

# Surfactant-Induced Postsynthetic Modulation of Pd Nanoparticle Crystallinity

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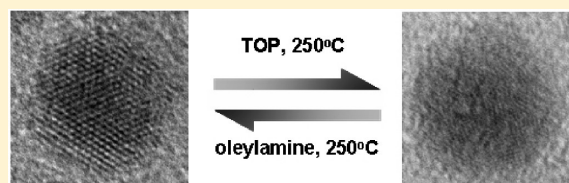
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 Supporting Information

**ABSTRACT:** Modulation of Pd nanoparticle (NP) crystallinity is achieved by switching the surfactants of different binding strengths. Pd NPs synthesized in the presence of weak binding surfactants such as oleylamine possess polyhedral shapes and a polycrystalline nature. When oleylamine is substituted by trioctylphosphine, a much stronger binding surfactant, the particles become spherical and their crystallinity decreases significantly. Moreover, the Pd NPs reconvert their polycrystalline structure when the surfactant is switched back to oleylamine. Through control experiments and molecular

dynamics simulation, we propose that this unusual nanocrystallinity transition induced by surfactant exchange was resulted from a counterbalance between the surfactant binding energy and the nanocrystal adhesive energy. The findings represent a novel postsynthetic approach to tailoring the structure and corresponding functional performance of nanomaterials.

**KEYWORDS:** Palladium nanoparticle, surfactant exchange, nanoparticle structure, crystallinity modulation



A wide range of nanomaterials are prepared by solution phase synthesis today. On the basis of the nanocrystal nucleation and growth from a homogeneous solution of the precursors, solution processing usually possesses the advantages of well control over particle size, shape, composition, and surface properties.<sup>1–3</sup> Among various factors governing the NP growth in solution phase,<sup>2</sup> surfactants that bind to and coat on the NP surface play a particularly important role. It is known that surfactants stabilize the NPs in solution and restrict their size in growth. Their binding selectivity on different crystal facets can also govern the anisotropic growth of NPs into various shapes such as cube,<sup>4,5</sup> rod,<sup>6–9</sup> and wire.<sup>10,11</sup> Moreover, the surfactants anchored on the surface to a large extent define the surface properties of the obtained NPs and thus have to be taken into account in further functionalization of such nanomaterials.<sup>12,13</sup> For example, ligand exchange, i.e., replacing the existing surfactant by another type, has been shown to be critical for self-assembly<sup>14,15</sup> and biomedical applications.<sup>16–18</sup> For most catalytic applications, however, surfactants have to be removed so that the inorganic surface of NPs can be exposed to reactants.<sup>19–22</sup> All of these indicate that further insights into the interplay between surfactants and NP surface are desired to acquire comprehensive understanding of NP surface chemistry and to optimize NP properties and performance for various applications.

Here we report the postsynthetic structure modulation of metallic Pd NPs induced by surfactant replacement. Pd NPs synthesized with oleylamine (OAm) as surfactant have a polyhedral

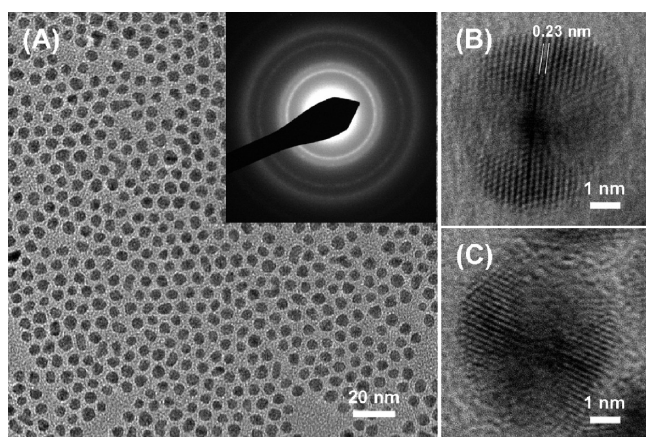
shape and a polycrystalline structure. When oleylamine is substituted by trioctylphosphine (TOP), a much stronger surfactant binding to Pd,<sup>23</sup> the NP shape is changed to near-spherical with NP crystalline size substantially reduced. The polycrystalline nature of the Pd NPs is further found to be recovered when the Pd–TOP NPs are aged in an OAm solution. After various control experiments and molecular dynamic simulations, we believe this unusual surfactant enabled modulation of NP crystallinity arises from a counterbalance between the surfactant binding energy and nanocrystal adhesive energy. Although surface-induced nanostructure transitions have been reported before, they have been limited only to metal oxides (e.g., ZrO<sub>2</sub>)<sup>24</sup> and IIB/VIA semiconductors such as ZnS.<sup>25–27</sup> To the best of our knowledge, there has been no report on such a modulation in metallic NPs.

