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Influence of Hydrogen on the Morphology of Platinum and Palladium Nanocrystals

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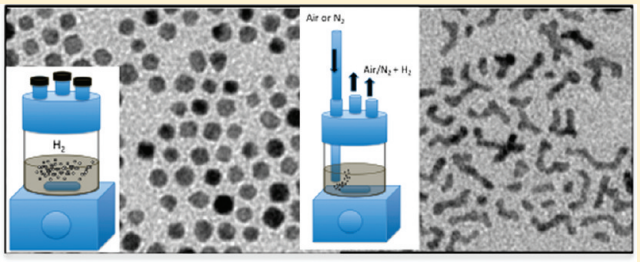
ABSTRACT: Palladium and platinum nanocrystals are synthesized by the liquid−liquid phase transfer method, which is a suitable way to produce anisotropic metallic nanoparticles and control their shape at the nanoscopic scale. The process leading to shape control is, however, quite complex as all the physical and chemical parameters could play an important role. In this paper, we have demonstrated the primordial role of the dissolved gases (O_2, H_2, N_2) in the solvent medium on the nanomorphology of platinum and palladium nanocrystals. In particular, it shows the specific role of H_2 in the formation of platinum nanocubes.



1. INTRODUCTION

Inorganic nanocrystals (NCs), especially the metal ones, are widely studied and used in chemical, biological, and physical devices. Understanding their properties and exploring their application are two major driving forces behind the synthesis of a large variety of nanomaterials.[1] As many of these properties are related to the surface of the NCs, efforts are underway to develop an understanding of how the shape of a nanoparticles influences its properties. In the last two decades, a large number of groups have developed new strategies to produce nanomaterials using the soft chemical route. Over the years, various methods of synthesis have been proposed. Among these, the phase transfer method developed by Brust et al.[2] is one of the main soft chemical routes to produce metallic nanoparticles on a large scale.[3−5] This method involves the transfer of the metal ion from a polar phase to a nonpolar phase using a transferring agent, followed by reduction in the emulsion of the metals complex.

The choice of platinum and palladium relates to their important role in chemistry: In catalysis, platinum is the most frequently used metal nowadays, but natural resources are scarce and there is a general need to minimize the use of this expensive metal. Both platinum and palladium NCs are excellent catalysts in synthetic organic chemistry[6,7] and many other applications such as environmental catalysis.[8,9] Both metals are also anticipated to be hydrogen storage media for hydrogen fuel cells.[10,11] For this, the size of the NCs has to be rather small, and the coating agent has to be efficient enough to prevent coalescence and weak enough not to interact too much with the nanoparticle surface. Furthermore, the crystallinity and shape of the nanoparticles can have a strong influence on the catalytic activity. Hence, larger efficiency of cubic platinum NCs in the fuel cells due to the highest efficiency of the {100} facets has been reported.[12] It is usually claimed that shape control is due to poisoning specific crystalline facets during the crystalline growth.[13,14] Particularly, the role of Br^- was mentioned in the formation of cubic metallic nanoparticles.[15−17] More recently, the influence of CO on the shape control of metallic nanocrystals has been reported.[14,18] Thus, gases could control the shape of the nanocrystals. We show here that, even if Br^- could play a role, other parameters are predominant in shape control. Here, we will examine the influence of environmental conditions, mainly the role of the dissolved gases (O_2, H_2, N_2) in the solvent medium on the shape of platinum and palladium NCs made by the wet chemistry route. This shows the specific role of H_2 on the nanomorphology of platinum and palladium.

2. EXPERIMENTAL PROCEDURES

Pd and Pt nanocrystals are synthesized by the phase transfer synthesis method presented by Brust et al.[2] Typically, it consists of metal ion transfer from an aqueous phase to an organic phase using an extractant molecule. The nanocrystals are obtained by chemical reduction.

2.1. Preparation of the Metallic Salt Solution. Aqueous solutions of 0.05 M $PtCl_4$ and $PdCl_2$ were prepared by dissolving the metallic salt in acid media to form the complexes H_2PtCl_6 and H_2PdCl_4.[19,20] These aqueous solutions were then mixed with 2×10^{-2} M tridecylammonium bromide (TDAB) dispersed in 80 cm^3 of toluene. To ensure maximum transfer of metal ions from the water phase to the organic phase, the transferring agent (TDAB) was present in large excess (corresponding to TDAB:$PtCl_4$/$PdCl_2$ = 2.5:1). The two-phase mixture was vigorously stirred until all the metallic complexes were transferred into the organic phase (30 min). The colorless water phase is then discarded.

