

A Simple Method for Producing Colloidal Palladium Nanocrystals: Alternating Voltage-Induced Electrochemical Synthesis

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Colloidal palladium nanocrystals (Pd-NCs) are important materials for many applications, such as heterogeneous catalysis,^[1–11] hydrogen purification-and-storage,^[12–14] chemical sensors,^[15,16] and electronics.^[17,18] Their performances are strongly dependent on their sizes, size distributions, shapes, and capping ligands.^[19–25] The structure-function relationship has stimulated tremendous effort to develop effective and efficient methods for synthesizing well-dispersed Pd-NCs. Currently, there are four main methods (Figure S1 in the Supporting Information): 1) the chemical reduction of Pd(II) or Pd(IV) anions PdX_n^{m-} ; ^[5,8,19,26] 2) the thermal decomposition of Pd compounds such as palladium acetylacetonate $\text{Pd}(\text{acac})_2$; ^[27–29] 3) the electrochemical reduction of Pd(II) or Pd(IV) anions PdX_n^{m-} ; and; ^[6,11,30–32] 4) the anodic dissolution of Pd electrode to PdX_n^{m-} anions followed by a cathodic deposition.^[33,34] The first three methods rely on expensive Pd(II) or Pd(IV) compounds, and the last two methods require specialized potentiostats. Therefore, it is highly desirable to produce high-quality Pd-NCs via simpler methods, particularly through environmentally friendly processes.^[35] Herein we report an alternating voltage induced electrochemical synthesis (AVIES) method, which allows for synthesizing well-dispersed, size-controlled, and single-crystalline colloidal Pd-NCs. This method involves only two Pd wires, a conventional transformer, and an electrolyte solution containing capping ligands. No special reducing agents are needed. It enables us to synthesize not only hydrophilic Pd-NCs, but also hydrophobic Pd-NCs. The reaction mechanism is unveiled to be a direct Pd-NC ejection off the Pd electrodes through cathodically reducing the PdO intermediates, which have been produced in the prior anodic half-cycles.

The concept of this AVIES method using aqueous solutions is demonstrated in **Figure 1**. A Variac transformer is connected to two Pd wires (0.5-mm in diameter) that are inserted in an electrolyte solution containing a common salt (e.g., NaCl) and capping ligands (e.g., polyvinylpyrrolidone (PVP), a hydrophilic polymer), **Figure 1A**. Then, as shown in

Figure 1B, an alternating voltage of 4 V and 60 Hz is applied to the two Pd electrodes through the transformer. Since the applied alternating voltage is zero-offset, the two Pd electrodes are electrochemically identical. Once the power is switched on, black flocculent substances start to diffuse away from both electrodes, accompanying vigorous bubbles of oxygen and hydrogen. The solution turns black after a few minutes (refer to Video S1 for more details). The solid products are purified through three cycles of centrifugation and water-washing, and can be re-dissolved in water, methanol, or ethanol for the subsequent characterization. More experimental details are discussed below as well as in the Supporting Information.

The synthetic reaction was first studied by ex-situ ultraviolet-visible absorption spectroscopy (UV-vis), shown in **Figure 2A** and **B** for the NaCl system. Once the reaction started, an absorption peak emerged at 276 nm, and its intensity proportionally increased with reaction time (**Figure 2** and **Figure S2**). In contrast, the purified solid products showed an absorption peak at 259 nm and a featureless absorption profile in the range of 300–700 nm (curve *i* in **Figure 2B**). The peak at 259 nm can be attributed to the metal-to-ligand charge transfer absorption between Pd and PVP.^[36,37] The remaining supernatant retained the peak at 276 nm (curve *ii*). A literature survey allowed us to assign this peak to the in-situ produced $[\text{PdCl}_{4-n}(\text{H}_2\text{O})_n]^{n-2}$ ions, which can also be generated from aging the Na_2PdCl_4 or K_2PdCl_4 aqueous solutions (curve *iii*).^[26,36,37]

The purified solid products were characterized and confirmed by transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), and X-Ray diffraction (XRD) to be Pd-NCs, shown in **Figures 2C–G**. The TEM images showed that the as-made Pd particles were well-dispersed nanospheres of 5 ± 1 nm in diameter and not dependent on the reaction time. The corresponding histograms of size-distributions are shown in **Figure S3**. This result is different from the synthetic methods of chemical reduction and thermal decomposition,^[26,27] but consistent with the electrochemical methods, where the sizes were controlled by the amplitudes of the applied voltages.^[30,33] The high-resolution TEM (HRTEM) image of a typical Pd-NC with clear lattice fringes throughout the entire NC, shown in the inset of **Figure 2F**, indicated the desired single-crystalline nature of the as-made Pd-NCs.^[19] The chemical compositions of the obtained Pd-NCs were determined by EDX (**Figure 2F**). The

