## 7. TEM characterization of Pd-PVP NPs obtained by photoreduction with sodium oxalate and sodium oxalate mixtures.



**Figure SI7:** TEM micrograph and size distribution for Pd-PVP NPs synthesized by photoreduction of  $\text{H}_2\text{PdCl}_4$  aqueous solution, 2 % w/v PVP, under batch experiment at 25 °C, irradiated with one 3 W Blue LED lamp (462 nm) for 20 min, with ratios Pd<sup>2+</sup>:citrate:oxalate: **a-** 1:8:2. **b-** 1:5:6. **c-** 1:3:7.

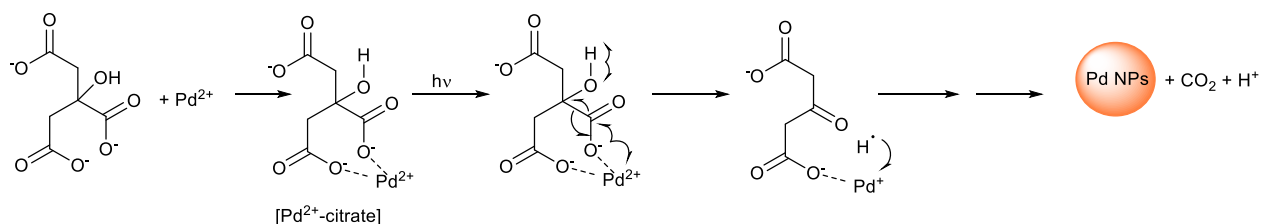
## 8. Synthesis of Pd-PVP NPs suspension under flow conditions

A solution of PVP (2 % w/v), sodium citrate (molar ratio Pd<sup>2+</sup>:PI 1:10) and a feedstock aqueous solution of  $\text{H}_2\text{PdCl}_4$  2 mM, was saturated by Ar and charged into the syringe. The syringe was connected through a mesoscale photochemical flow reactor (6.56 mL with 0.75 mm ID FEP-tubing) and the mixture was continuously irradiated for 10 min through a blue-LED reactor (15 x 3W at 462 nm). Finally, the NPs were collected in an open glass vial to ensure that the reaction stops.



**Figure S18:** TEM micrograph and size distribution for Pd-PVP NPs synthesized by photoreduction of  $\text{H}_2\text{PdCl}_4$  2mM, 2 % w/v PVP, under continuous photo-flow experiment at 25 °C, irradiated with Blue LED lamp (3 W, 462 nm), with ratio  $\text{Pd}^{2+}$ :citrate:oxalate: 1:4:6: **a-** 10 min in water (single-phase); **b-** 5 min in water: Hexane (segmented-phase) experiment and **c-** 5 min in water: MTBE (segmented-phase) experiment.

## 9. Mechanisms Proposed for the photoreduction of $\text{Pd}^{2+}$ by citrate salts



**Figure S19:** Plausible mechanisms for the photoreduction of  $\text{Pd}^{2+}$  by citrate salts

A photoinduced electron transfer process comprising a complex  $[\text{Pd}^{2+}\text{-citrate}]$  is proposed. By photoexcitation of the complex  $[\text{Pd}^{2+}\text{-citrate}]$ , upon decarboxylation of citrate, electrons are injected into the metal resulting in the formation of radical  $\text{H}\cdot$ . Following, the radical  $\text{H}\cdot$  releases

an electron to the formed [Pd<sup>+</sup>] intermediate, producing [Pd<sup>0</sup>] complex, which eventually leads to the formation of Pd nuclei together with 3-OA and CO<sub>2</sub>.<sup>1,2</sup> Further adsorption of Pd<sup>0</sup> onto the Pd nuclei leads to a growth of Pd NPs. In that process, the presence of PVP polymer chains, along with citrate/3-OA anions adsorbed onto the Pd NPs surface, suppresses aggregation Pd NPs due to the steric repulsion in combination with electrostatic repulsion.