2.2. Chemical Reduction of the Metallic Salt. *Procedure I: Reduction in the Presence of Capping Agent (Figure 1A).* 6.52×10^{-3} mol of dodecylamine ($C_{12}NH_2$) Capping Agent (CA) is added under stirring to 20 cm^3 of the obtained organic solution

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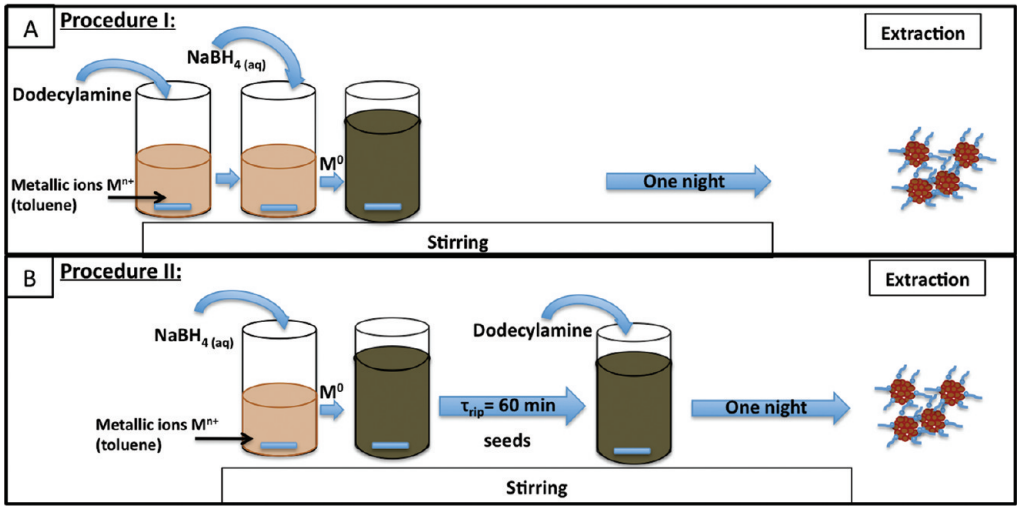

Figure 1. Schematic description of the two procedures used to synthesized metallic nanoparticles. For procedure I, the capping agent is added before the reducing agent (A), whereas in procedure II, the capping agent is added one hour after the addition of the reducing agent (B).