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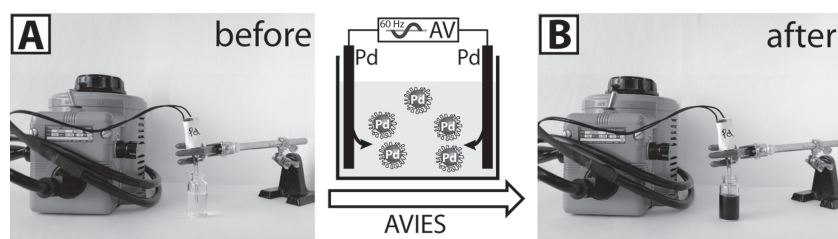


Figure 1. Illustration of the AVIES method for synthesizing colloidal Pd-NCs: (A) The state before turning on the Variac transformer; (B) the state after turning on the Variac transformer.

copper signal was from the TEM grid along with most of the carbon signal, and the rest of the carbon and the oxygen signal came from PVP. XRD data in Figure 2G confirmed that the products were face-centered-cubic (fcc) Pd-NCs.^[23,35] In order to tune the crystal sizes, we studied the effects of a series of experimental conditions and found that (**Figure 3** and **Figure S4**): a) the crystal sizes and the morphologies were also dependent to different extent on the concentration of PVP (10–50 mg/mL), the concentration of NaCl (3–6 M),

and the voltage in the range of 4–6 V (the reaction speeds were too slow at <3 V, and insoluble aggregates were dominant at >7 V); b) the natural pH at 3.4 for the NaCl solutions containing 30 mg/mL of PVP happened to be a good condition, the yield of Pd-NCs obtained at pH = 1.6 was very low, and the Pd-NCs obtained at pH = 11.4 were mostly fused aggregates.

The next step was to understand the reaction mechanism, i.e., how the Pd-NCs were formed. The in situ generation of the $[\text{PdCl}_{4-n}(\text{H}_2\text{O})_n]^{n-2}$ ions originating from hydrolysis of the PdCl_4^{2-} ions (**Figure 2B**) pointed to the possibility that Pd-NCs were produced through a cathodic reduction of the $[\text{PdCl}_{4-n}(\text{H}_2\text{O})_n]^{n-2}$ (or PdCl_4^{2-}) intermediates, which had been generated during the previous anodic processes. To prove or disprove this, we replaced NaCl with Na_2PdCl_4 and changed the alternating voltage to 1 V, which is low enough to avoid a direct etching of the Pd wires and high enough to produce Pd-NCs if the electrochemical process herein was comparable with that of a conventional three-electrode setup.^[33] However, no colloidal particles were generated. Furthermore, we changed the alternating voltage to a direct voltage. Again, we did not observe any colloidal particles. These results indicated that the $[\text{PdCl}_{4-n}(\text{H}_2\text{O})_n]^{n-2}$ (or PdCl_4^{2-}) ions cannot be the intermediates for generating Pd-NCs in the AVIES process, but simply the inherent byproducts.

To further understand the reaction mechanism, on the basis of a typical AVIES reaction (3 M NaCl and 30 mg/mL PVP), we replaced the alternating voltage with a 4-V direct voltage applied through a potentiostat and converted the single compartment to two compartments by inserting a porous membrane between the two Pd wires, **Figure 4A**. We observed brown colloidal substances along with oxygen bubbles over time in the anodic (+) compartment. In contrast, no changes could be observed in the cathodic (–) compartment, besides the expected evolution of hydrogen. The UV-vis absorption spectrum of the anodic compartment was the same as that of a typical AVIES reaction, whereas that of the cathodic compartment was the same as that of the blank solution (**Figure 4B**). XRD and TEM data in **Figure 4C** and **D** showed that the solid products collected from the anodic compartment were amorphous substances. The essential difference of the EDX spectrum in **Figure 4E**, in contrast to that of Pd-NCs in **Figure 2B**, was a much stronger signal of oxygen (the signal of Ni was assigned to impurities in the Cu