The synthesis of polycrystalline Pd NPs with OAm as the surfactant (denoted as Pd–OAm1) was modified from a previously reported procedure.<sup>28</sup> Pd(II) acetylacetonate was dissolved in OAm at room temperature and then heated to 60 °C when a morpholine borane (MB) complex in OAm solution was injected to initiate the nucleation. Immediately after MB injection, the heating temperature was raised to 90 °C for NP growth and kept at this temperature for 0.5 h to obtain Pd–OAm1 NPs (see the Supporting Information for details). Figure 1A shows a representative transmission electron microscopy (TEM) image of the

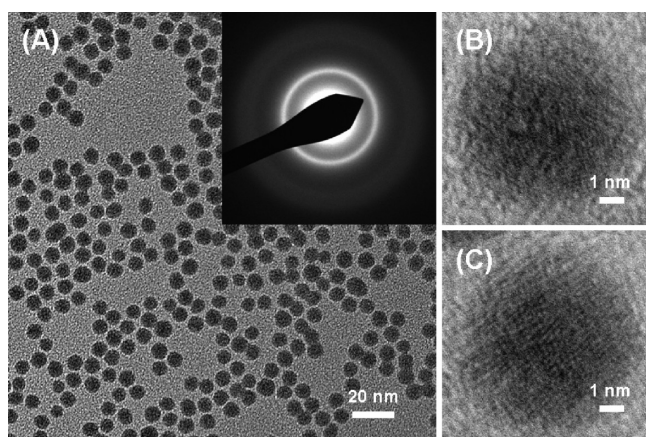
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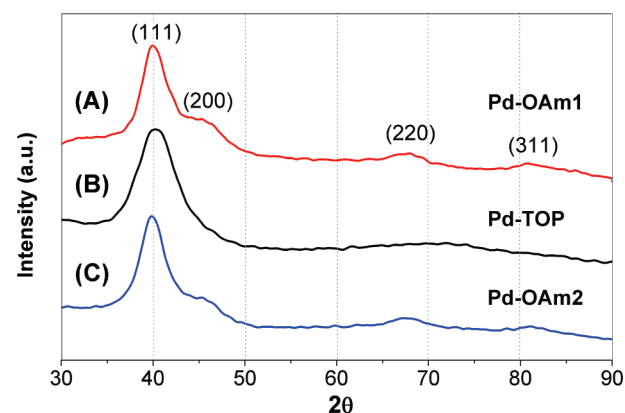
**Figure 1.** (A) TEM image and SAED pattern (inset). (B) and (C) HRTEM images of the as prepared 6.3 nm Pd–OAm1 NPs.



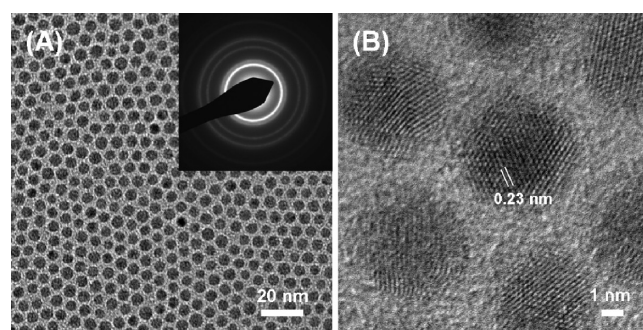
**Figure 2.** (A) TEM image and SAED pattern (inset). (B) and (C) HRTEM images of the as prepared 7.1 nm Pd–TOP NPs.

as-synthesized monodisperse  $6.3 \pm 0.6$  nm Pd–OAm1 NPs (Figure S1A, Supporting Information). A high-resolution TEM (HRTEM) study shows that the NPs have a polycrystalline structure (panels B and C of Figure 1). The lattice fringe was measured to be 0.23 nm, close to the spacing of the (111) planes in face centered cubic (fcc) Pd (0.223 nm). Selected area electron diffraction (SAED) pattern (inset in Figure 1A) shows four diffused rings, which can be assigned to the diffractions from (111), (200), (220), and (311) planes of an fcc Pd phase. The polycrystalline nature of the as-synthesized Pd–OAm1 NPs is consistent with the results from a previous study.<sup>28</sup>