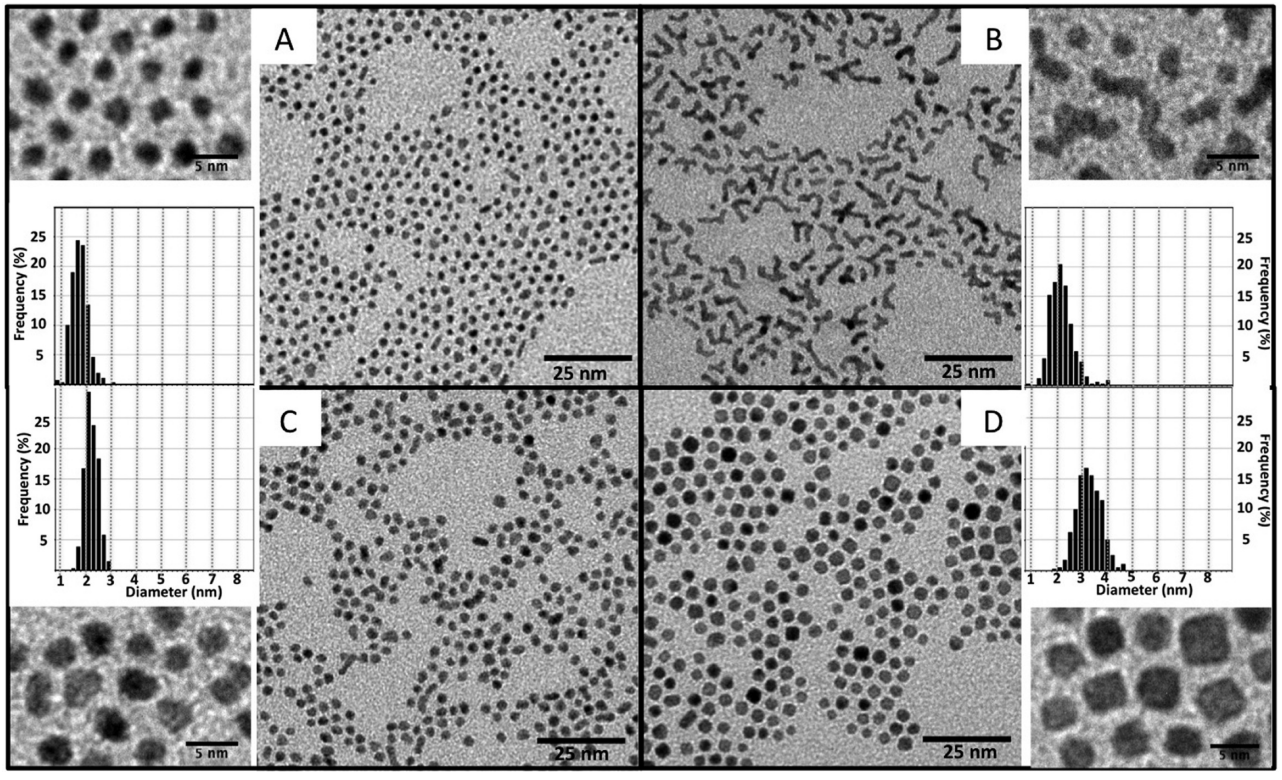

Figure 2. Pt nanocrystals obtained after extraction and redispersion in toluene. Pt nanocrystals produced in open air under oxygen flow from procedure I (A) or procedure II (B) and Pt nanocrystals produced under hydrogen (glovebox) from procedure I (C) or procedure II (D). Higher TEM magnification and corresponding size distributions are presented in insets.

containing the metallic complexes. A freshly prepared aqueous solution of $NaBH_4$ (10 cm^3, 0.4 $mol{\cdot}L^{-1}$) is dropwise added under stirring, yielding an emulsion. This induces the reduction of the metallic salt at the interface of the organic and aqueous phases. Both the reducing agent and the capping agent are added in large stoichiometric excess relative to the palladium/platinum ($NaBH_4$:Pd/Pt = 17:1 and CA:Pd/Pt = 22:1). The emulsion turns relatively rapidly from orange to dark brown. The reaction takes place for one night, after which the stirring is turned off and the organic phase, containing the metal nanoparticles, is collected and evaporated using a Rotavapor. The black paste obtained is then washed with 40 cm^3 of ethanol. Then, the turbid solution is centrifuged and the supernatant is discarded. This operation is repeated twice. After the last centrifugation, the precipitate is redispersed in 4 cm^3 of toluene. The final solution contains the coated $C_{12}NH_2$ nanoparticles in toluene.

Procedure II: Reduction Followed by the Addition of Capping Agent (Figure 1B). In this case, the freshly prepared aqueous solution of $NaBH_4$ (10 cm^3, 0.4 $mol{\cdot}L^{-1}$) is dropwise added under stirring to 20 cm^3 of the organic solution containing the metallic complexes. The reduction occurs in the emulsion phase, at the interface of the organic and aqueous phases, which results in a color change from orange to dark brown. After 60 min (ripening time τ_{rip}), 6.52 × 10^{-3} mol of dodecylamine ($C_{12}NH_2$) capping agent is then added. The chemical

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Table 1. Size and Size Distribution of Extracted Pt and Pd NCs Obtained from Procedure I and Procedure II in the Presence of O_2 and H_2

	Pt		Pd	
	Air	H_2	Air	H_2
Proc I	1.8 ± 0.3 nm	2.3 ± 0.3 nm	1.9 ± 0.3 nm	3.0 ± 0.4 nm
Proc II	1.8 ± 0.3 nm	3.2 ± 0.5 nm	5.2 ± 0.9 nm	2.4 ± 0.5 nm