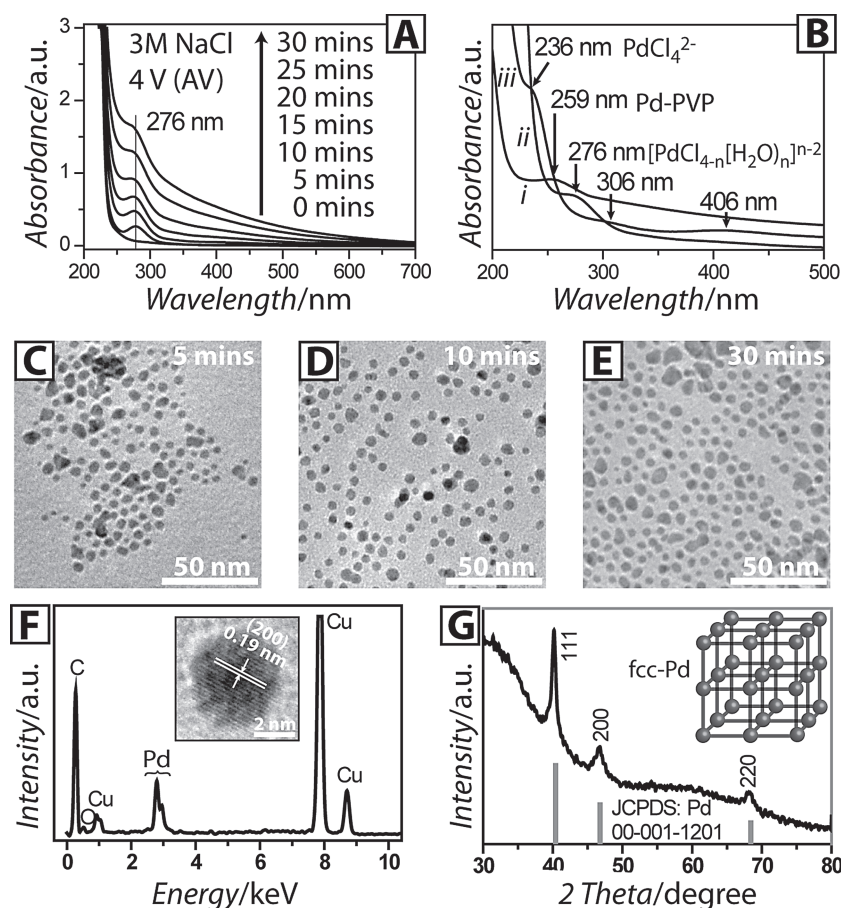


Figure 2. Studies of the AVIES reaction for synthesizing Pd-NCs using an alternating voltage of 4 V, 3 M NaCl, and 30 mg/mL of PVP. Unless otherwise specified, the reaction time was 30 min. (A) Time evolution of the UV-vis spectra. (B) Comparison of the UV-vis spectra of the purified Pd-NCs (i), the remaining supernatant (ii), and a freshly-made PdCl_4^{2-} solution (iii). (C) to (E) are the TEM images of the purified Pd-NCs obtained at the reaction times of 5 min, 10 min and 30 min, respectively. (F) The EDX spectrum of the obtained Pd-NCs and the HRTEM image of an exemplary Pd-NC. (G) XRD patterns of the synthesized Pd-NCs (red lines) and the face-centered cubic Pd standard (black sticks).