#### **10. Representative procedure for the Suzuki-Miyaura cross-coupling reaction catalyzed by Pd-PVP NPs.**

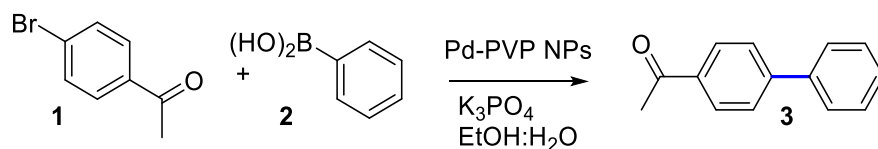
Into a 10 mL tube reaction with a Teflon screw-cap septum equipped with a magnetic stirrer *p*-bromoacetophenone (**1**) (0.25 mmol), arylboronic acid (**2**) (0.375 mmol) and K<sub>3</sub>PO<sub>4</sub> (0.75 mmol) were placed. Then, EtOH (0.5 mL) and water (to obtain a total volume of 1.5 mL taking into account the volume of Pd-PVP NPs solution) were added. At last, the 52 μL of Pd-PVP NPs 2mM (0.04 mol%) was added. The reaction mixture was heated in an oil bath for 1 hour. After being cooled to room temperature, the mixture was opened to the air, diluted with water and then extracted three times with ethyl acetate (5 mL each). The biaryl product was purified by silica-gel column chromatography after being dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The product was quantified by GC employing benzophenone as internal standard. The pure product was compared with authentic samples by GC, GC-MS and <sup>1</sup>H NMR. All the spectroscopic data were in agreement with those previously reported for the product 1-(biphenyl-4-yl)ethanone (**3**).<sup>3</sup>

TOF values were calculated using the following equation:

$$TOF = \frac{n(ArBr)}{n(total Pd) \times t}$$

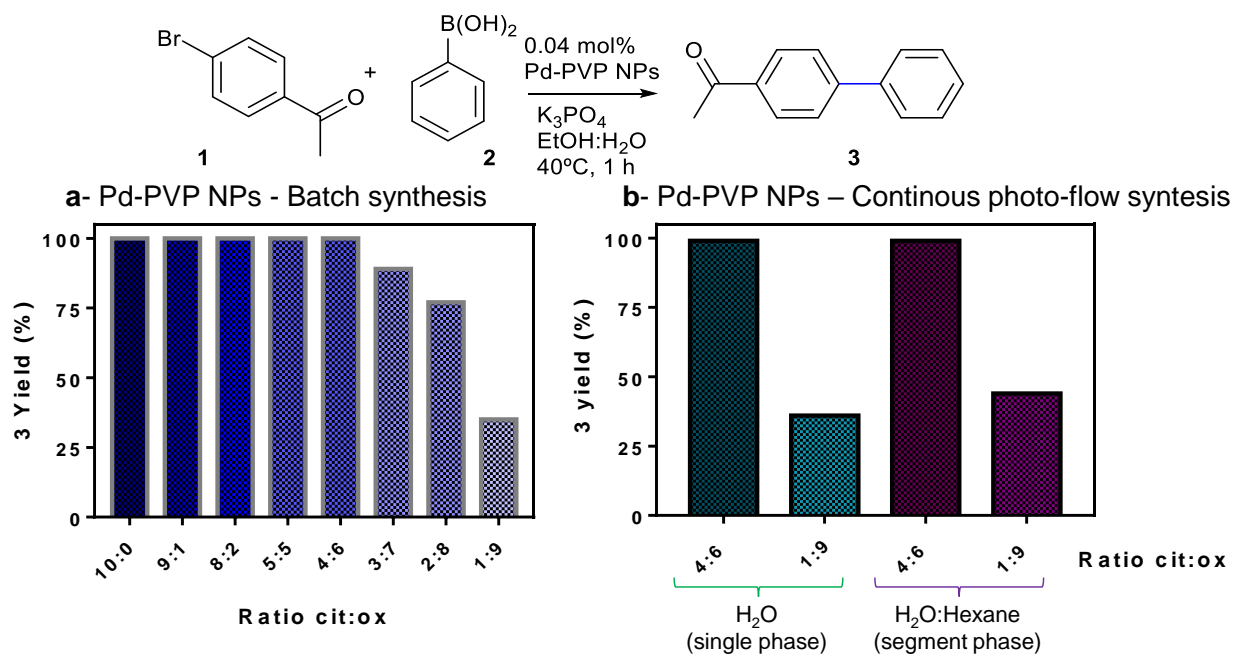
where  $n_{(Ar-Br)}$  is the number of moles of Ar-Br converted (mol),  $n_{(total Pd)}$  is the moles of total Pd (mol) added to the reaction, and  $t$  is the reaction time (h).