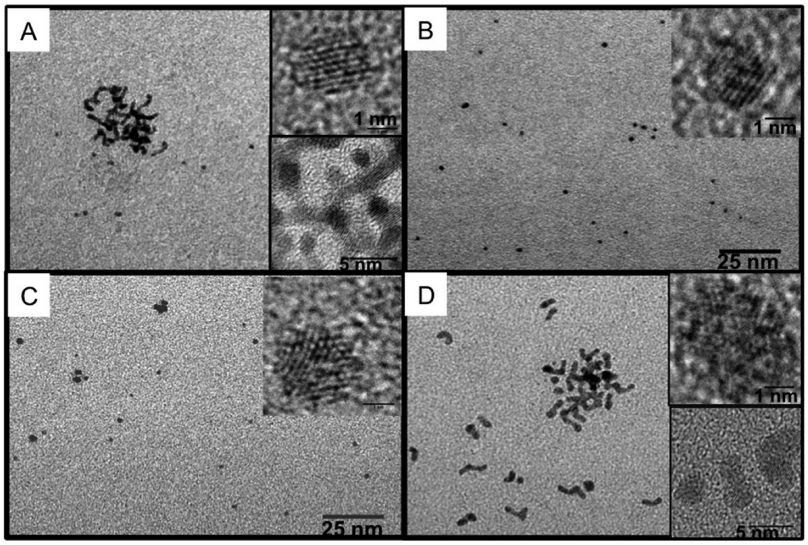

Figure 3. TEM and High Resolution TEM of seeds obtained after one hour of reduction, just before the addition of the capping agent. Pt seeds obtained in open air under oxygen flow (A) and under Hydrogen (glovebox) (B) and Pd seeds obtained in open air under oxygen flow (C) and under Hydrogen (glovebox) (D).

bath is kept under stirring for one night, then the nanocrystals are extracted following the procedure described above. The final solution contains the coated $C_{12}NH_2$-nanoparticles in toluene.

2.3. Environmental Effect. The synthesis of Pt/Pd NCs has been performed either under oxygen (air flow) or in the absence of oxygen (in a glovebox), under hydrogen atmosphere or under N_2 flow. In this last case, degassed solutions are used.

Hydrogen is naturally produced by the chemical reduction. To perform the reaction under saturated H_2 atmosphere, a closed screw cap with three ports is used and the reducing and capping agents are injected through a silicone septum. In order to see the influence of hydrogen atmosphere on the nanoparticles, we performed the same syntheses with open screw cap and by bubbling N_2 into the chemical bath, during and after the reduction, to drive out the hydrogen formed. The same procedure is used for oxygen except that the syntheses are made in open air under air flow.

3. RESULTS AND DISCUSSION

Reducing metallic salt by $NaBH_4$ is a well-known method to produce hydrogen. The borohydride ion spontaneously hydrolyzes in aqueous solution to give hydrogen as follows:

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2$$

This reaction is rather slow in pure water;[21] however, the presence of metal salts can catalyze or participate in this decomposition yielding the formation of metallic particles.[22] This last process is considerably faster.[21] The chemistry of the borohydride reduction of metal ions has been found to be quite complex, and the nature of the products depends on the experimental conditions,[23] but in any case, H_2 is one of the products of the reaction. Indeed, there are at least 4 mol of H_2 formed from 1 mol of $NaBH_4$, which in turn could produce, in a closed vessel, a high pressure of hydrogen.[24] It is known that H_2 strongly interacts with noble metal as platinum and palladium. This is one of the driving forces of their use in catalysis and notably for fuel cells.[10,11] Thus, we must ask ourselves about the influence of H_2, produced during the reaction, on the structure of the metallic NCs formed from colloidal chemistry (shape, size, and so forth). For that, we develop a synthetic procedure, which allows us to focus on the role of the dissolved gas on the morphology of platinum and palladium NCs. It has been previously reported that synthesis of cubic platinum NCs could not be achieved from colloidal systems in the open air.[16] Continuously bubbling air (i.e., 20% of O_2) or nitrogen (under glovebox) in the chemical bath, using an open vessel, allows us to drive out the hydrogen formed during the reaction and then to compare the role of these two gases. In a second step, operating under nitrogen glovebox and working with degassed solutions in closed vessels allows us to investigate, by comparison, the specific role of H_2.

3.1. Synthesis of Platinum NCs in Open Air. Metallic nanocrystals can be synthesized considering two procedures (Figure 1): the capping agent (dodecylamine $C_{12}NH_2$) is added either before (procedure I, Figure 1A) or one hour after (i.e., the ripening step) the addition of the reducing agent (procedure II, Figure 1B). Figure 2 shows the coated Pt NCs obtained after extraction and their redispersion in toluene. They are synthesized in open air under oxygen flow. Faceted Pt NCs characterized by a diameter of 1.8 ± 0.3 nm are obtained from procedure I (Figure 2A and inset; Table1). Differently, in procedure II, where the capping agent is added one hour after the reduction, wormlike particles having the same cross-sectional diameter of 1.8 ± 0.3 nm are observed (Figure 2B, Table1). This is surprising, because in the liquid−liquid phase transfer synthesis, adding the capping agent after the reducing