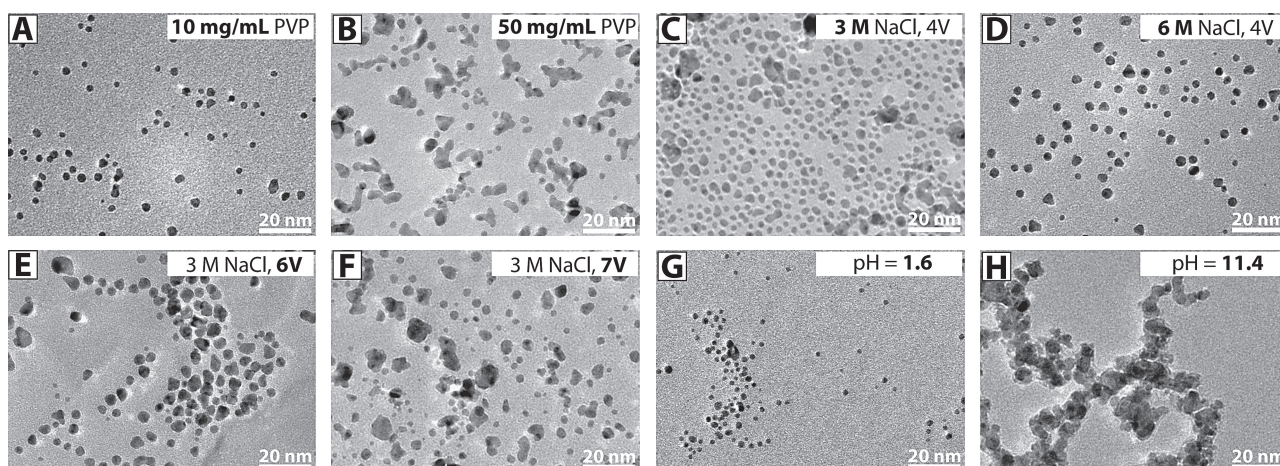


Figure 3. TEM images of Pd-NCs obtained by tuning one specific experimental condition versus the typical conditions for each image: (A) 10 mg/mL PVP; (B) 50 mg/mL PVP; (C) 3 M NaCl; (D) 6 M NaCl; (E) 6 V voltage; (F) 7 V voltage; (G) pH = 1.6; and (H) pH = 11.4.

TEM grid). Since the above-described amorphous substances were produced through an anodic process and it has been reported that Pd-NCs can be synthesized by cathodically reducing PdO nanoparticles,^[9] they were assigned to amorphous PdO. Therefore, we proposed the following reaction mechanism for our AVIES method: First, amorphous PdO nanoparticles were formed as a result of the anodic oxidation of the Pd atoms on the electrode surfaces and the electrochemical etching of the neighboring Pd atoms to form the water-soluble $[\text{PdCl}_{4-n}(\text{H}_2\text{O})_n]^{n-2}$ byproducts. Afterward, PdO

nanoparticles were reduced by electrons (or freshly-produced hydrogen atoms) during the subsequent cathodic processes to produce and release Pd-NCs.^[9] Last, PVP in the surrounding capped the nascent Pd-NCs and dispersed them into the bulk solution. Although PdO was amorphous in the mock study in Figure 4, the real PdO intermediates in the AVIES reactions were more likely to be crystalline; the verification research is underway.

With unveiling the above-determined synthetic mechanism, we inferred that this AVIES method should also be applicable to other electrolytes. Interestingly, we achieved not only well-dispersed Pd-NCs, but also size-control by using different alkali-metal halogenides. For example, smaller Pd-NCs of 1.4 ± 0.2 nm were produced from 3 M KI and larger Pd-NCs of 6 ± 1 nm from 3 M KBr, shown by the TEM and HRTEM images in **Figure 5** and Figure S5. The Pd-NCs made from 3 M NaBr (~ 4.0 nm), 3 M LiCl (~ 6.6 nm), 3 M LiBr (~ 6.6 nm), and 3 M KCl (~ 7.4 nm) solutions are shown in Figure S6. Although the mechanism of this electrolyte-dependent size-control is unclear for now, it may be associated with the different capabilities of these electrolytes in forming the PdCl_4^{2-} and/or the $[\text{PdCl}_{4-n}(\text{H}_2\text{O})_n]^{n-2}$ ions (Figure S7).^[26] In addition, methanol could also be used as the solvent to replace water for synthesizing PVP-passivated Pd-NCs, and the sizes were smaller than those from the water systems (Figure S8).

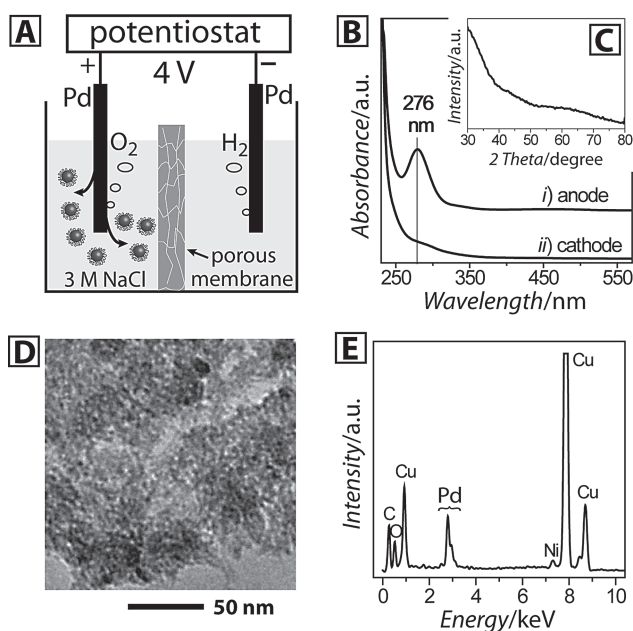


Figure 4. Mechanistic study of the AVIES method. (A) Scheme of the experimental setup by using a direct voltage provided by a potentiostat and two separate compartments created by a porous membrane. (B) UV-vis absorption spectra of the solutions from the anodic (+) compartment (i) and the cathodic (–) compartment (ii). (C) to (E) are the XRD pattern, TEM image, and EDX spectrum of the solid products collected from the anodic compartment, respectively.