**Table S11:** Suzuki-Miyaura coupling reaction catalyzed by colloidal Pd-PVP NPs prepared with sodium citrate as PI under batch conditions.<sup>a</sup>



| Catalyst                                   | % Pd mol | Temp. (°C) | time (h) | Conversion <b>1</b> (%) <sup>b</sup> | Yield <b>3</b> (%) <sup>c</sup> | TOF (h <sup>-1</sup> ) <sup>d</sup> |
|--|----------|------------|----------|--------------------------------------|---------------------------------|-------------------------------------|
| Pd-PVP NPs                                 | 0.33     | 90         | 2        | 99                                   | 99                              | 150                                 |
|  | 0.10     | 90         | 2        | 99                                   | 99                              | 495                                 |
|  | 0.10     | 90         | 1        | 99                                   | 99                              | 990                                 |
|  | 0.10     | 60         | 1        | 99                                   | 97                              | 990                                 |
|  | 0.10     | 40         | 1        | 99                                   | 95                              | 990                                 |
|  | 0.04     | 40         | 1        | 97                                   | 93                              | 2425                                |
|  | 0.04     | 30         | 1        | 98                                   | 98                              | 2150                                |
|  | 0.04     | 30         | 0.25     | 86                                   | 83                              | 8600                                |
| --   | --       | 40         | 1        | 0                                    | 0                               | 0                                   |
| H <sub>2</sub> PdCl <sub>4</sub> + citrate | 0.04     | 40         | 1        | 59                                   | 59                              | 1476                                |

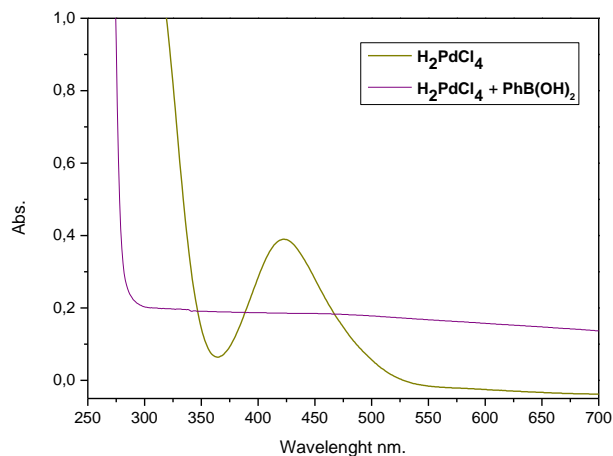
<sup>a</sup> Reactions conditions: in a 10 mL reaction tube 4-bromoacetophenone (**1**) (0.25 mmol), phenylboronic acid (**2**) (0.375 mmol) K<sub>3</sub>PO<sub>4</sub> (0.75 mmol), EtOH (0.5 mL), water (1.45 mL) and 50 μL of Pd-PVP NPs were placed and the reaction was stirred and heated in an oil bath for the indicated time. <sup>b</sup> Determine in relationship to the amount of initial substrate **1**. <sup>c</sup> GC yields. The yields reported represent at least the average of two reactions. <sup>d</sup> TOF (Turnover Frequency: mol substrate converted per mol of Pd per hour). This represent at least the average of two reaction



**Figure S110:** Comparison of the catalytic activity of Pd-PVP NPs in Suzuki-Miyaura cross coupling reaction between 4-bromoacetophenone (**1**) and phenylboronic acid (**2**) at 40 °C for 1 hour, obtained with different ratios of sodium citrate:sodium oxalate as PIs under: **a-** batch synthesis. **b-** Continuous photo-flow synthesis under single-phase regime (H<sub>2</sub>O- green columns) and segmented flow regime (H<sub>2</sub>O-Hexane- purple columns).