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agent usually leads to larger spherical NCs.[25] This observation shows that, during the ripening time (one hour), no condensation growth occurs, but rather a growth by aggregation of the 1.8 nm nanoparticles. This indicates that the initial seeds are limited in growth but can aggregate to form wormlike structure having the same lateral size. Such behavior has already been observed for Pt nanoparticles synthesized in open air in other colloidal systems such as reverse micelles.[19] To confirm this assumption, TEM and HRTEM have been carried out on the seed obtained from procedure II, just before the addition of the capping agent $C_{12}NH_2$ (Figure 3). In this case, a drop of solution is taken directly from the chemical bath and deposited on a TEM grid. Figure 3A shows that both isolated faceted and wormlike Pt nanoparticles are observed. HRTEM (inset Figure 3A) clearly confirms that wormlike particles are composed of aggregated nanocrystals, which are characterized by an FCC structure and are similar to the isolated one. It confirms also that this aggregation appears during the ripening step. Thus, adding the capping agent only allows stabilization of the wormlike structure, which can be extracted. In procedure I, the capping agent is added prior to the reducing agent, so that the initial growth of the seeds occurs in the presence of the capping agent, which in turn prevents the aggregation, yielding isolated quasi-spherical nanocrystals (Figure 2A). Clearly, the order of addition of reagents plays an important role in controlling shape.

3.2. Synthesis under Nitrogen Atmosphere: The Role of Hydrogen and Nitrogen. Similar syntheses of Pt NCs are performed in the absence of oxygen, under hydrogen atmosphere. If the reducing agent is added before (procedure I), the Pt nanoparticles obtained are similar, but somewhat larger (2.3 ± 0.3 nm) than under oxygen (Figure 2C, Table 1). The effect of hydrogen is, however, greatly evidenced in procedure II as instead worms, cubic NCs of 3.2 ± 0.5 nm (Figure 2D, Table 1), are obtained. Different from what is observed under oxygen, larger particles are obtained from procedure II as expected (see above), but now the shape is strongly modified. In procedure II, the growth of the NCs results from condensation of the atoms on the first seeds; usually, this yields quasi-spherical NCs. Formation of cubic NCs, in an isotropic liquid medium, could only be understood if some species interact with the initial fcc-crystallized seeds to direct a selective growth of the (111) facets and prevent the growth of the (100) facets. In the literature, it is often claimed that Br^- leads to cubic nanomorphology through its adsorption on the (100) faces.[15,17,26] In our case, Br^- is always present in the chemical bath regardless of the dissolved gas used, but cubes are only observed under H_2 atmosphere. Then, the exclusive role of this ion on the nanomorphology control of the Pt nanoparticles can be excluded. In addition, Peng et al., in a recent monograph, report different liquid synthesis leading to the formation of cubic platinum nanoparticles. It appears that many of them involve the presence of H_2.[27] Indeed, platinum cubes can be obtained without the presence of Br^- but never in the absence of H_2. Different from synthesis under O_2 flow, the TEM and HRTEM made on the seeds deposited after one hour of reduction (i.e., just before adding the capping agent) show the formation of only small, isolated faceted particles well-crystallized in an FCC structure (Figure 3B and insets). This means that the aggregation is inhibited through the stabilization of the nanoparticles. At this step, no dodecylamine is present in solution, but only ions (such as Br^-) and/or the dissolved gas (H_2). Compared with the same synthesis in open air, under a permanent flow of O_2 the only change in the chemical bath is the dissolved gas. The absence of worms through the stabilization of nanoparticles could then be attributed to the presence of H_2, which adsorbs at the metallic surface of the fcc platinum seed. It is well-known that H_2 adsorbs spontaneously and strongly to the Pt surfaces.[28,29] Its affinity for the Pt surface is higher than O_2.[30] Thus, isolated well-crystallized Pt FCC seeds are present in solution (Figure 3B) and can grow slowly, after the adding of the dodecylamine and prior to the extraction from the chemical bath 16 h after (Figure 1B). This growth occurs in the presence of Br^- and dodecylamine under high-pressure H_2, yielding platinum nanocubes. At this step, the system behaves like a microemulsion, where TDAB and dodecylamine form the interface. It has been previously demonstrated that long chain alkylamine ($n \geq 14$) stays at the interface making the palisade layer static as compared to the palisade layer formed with the short chain alkylamines.[19] This effect is analogous to the one seen for other surfactant systems, where the lifetime of the colloidal aggregate has been found to depend on the length of an added co-surfactant.[31] A more dynamic interface will favor the growth of the initial seeds either by transport of new platinum−TDA complexes from the bulk toluene phase into the interface of the water droplets, where they release platinum to the growing nanoparticle,[19] or by the condensation of the monomer Pt^0. Thus, decreasing the lifetime of the capping agent into the palisade layer in the chemical bath favors homogeneous growth of the NCs prior to their extraction. Indeed, decreasing the adsorption of dodecylamine, which is only weakly bound to the platinum surfaces,[32] will decrease the lifetimes of the capping agent at the interfaces and thus favors the controlled growth of the FCC seeds yielding nanocubes. It has been reported that the presence of adsorbed H_2 excess on a platinum surface increases the mobility of NH_2 at surfaces (i.e., decreases the lifetime at the surfaces).[23] Thus, in our case, where a large amount of H_2 is present, we can assume a decrease of the lifetime of dodecylamine at the interface compared to synthesis under O_2 flow.