Tuning of the NP crystallinity was achieved by replacing OAm with TOP as the surfactant. After the growth of Pd NPs in oleylamine at 90 °C, TOP was added to the solution in situ. The solution temperature was then raised to 250 °C and kept at this temperature for 1 h. The Pd NPs separated from this TOP treatment (Pd–TOP) were checked by energy-dispersive X-ray spectroscopy (EDS) after washing with ethanol. The observation of phosphorus (P) and a Pd/P atomic ratio of 84/16 indicated the accomplishment of surfactant exchange (Figure S2A, Supporting Information). The Pd–TOP NPs have a nearly spherical shape, and their size is increased to  $7.1 \pm 0.6$  nm (Figure 2A and Figure S1B (Supporting Information)). HRTEM images (panels B and C of Figure 2) show a nanostructure with reduced crystallinity in comparison with the Pd–OAm1 NPs. The SAED



**Figure 3.** XRD patterns of (A) Pd–OAm1 NPs, (B) Pd–TOP NPs, and (C) Pd–OAm2 NPs.



**Figure 4.** (A) TEM image and SAED pattern (inset). (B) HRTEM image of the as prepared 5.9 nm Pd–OAm2 NPs.

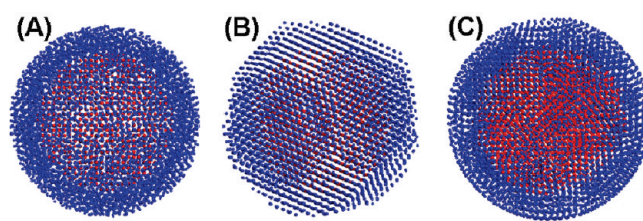
pattern (inset of Figure 2A) shows only the fuzzy (111) ring. The reduced crystallinity in Pd–TOP NPs was further characterized by X-ray diffraction (XRD) patterns (Figure 3). The Pd–OAm1 NPs gave four characteristic diffraction peaks corresponding to (111), (200), (220), and (311) of fcc Pd, while Pd–TOP NPs show only one broader (111) peak. The increase in (111) peak width and the disappearance of the other high-angle diffraction peaks confirm that the crystalline domains in the Pd–TOP NPs became much smaller after the surfactant exchange.

Interestingly, the above structure change can be reversed when TOP is replaced again by OAm. This was done by heating the Pd–TOP NPs in an OAm solution at 250 °C (the obtained NPs were denoted as Pd–OAm2). Though TOP binds more strongly to Pd than OAm, partial replacement of TOP by OAm on the particle surface still occurred in the OAm-rich environment at the elevated temperature, as confirmed by elemental analysis of the Pd–OAm2 NPs. EDS analyses show that the Pd/P atomic ratio was changed from 84/16 for Pd–TOP to 93/7 for Pd–OAm2 NPs (Figure S2A,B, Supporting Information). Figure 4A shows the TEM image of the Pd–OAm2 NPs. They are still in near spherical shape as in Pd–TOP NPs but their size is slightly reduced to  $5.9 \pm 0.5$  nm (Figure S1C, Supporting Information). The HRTEM image (Figure 4B) shows the clear lattice fringes of fcc Pd (111) planes. XRD also confirms the higher crystallinity of Pd–OAm2 NPs than Pd–TOP NPs, where four diffraction peaks are observed. The crystal domain size calculated from the line broadening of (111) peak based on Scherrer's equation was 2.9 nm for Pd–OAm2, close to the value (2.7 nm) for Pd–OAm1 and much larger than that (2.0 nm) for Pd–TOP NPs.



The observed crystallinity change upon surfactant exchange between TOP and OAm seems to indicate that the chemical nature of the surfactant has an effect on the NP structure and crystallinity. While the detailed mechanism remains elusive, several factors were first recognized to be critical for attaining the postsynthetic modulation of NP crystallinity in solution. At first, TOP is essential for reducing the Pd NP crystallinity. Without TOP, heating the Pd–OAm1 NPs in OAm at 250 °C (for 1 h) resulted in particle aggregation and increase in crystalline domain sizes (Figures S3 and S4, Supporting Information). This elevated temperature (~250 °C) also seems to be crucial for the structure change. If the Pd–OAm1 NPs were treated with TOP at 90 °C, no dramatic change was observed in particle size, shape, or crystallinity (Figures S3 and S5, Supporting Information). This could be due to the incomplete surfactant exchange at this temperature, as revealed by a higher Pd/P atomic ratio of 96/4 determined by EDS analysis (Figure S2C, Supporting Information). This indicates that the NPs treated at 90 °C have less P than the Pd–TOP NPs (84/16) obtained at 250 °C. Furthermore, the replacement of TOP by OAm can be identified as the key for the reversion from disordered (Pd–TOP) to polycrystalline (Pd–OAm2) NPs. When the ligand exchange was blocked by the presence of extra TOP in the solution, the reversion process was hindered and small crystalline domains remained in the Pd NPs even after aging at 300 °C for 1 h (Figures S3 and S6, Supporting Information). It is also noticed that the Pd NPs show significant volume changes during the treatments, with +43.1% from Pd–OAm1 to Pd–TOP and –42.6% from Pd–TOP to Pd–OAm2. This is likely to be mainly caused by the crystallinity changes despite other possible factors like the different synthetic conditions. It is reasonable to believe that the Pd–TOP NPs with reduced crystallinity contain a large number of defects (such as vacancy) in the particles, which might cause the substantial volumetric expansion.