### 11. *In situ* reduction of H<sub>2</sub>PdCl<sub>4</sub> by phenylboronic acid.

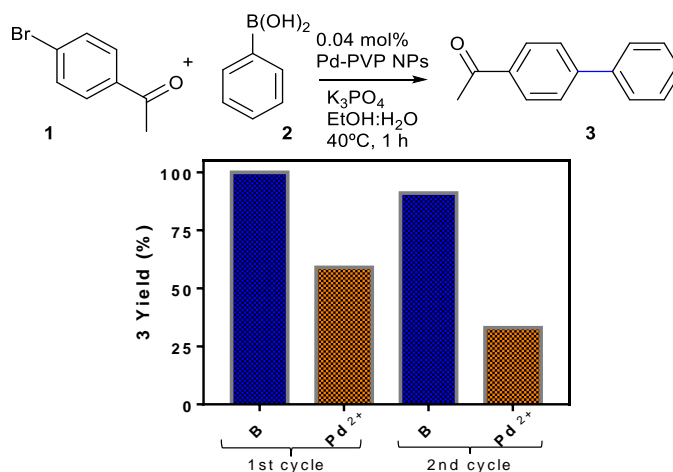
The *in situ* reduction of H<sub>2</sub>PdCl<sub>4</sub> precursor by phenylboronic acid was evaluated. For that, in a 10 mL vial, 2 mL of H<sub>2</sub>PdCl<sub>4</sub> 2 mM aqueous solution was placed and then 10 mg of phenylboronic acid were added at room temperature under vigorous stirring. After a few seconds, a sudden change of colour from yellow to dark brown was observed. The process was followed by UV-vis spectroscopy, which confirmed the disappearance of the H<sub>2</sub>PdCl<sub>4</sub> absorption band at 423 nm after only 4 minutes of reaction.



**Figure S111:** Optical absorption spectra of  $\text{H}_2\text{PdCl}_4$  2 mM aqueous solution (green line) and  $\text{H}_2\text{PdCl}_4$  + phenylboronic acid (1:20 ratio) after 4 minutes of mixture (purple line).

## 12. Representative procedure for catalyst reuse experiment in the Suzuki-Miyaura cross-coupling reaction

The reuse test of Pd-PVP NPs was performed after carried out the reaction following the procedure previously described in Section 10. The same reaction mixture was used by addition of fresh amounts of reactants. The experiment was performed three times by consecutive addition of a new batch of *p*-bromoacetophenone (**1**) (0.25 mmol), arylboronic acid (**2**) (0.375 mmol) and  $\text{K}_3\text{PO}_4$  (0.75 mmol), EtOH (0.25 mL) and water (0.75 mL). The reaction mixture was stirred at 40 °C for 1 h. After this time, the reaction was monitored by CG analyses.



**Figure SI12:** Reusing experiment in Suzuki-Miyaura cross-coupling reaction between 4-bromoacetophenone (**1**) and phenylboronic acid (**2**) of Pd-PVP NPs with sodium citrate as PI under batch (B) and a mixture  $\text{H}_2\text{PdCl}_4$ - sodium citrate.

**Table SI 2:** Comparison of catalytic activity of Pd-PVP NPs and some selected Pd-based catalysts in the literature for Suzuki-Miyaura cross-coupling reaction between 4-bromoacetophenone (**1**) and phenylboronic acid (**2**).