In procedure I, the coating agent is present prior to the reduction (Figure 1A). During the reduction, Pt^0 atoms and H_2 will be produced simultaneously in the presence of amine, and then a competition between H_2 and dodecylamine adsorptions at the metallic surface arises. Different from synthesis under O_2 flow, the larger size obtained under H_2 shows that the capping agent does not block the growth of the nanoparticles. This confirms the assumption made above that the interface between $C_{12}NH_2$ and the metallic surface under H_2 is more dynamic than in the open air and/or that the affinity of H_2 is strong enough to desorb the dodecylamine and then allows the NCs to continue their growth before the extraction.

Thus, H_2 plays a double role in the growth: first, it protects initial seeds from the aggregation (Figure 3B); and second, by decreasing the adsorption of the capping agent, it favors controlled growth on (111) facets in the presence of the capping agent and Br^-, yielding the cubic shape. To confirm the specific role of H_2, similar investigations have been undertaken, in a glovebox with degassed solution, but under N_2 flow in open vessels, to drive out the H_2 formed during the reaction. Figure 4A shows that, in this case, procedure II yields wormlike structure similar to that obtained in open air, under O_2 flow: no specific shape as cubes is obtained. HRTEM and TEM show the seeds prior to the addition of capping agent (Figure 4B and insets). Again, they are similar to that obtained under O_2 flow in open air. Thus, N_2 cannot protect the seeds from

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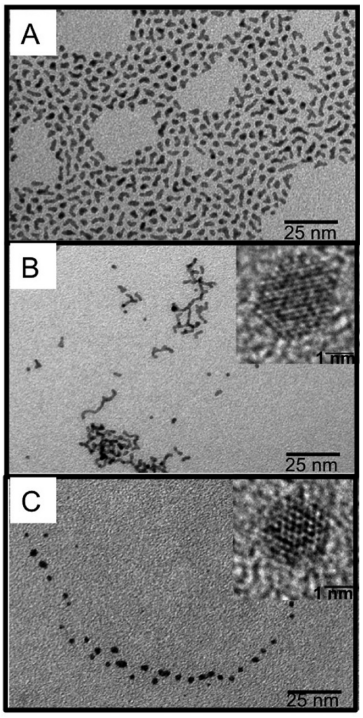

Figure 4. Nanocrystals produced under nitrogen flow (under glovebox) from procedure II. TEM images of Pt nanocrytals obtained after extraction (A). The Pt (B) and Pd (C) seeds obtained before the addition of capping agent and their HRTEM in inserts.

aggregation, and finally, wormlike structures are obtained at the end of the reaction. This confirms the specific role of hydrogen in the control of nanomorphology of platinum NCs. We cannot exclude a kinetic effect on the morphology of the metal nanoparticles, as the reduction rate of the metal can vary in the presence of H_2. However, the reduction step is fast (at the minute scale), compared to the growth process, which takes place in 16 h (after addition of the capping agent). In fact, the growth kinetics is complex and is always an open field. As an example, the final size of the nanocrystals strongly depends on the aging time before the extraction. Furthermore, preliminary in situ investigation of the growth process by X-ray scattering measurements indicates the presence of O_2 in the solution, totally inhibiting the growth process after addition of the capping agent, when under H_2 it takes places in 16 h leading to the cubic shape.[33] This confirms the predominant role of H_2 in the growth of the platinum nanocubes.