Qualitative understanding of the NP crystallinity modulation was further provided by molecular dynamics simulation using the open source software Lammmps distributed by Sandia National Laboratories.<sup>29</sup> The embedded atom method potential<sup>30</sup> for Pd was applied. All simulations were performed using NVT ensemble (or canonical ensemble, the number of atoms ( $N$ ), volume of the system ( $V$ ), and the system temperature ( $T$ ) are kept constant) integration in Lammmps at 600 K. A constant time step of 1 fs was used. We first heated the 5 nm particle to a high temperature (e.g., 3000 K) and then cooled it quickly to 600 K, to establish an initial amorphous state of the particle as shown in Figure 5A. By relaxing the amorphous particle in vacuum for 2 ns, we could see that the particle crystallized (Figure 5B), implying the preferential crystallization of Pd NPs in the absence of surfactants or in the presence of a weak surfactant. However, if we applied a spherical potential wall on the particle in order to mimic the confinement introduced by the strong surfactant,<sup>23,25</sup> we found that the potential wall exerted a surface tension on the amorphous particle, and the crystallization tendency of atoms was suppressed. The particle remained amorphous after the same relaxation (2 ns), as shown in Figure 5C. Considering that the confinement effect by surfactant was likely to be determined by the binding energy between the surfactant and particle surface atoms, the observed reversible modulation of NP crystallinity is thus postulated to have resulted from the interplay of the surfactant binding energy and the crystal adhesive energy in the NPs.<sup>31</sup>



**Figure 5.** (A) Initial amorphous 5 nm Pd NP (blue, atoms at the 1 nm surface layer; red, inner atoms). (B) Crystallization of the amorphous Pd particle in vacuum. (C) The Pd particle remained to be amorphous if the particle was confined by surface tension.

The results from the control experiments and simulation reinforced that the binding strength of surfactants plays a key role in determining the crystallinity of Pd NPs, which could be potentially utilized to control the structure and properties of the solution processed NPs. Our preliminary studies show that the Pd NPs have distinct magnetic properties when different surfactants are present on the surface, with Pd–OAm1 being ferromagnetic and Pd–TOP paramagnetic at 5 K (Figure S7, Supporting Information).<sup>32</sup> The research thus opens a new direction for postsynthetic modulation of nanostructures and their functional performance.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Additional figures and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ REFERENCES

- (1) Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A. *Chem. Rev.* **2005**, *105*, 1025–1102.
- (2) Cushing, B. L.; Kolesnichenko, V. L.; O'Connor, C. J. *Chem. Rev.* **2004**, *104*, 3893–3946.
- (3) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545–610.
- (4) Sun, Y. G.; Xia, Y. N. *Science* **2002**, *298*, 2176–2179.
- (5) Wang, C.; Daimon, H.; Lee, Y.; Kim, J.; Sun, S. J. *Am. Chem. Soc.* **2007**, *129*, 6974–6975.
- (6) Peng, X.; Manna, L.; Yang, W.; Wickham, J.; Scher, E.; Kadavanchi, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59–61.
- (7) Gao, J. X.; Bender, C. M.; Murphy, C. J. *Langmuir* **2003**, *19*, 9065–9070.
- (8) Liu, Y.; Peng, S.; Ding, Y.; Rong, C.; Kim, J.; Liu, J. P.; Wang, Z. L.; Sun, S. *Adv. Funct. Mater.* **2009**, *19*, 3146–3150.
- (9) Yin, Y.; Alivisatos, A. P. *Nature* **2005**, *437*, 664–670.