| Catalyst                                    | Catal. load. (% mol) | Reaction medium         | Base                            | Temp (°C) | Time (h) | TOF ( $\text{h}^{-1}$ ) <sup>ref</sup> |
|---|----------------------|-------------------------|---------------------------------|-----------|----------|--|
| Pd-PVP NPs                                  | 0.04                 | EtOH: H <sub>2</sub> O  | K <sub>3</sub> PO <sub>4</sub>  | 30        | 0.25     | 8600 <sup>This work</sup>              |
| Pd NPs                                      | 0.20                 | H <sub>2</sub> O        | K <sub>2</sub> CO <sub>3</sub>  | 50        | 5        | 90 <sup>4</sup>                        |
| Pd NPs <sup>a</sup>                         | 3                    | H <sub>2</sub> O        | Na <sub>2</sub> CO <sub>3</sub> | 60        | 11       | 3 <sup>5</sup>                         |
| Pd/C (10 %) <sup>b</sup>                    | 0.5                  | i-PrOH:H <sub>2</sub> O | K <sub>3</sub> PO <sub>4</sub>  | r. t.     | 3        | 61 <sup>6</sup>                        |
| PdO/Ce <sub>x</sub> O <sub>y</sub>          | 1 mg                 | EtOH:H <sub>2</sub> O   | NaOH                            | 70        | 1        | 13944 <sup>7</sup>                     |
| BN@NHC-Pd <sup>c</sup>                      | 0.02                 | EtOH:H <sub>2</sub> O   | K <sub>2</sub> CO <sub>3</sub>  | r. t      | 1        | 4700 <sup>8</sup>                      |
| Pd(OAc) <sub>2</sub> + P-ligand             | 0.0001               | H <sub>2</sub> O        | K <sub>2</sub> CO <sub>3</sub>  | 100       | 2        | 385000 <sup>9</sup>                    |
| PdCl <sub>2</sub> + N,O-ligand              | 0.30                 | H <sub>2</sub> O        | K <sub>2</sub> CO <sub>3</sub>  | 90        | 2        | 157 <sup>10</sup>                      |
| PdCl <sub>2</sub> + N,N-ligand <sup>d</sup> | 0.005                | H <sub>2</sub> O        | K <sub>3</sub> PO <sub>4</sub>  | 100       | 6        | 3100 <sup>11</sup>                     |



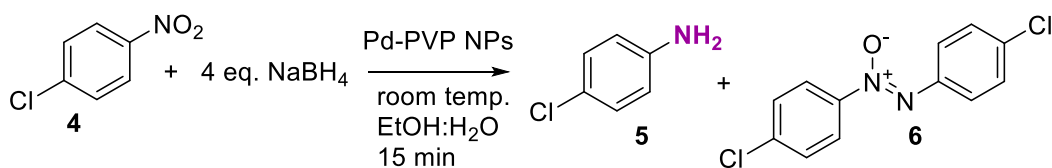
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a- Pd NPs stabilized with proline-based amphiphile PS-750-M. 4-Chlorophenylboronic acid was used. b- 4-Bromobenzaldehyde was used. c- Boron nitride was used as support. d- Formation of the Pd NPs was detected under the catalytic reaction.

### **13. Representative procedure for the nitroaromatic reduction catalyzed by PVP-Pd NPs.**

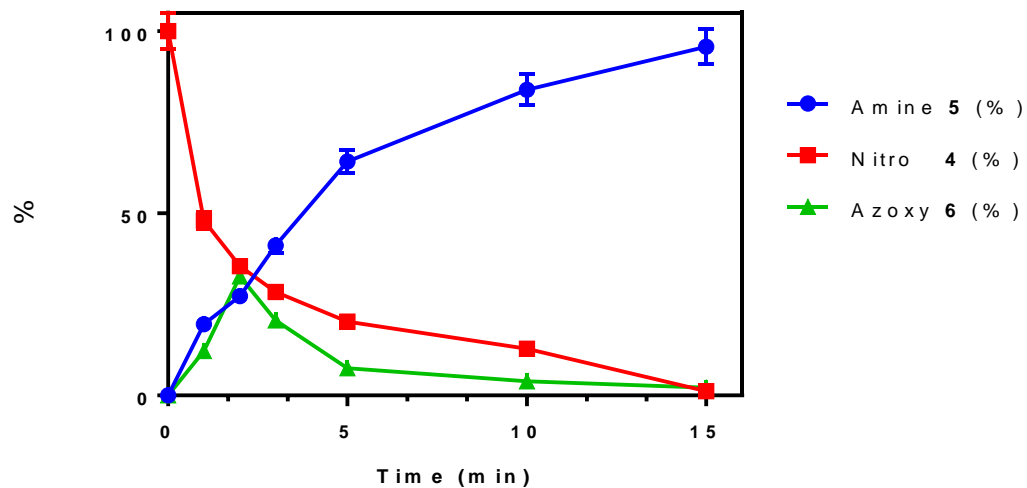
Into a 25 mL bottom round flask equipped with a magnetic stirrer, *p*-chloronitrobenzene (4, 0.25 mmol) was dissolved in EtOH (0.5 mL) and 1 mL of water was added. Then 125  $\mu$ L of colloidal dispersion of PVP-Pd NPs was added. Finally, under vigorous stirring, a solution of 1 mmol of NaBH<sub>4</sub> in H<sub>2</sub>O (2 mL) was dropped. At this stage, an intense color change took place, and effervescence evolution was observed. The reaction was stirred for 15 minutes at room temperature, and then it was diluted with water and extracted three times with ethyl acetate (5 mL each). The reaction mixture was analyzed by GC and GC-MS after being dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The product was quantified by GC employing benzophenone as internal standard. The amine product was compared with authentic samples by GC, GC-MS and <sup>1</sup>H NMR. All the spectroscopic data were in agreement with those previously reported for the product 4-chloroaniline (**5**).<sup>12</sup>