3.3. Case of Palladium Nanocrystals. As for platinum, palladium is often used in catalysis even in combination with platinum. They belong to the same chemical group, but their behavior differs especially concerning the interaction with H_2. Contrary to platinum, palladium can not only adsorb, but also absorb large quantities of hydrogen. In fact, H_2 can dissociate at surfaces, and then atomic H can diffuse into the lattices to form hydrides, PdH_x.[34] This occurs at a pressure lower than 1 bar and at room temperature. It has been recently reported that, when the size of the Pd particle approaches the nanometric scale, the probability of forming Pd-hydrides increases compared to the bulk state. This is due to the high specific surface area in the case of the nanoparticle. Indeed, the presence of H_2 changes the structure of the surface, which is no longer metallic and becomes amorphous.[35] Thus, as the shape control and the growth process in liquid−liquid phase transfer synthesis is strongly dependent on binding of the capping agent on the metallic surfaces (see above), we can expect different behavior in the case of palladium as the anchoring of the capping agent depends on the state of the surfaces.

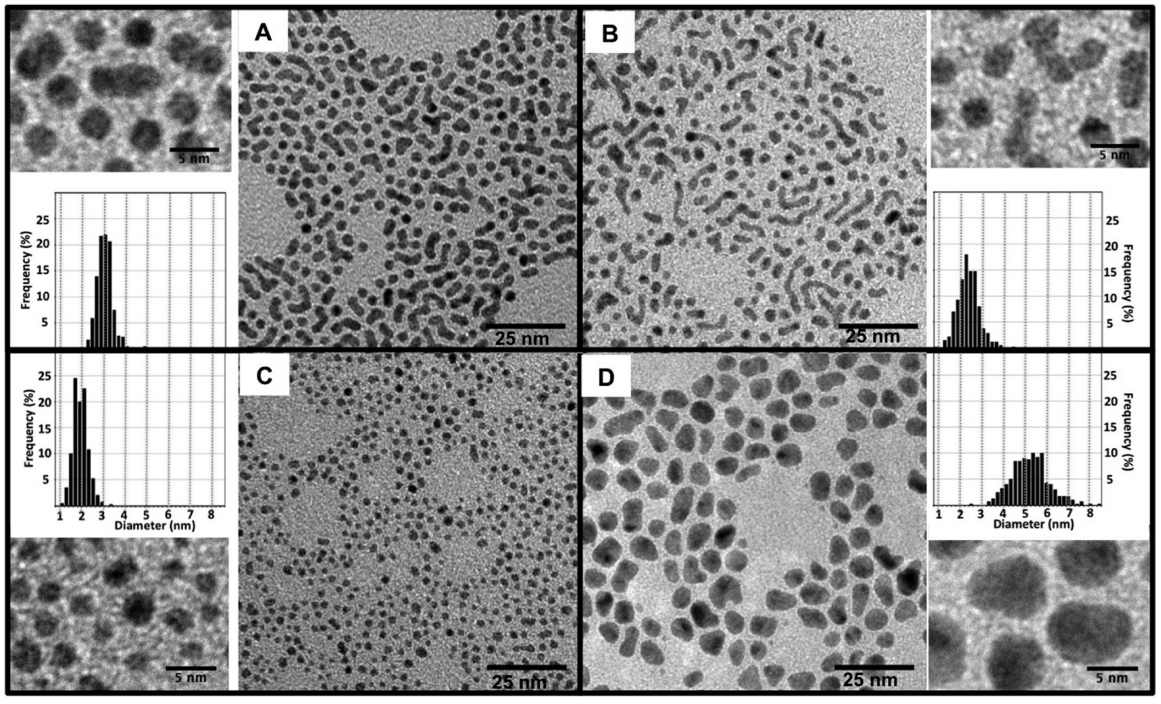

Figure 5. Pd nanocrystals obtained after extraction and redispersion in toluene. Pd nanocrystals produced in open air under oxygen flow for procedure I (A) or for procedure II (B) and Pd nanocrystals produced under hydrogen (glovebox) for procedure I (C) or for procedure II (D). Higher TEM magnification and corresponding size distributions are presented in insets.