- (10) Sun, Y. G.; Gates, B.; Mayers, B.; Xia, Y. N. *Nano Lett.* **2002**, *2*, 165–168.
- (11) Wang, C.; Hu, Y. J.; Lieber, C. M.; Sun, S. J. *Am. Chem. Soc.* **2008**, *130*, 8902–8903.
- (12) Litran, R.; Sampedro, B.; Rojas, T. C.; Multigner, M.; Sanchez-Lopez, J. C.; Crespo, P.; Lopez-Cartes, C.; Garcia, M. A.; Hernando, A.; Fernandez, A. *Phys. Rev. B* **2006**, *73*, No. 054404.
- (13) Garitaonandia, J. S.; Insausti, M.; Goikolea, E.; Suzuki, M.; Cashion, J. D.; Kawamura, N.; Ohsawa, H.; de Muro, I. G.; Suzuki, K.; Plazaola, F.; Rojo, T. *Nano Lett.* **2008**, *8*, 661–667.
- (14) Park, S. Y.; Lytton-Jean, A. K. R.; Lee, B.; Weigand, S.; Schatz, G. C.; Mirkin, C. A. *Nature* **2008**, *451*, 553–556.
- (15) Grzelczak, M.; Vermant, J.; Furst, E. M.; Liz-Marzan, L. M. *ACS Nano* **2010**, *4*, 3591–3605.
- (16) Choi, H. S.; Liu, W.; Misra, P.; Tanaka, E.; Zimmer, J. P.; Ipe, B. I.; Bawendi, M. G.; Frangioni, J. V. *Nat. Biotechnol.* **2007**, *25*, 1165–1170.
- (17) Cheng, K.; Peng, S.; Xu, C. J.; Sun, S. J. *Am. Chem. Soc.* **2009**, *131*, 10637–10644.
- (18) Yavuz, M. S.; Cheng, Y. Y.; Chen, J. Y.; Cobley, C. M.; Zhang, Q.; Rycenga, M.; Xie, J. W.; Kim, C.; Song, K. H.; Schwartz, A. G.; Wang, L. H. V.; Xia, Y. N. *Nat. Mater.* **2009**, *8*, 935–939.
- (19) Wang, C.; Wang, G. F.; van der Vliet, D.; Chang, K. C.; Markovic, N. M.; Stamenkovic, V. R. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6933–6939.
- (20) Wang, C.; van der Vliet, D.; Chang, K. C.; You, H. D.; Strmcnik, D.; Schluter, J. A.; Markovic, N. M.; Stamenkovic, V. R. *J. Phys. Chem. C* **2009**, *113*, 19365–19368.
- (21) Chen, J. Y.; Lim, B.; Lee, E. P.; Xia, Y. N. *Nano Today* **2009**, *4*, 81–95.
- (22) Peng, Z. M.; Yang, H. *Nano Today* **2009**, *4*, 143–164.
- (23) Yang, Z.; Klabunde, K. J. *J. Organomet. Chem.* **2009**, *694*, 1016–1021.
- (24) Kirsch, B. L.; Riley, A. E.; Gross, A. F.; Tolbert, S. H. *Langmuir* **2004**, *20*, 11247–11254.
- (25) Zhang, H. Z.; Gilbert, B.; Huang, F.; Banfield, J. F. *Nature* **2003**, *424*, 1025–1029.
- (26) Gilbert, B.; Huang, F.; Lin, Z.; Goodell, C.; Zhang, H.; Banfield, J. F. *Nano Lett.* **2006**, *6*, 605–610.
- (27) Epifani, M.; Pellicer, E.; Arbiol, J.; Sergeant, N.; Pacnier, T.; Morante, J. R. *Langmuir* **2008**, *24*, 11182–11188.
- (28) Mazumder, V.; Sun, S. J. *Am. Chem. Soc.* **2009**, *131*, 4588–4589.
- (29) Plimpton, S. J. *Comput. Phys.* **1995**, *117*, 1–19.
- (30) Foiles, S. M.; Baskes, M. I.; Daw, M. S. *Phys. Rev. B* **1986**, *33*, 7983–7991.
- (31) Wang, C.; Tian, W.; Ding, Y.; Ma, Y.-q.; Wang, Z. L.; Markovic, N. M.; Stamenkovic, V. R.; Daimon, H.; Sun, S. J. *Am. Chem. Soc.* **2010**, *132*, 6524–6529.
- (32) Bulk Pd itself is paramagnetic. However, in the form of NPs with organic ligands present on the surface, Pd NPs can possess ferromagnetic properties due to charge transfer from Pd to the ligands (ref 12). It is interesting that, unlike that reported before, the Pd-TOP NPs in this study did not show ferromagnetic behavior, which might be correlated to their highly disordered crystal nature and presence of amorphous layers on the surface (See, for example: Shinohara, T.; et al. *Phys. Rev. Lett.* **2003**, *91*, No. 197201). It might also be possible that the Pd-TOP NPs are superparamagnetic, but the anisotropy is so low that thermal fluctuations overcome the anisotropy to make the magnetization appear paramagnetic.