**Table S1 3:** Reduction of nitro group in 4-chloronitrobenzene (**4**) catalyzed by colloidal Pd-PVP NPs.<sup>a</sup>



| Entry | Catalyst                                   | Pd loading (mol %) | Time (min) | Yield ( <b>5</b> ) (%) <sup>c</sup> | Yield ( <b>6</b> ) (%) <sup>c</sup> | TOF (min <sup>-1</sup> ) <sup>d</sup> |
|-------|--|--------------------|------------|-------------------------------------|-------------------------------------|---------------------------------------|
| 1     | --   | 0                  | 15         | 0                                   | 0                                   | 0                                     |
| 3     | Pd-PVP NPs Citrate                         | 0.1                | 15         | 96                                  | <5                                  | 66                                    |
| 4     |  |                    | 10         | 67                                  | <5                                  | 92                                    |
| 5     |  |                    | 5          | 40                                  | 7                                   | 140                                   |
| 6     | Pd NPs Citrate                             | 0.1                | 15         | 31                                  | 5                                   | 20                                    |
| 7     | Pd-PVP NPs cit:ox 8:2                      | 0.1                | 15         | 83                                  | 8                                   | 54                                    |
| 8     | Pd-PVP NPs cit:ox 5:5                      | 0.1                | 15         | 90                                  | <5                                  | 59                                    |
| 9     | Pd-PVP NPs cit:ox 2:8                      | 0.1                | 15         | 99                                  | <5                                  | 65                                    |
| 10    | Pd-PVP NPs cit:ox 1:9                      | 0.1                | 15         | 89                                  | <5                                  | 58                                    |
| 11    | Pd-PVP NPs cit:ox 1:9<br>flow single phase | 0.1                | 15         | 99                                  | <5                                  | 65                                    |

<sup>a</sup> Reactions conditions: in a 5 mL scintillation vial was placed *p*-chloronitrobenzene (**4**, 0.25 mmol), 0.5 mL EtOH (0.5 mL), 1 mL of water, the needed amount of colloidal dispersion of PVP-Pd NPs was added. Then, a solution of 1 mmol of NaBH<sub>4</sub> in H<sub>2</sub>O (2 mL) was dropped, and the mixture was stirred for 15 min. <sup>b</sup> Determine in relationship to the amount of initial substrate **4**. <sup>c</sup> GC yields. The yields reported represent at least the average of two reactions. <sup>d</sup> TOF (Turnover Frequency: mol substrate converted per mol of Pd per hour).



**Figure SI13:** Time evolution for the reduction of 4-chloronitrobenzene by  $\text{NaBH}_4$  and catalyzed with Pd-PVP NPs: Nitro 4 (Red square), Amine 5 (Blue circle), Azoxy 6 (Green triangle).

## 14. References

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