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Figure 5 shows the coated Pd NCs after extraction and redispersion in toluene. They are obtained in a glovebox under hydrogen for procedure I (Figure 1A) and procedure II (Figure 1B). Spherical particles with a few short worms, characterized by diameter and/or cross-sectional diameter of 3.0 ± 0.4 nm, are observed from procedure I (Figure 5A). Similar morphologies are obtained from procedure II, but particles are characterized by a lower size (2.4 ± 0.5 nm) instead of a larger expected, as the capping agent is added 1 h after the reducing agent (Figure 5B, Table 1). Different from the case of platinum, no specific shape is observed. The seeds, observed at the end of the ripening step without capping agent, are mainly wormlike (Figure 3D) and the HRTEM (insert Figure 3D) shows a crystallized FCC core with an amorphous shell. As explained above, this amorphization of the surfaces could be due to H_2 absorption, leading to palladium hydride. It is not due to the nature of the materials, as the same experiments made under O_2 flow (Figure 3C) or N_2 flow (Figure 4C) show that the seed are perfectly crystallized without this core−shell structure.

It is known that self-assembled monolayers could only be obtained on well-crystallized surfaces. Thus, in our case as the surface of nanoparticles is amorphous, the capping layer should present numerous defects and/or its binding with the surface (hydride) differs from that of pure metal. As a consequence, dodecylamine layer cannot protect efficiently from aggregation. This yields wormlike structures coexisting with spherical ones, whatever the synthetic procedure is.

Surprisingly, the characteristic size decreases in procedure II compared to procedure I. Again, this is probably an effect of hydrogen absorption. Here, as the coating agent is added 1 h after the reducing agent, the seeds of palladium are exposed to high pressure of H_2, which yields formation of hydride.[34,35] This effect is even more important as the size decreases.[35] Thus, this change in the surface could inhibit the growth by condensation of Pd^0 on the seed. However, as the dodecylamine is only weakly bound to the surfaces, it cannot prevent aggregation of palladium hydride NCs. In this case, the growth process is similar to what has been observed for platinum in open air (Figure 2B). For procedure I, the coating agent is present prior to the reduction (Figure 1A). Hence, there is competition between H_2 and dodecylamine: to form hydride, hydrogen must first desorb the dodecylamine, but this process is not blocked by the capping layer.[34] This is due to weak interaction of the amine group with the metallic surfaces. Thus, in this case, dodecylamine partly passivates the surfaces allowing the NCs to grow by condensation and/or aggregation. This delayed effect of H_2, due to the presence of the capping agent, could then explain the larger size obtained from this procedure.

Synthesis in open air, under O_2 flow, confirms the role of capping molecules on the growth process (Figure 5C). By using procedure I, only spherical nanocrystals similar to that obtained for platinum with the same procedure are obtained. Here, dodecylamine, added before the reducing agent, protects the seed from further growth. There is no specific action of H_2, which is contuously being driven out by O_2, so the size and shape are similar for palladium and platinum (Table 1). Palladium obtained by procedure II in open air (i.e., under O_2 flow) (Figure 5D) is, however, strongly different compared to platinum. Large (5.2 ± 0.3 nm, Table 1) and unshaped palladium NCs are collected after extraction. This strong increase in size, compared to procedure I, is what is usually expected by using the liquid−liquid phase transfer method and observed in the case of gold NCs.[25] This shows that, different from the case of platinum, where worms are obtained by aggregation of spherical seeds (see above), the palladium seed can grow continuously by condensation of Pd^0 on stable nuclei. This difference of behavior also indicates that the binding of dodecylamine with platinum is probably stronger than the binding of dodecylamine with palladium. This could be due to the nature of the metal and/or to the influence of oxygen on the anchoring of the dodecylamine. As a matter of fact, Figure 3C shows that, prior to the addition of dodecylamine, only isolated spherical NCs are obtained for palladium, different from the case of platinum where wormlike structures are observed (Figure 3A). Hence, growth occurs on isolated spherical seeds yielding larger NCs.

4. CONCLUSION

In summary, properly designed wet chemical synthesis, even in liquid isotropic solutions, offers a suitable way to produce anisotropic metallic nanoparticles and to control their shape at the nanoscopic scale. We have demonstrated the complexity of this process under several chemical conditions, where all the parameters could play an important role. Different from what is often reported, shape control of colloidally synthesized metallic NCs is not only due to the poisoning facets of crystalline seeds by halide such as Br^-. We have demonstrated the primordial role of the dissolved gases issued either from air or as a byproduct of the reaction, which may strongly influence the shape of the NC. Indeed, they can perturb the dynamics of the capping layer at NC surfaces and also the nature of the metallic surfaces. This illustrates the complexity of the control of nanomorphology, as it needs fine-tuning of these various physicochemical parameters to establish a general framework of anisotropic growth of metallic nanoparticles in solution. Finally, it is demonstrated that platinum nanocubes are obtained only if H_2 is present in solution.

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Notes

The authors declare no competing financial interest.

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