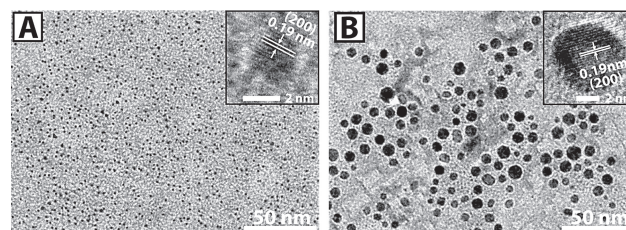


Figure 5. Size control of the Pd-NCs by tuning the electrolyte identities. (A) TEM image of the Pd-NCs (1.4 ± 0.2 nm) made from 3 M KI. (B) TEM image of the Pd-NCs (6 ± 1 nm) made from 3 M KBr.

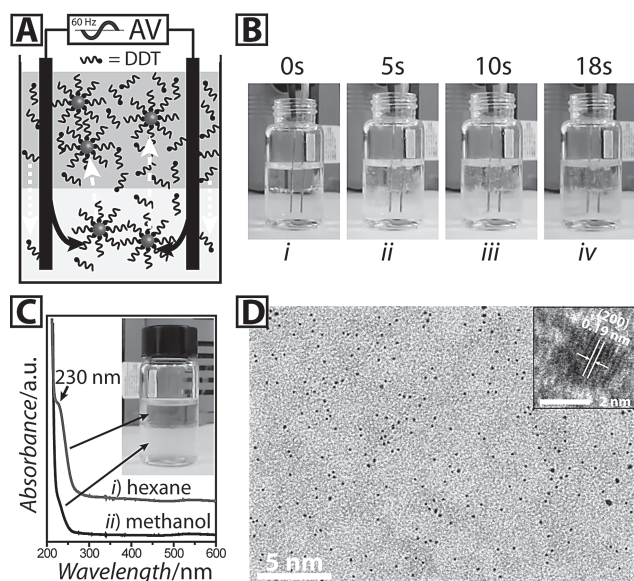


Figure 6. Demonstration of the two-phase AVIES method for directly synthesizing hydrophobic Pd-NCs. (A) Scheme showing how DDT-passivated Pd-NCs are first produced in the methanol phase (bottom) and then accumulated in the hexane phase (top). (B) A series of sequential optical images of the synthesis. (C) UV-vis absorption spectra of the methanol phase (i) and the hexane phase (ii). (D) TEM image of the obtained DDT-passivated Pd-NCs. The HRTEM image in the inset shows an exemplary single-crystalline Pd-NC.

Besides synthesizing the above-demonstrated hydrophilic Pd-NCs, we also produced hydrophobic Pd-NCs, which are preferred for some applications,^[11,38,39] by replacing the original ligands PVP with DDT (1-dodecanethiol) through a methanol/hexane two-phase ligand exchange process (Figure S9). The completeness of the ligand exchange was confirmed by Fourier transform infrared (FTIR) spectroscopy. The PVP-passivated Pd-NCs showed all the characteristic features of pure PVP.^[40] After the DDT treatment, only the characteristic features of DDT were detectable, where the disappearance of the ν_{S-H} signal confirmed the formation of the Pd-S bonds.^[41,42]

While the above-described ligand exchange process is widely used to produce hydrophobic Pd-NCs, a direct synthesis is more desirable.^[43,44] However, this poses a challenge to the AVIES method, because dissolving electrolytes requires polar solvents and dissolving hydrophobic ligands needs non-polar solvents. To mitigate this problem, we developed a two-phase AVIES method, using methanol to dissolve the electrolytes (such as NaBr) and hexane to dissolve the ligands (such as DDT), **Figure 6**. Interestingly, the Pd-NCs were formed in the methanol phase (bottom) and then spontaneously accumulated in the hexane phase (top), because of the poor solubility of DDT in methanol. The depletion of DDT in the methanol phase, due to the formation of DDT-passivated Pd-NCs, resulted in a continuous diffusion of DDT from the hexane phase to the methanol phase (Figure 6A). This process is highlighted in Figure 6B by a series of sequential optical images of the synthesis, particularly by the fact that the yellow color surrounding the two Pd wires in panel b is much stronger than the solution body (refer to Video S2 for

more details). After a simple shaking, the produced Pd-NCs diffused into the hexane phase, which was confirmed by the featureless absorption spectrum of the methanol phase and the metal-to-ligand charge transfer absorption peak at 230 nm for the hexane phase (Figure 6C).^[36,37] The fact that the PdBr_4^{2-} ions were not observed in this reaction, different from the aqueous-phase AVIES reactions,^[26] may be due to the poor solubility of the PdBr_4^{2-} ions in methanol. This result indicated that the PdBr_4^{2-} ions herein were not the intermediates for producing the Pd-NCs, and consistent with our above-proposed reaction mechanism for the aqueous-phase AVIES method. The obtained Pd-NCs were narrowly-dispersed, single-crystalline nanospheres in the range of 1.6 ± 0.3 nm (Figure 6D and Figure S10). In addition, other electrolytes (such as LiBr and LiCl) and capping ligands (such as hexanethiol (HT) and octadecanethiol (ODT)) could also be used. More importantly, a post-synthesis purification may be avoidable for this two-phase AVIES method, due to its inherent capability of self-purification, if the added ligands can be fully consumed and the selected electrolyte has negligible solubility in the hexane phase.

Our preliminary data showed that this simple AVIES method could also be generalized to other metals, such as Au and Ag (Figure S11). The well-dispersed Au-NCs of 17 ± 2 nm in diameter and Ag-NCs of 2.0 ± 0.7 nm in diameter were synthesized by using 2.7 M KNO_3 solutions, 4 V voltages, and 30 min of reaction time.

In summary, we have demonstrated a simple method for synthesizing well-dispersed, size-controlled (1–7 nm in diameter), and single-crystalline colloidal Pd-NCs. This method is definitely adoptable by any research lab, since it requires neither expensive Pd compounds nor specialized equipment. It can also be easily scaled up by using Pd electrodes of larger surface areas and better-designed electrochemical cells. The obtained Pd-NCs can be either hydrophilic or hydrophobic, depending on the employed capping ligands. The mechanistic study has showed that the Pd-NCs are directly released from the Pd electrodes through a cathodic reduction of the PdO intermediates, which have been generated in the preceding anodic processes. Moreover, this generality of this method has been successfully demonstrated to other metals such as Au and Ag. The future work will be to expand this method to bimetallic alloys, control NC shapes and study the catalytic applications of the synthesized NCs.

Experimental Section

Synthesis of Pd-NCs through the Single-Phase AVIES Method:

Two Pd wires (diameter = 0.5 mm and length = 4 cm) were connected to a Variac transformer and inserted into a 5 mL of aqueous solution that contained a supporting electrolyte (the identity and concentration are stated specifically at appropriate places, such as 3 M NaCl) and a polymer stabilizer PVP (30 mg/mL). Once the transformer was turned on, typically at 4–5 V, vigorous bubbles (a mixture of oxygen and hydrogen) and black flocculent substances started to diffuse away out from both wires. Ex-situ UV-vis spectroscopy was used to monitor the reaction. After 10–30 min, the reaction solution turned dark. The black solid products were

purified through three times of centrifugation at 14.6×10^3 rpm for 30–60 min (on a Legend 14 centrifuge), using nanopure water as the washing/dispersing solvent. The products were then dispersed in water, methanol or ethanol, for further characterization such as XRD and TEM. This AVIES method can also use methanol instead of water as the solvent for those electrolytes that have high solubility in methanol, such as NaBr, LiBr, and LiCl.

Synthesis of Pd-NCs through the Two-Phase AVIES Method: Here we use NaBr and 1-dodecanethiol (DDT) as examples to describe the experimental details. First, a 2 mL of 1M NaBr solution in methanol (75% of the saturation concentration), 2 mL of hexane, and 0.5 mL of DDT were mixed in a 6-mL vial. Then, two Pd wires were submerged in both phases of hexane and methanol. Afterward, an alternating voltage of 4 V was applied to the two Pd wires through a Variac transformer. Consequently, Pd-NCs were formed in the methanol phase (indicated by the strong yellow color) and then diffused into the hexane phase. Other electrolytes (such as LiBr and LiCl) and other thiols (such as 1-hexanethiol HT and 1-octadecanethiol ODT) also worked for this two-phase AVIES method.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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