Nanoparticle Catalysis

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The Origin of Shape Sensitivity in Palladium-Catalyzed Suzuki–Miyaura Cross Coupling Reactions**

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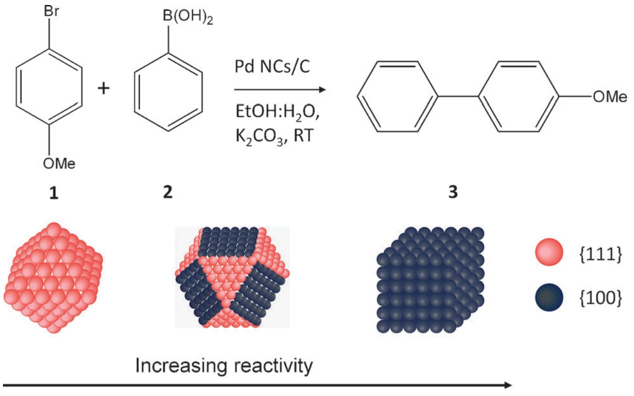
Abstract: *The shape sensitivity of Pd catalysts in Suzuki–Miyaura coupling reactions is studied using nanocrystals enclosed by well-defined surface facets. The catalytic performance of Pd nanocrystals with cubic, cuboctahedral and octahedral morphologies are compared. Superior catalytic reactivity is observed for Pd NCs with {100} surface facets compared to {111} facets. The origin of the enhanced reactivity associated with a cubic morphology is related to the leaching susceptibility of the nanocrystals. Molecular oxygen plays a key role in facilitating the leaching of Pd atoms from the surface of the nanocrystals. The interaction of O_2 with Pd is itself facet-dependent, which in turn gives rise to more efficient leaching from {100} facets, compared to {111} facets under the reaction conditions.*

The Suzuki–Miyaura reaction is a highly utilized reaction for aryl–aryl bond formation in organic synthesis due to its synthetic versatility.[1] The use of heterogeneous catalysts in Suzuki–Miyaura coupling is particularly appealing as it allows for ligand-free methodologies and facilitates easy purification and metal recovery.[2] The exquisite control of size and shape dispersion possible in solution-based colloidal synthesis has attracted much interest in studying the structure sensitivity of reactions catalyzed by noble metal nanocrystals (NCs).[3] The origin of shape sensitivity in Suzuki–Miyaura coupling is controversial and is further challenged by the debate concerning the heterogeneous or homogeneous nature of the reaction mechanism. El-Sayed et al.[4] demonstrated that tetrahedral Pt NCs catalyzed the cross coupling of phenylboronic acid and iodobenzene, while the use of spherical Pt nanoparticles gave no conversion. They attributed the difference in reactivity to the sharp edges of the tetrahedral particles. Pd NCs with high-index surface facets have displayed enhanced reactivity compared to low-index facets.[5] However, NCs with high-index surfaces are more susceptible to leaching and the higher activity may simply reflect greater dissolution of active molecular Pd.[6] Several studies demonstrate that NC-catalyzed Suzuki coupling reactions proceed via a homogeneous mechanism, where the particle serves as a source of soluble Pd that is leached from the surface.[7] Conversely, strong evidence for surface-mediated catalytic processes are also reported, such as spatially controlled coupling reactions using a Pd-coated AFM probe[8] and in situ X-ray absorption studies,[9] which identify edge and corner atoms as the active sites. Recently, Pd-supported carbon nanotubes were found to be resistant to leaching under Suzuki–Miyaura conditions but changes to the nanoparticle surface structure and chemistry were observed.[10] The existence of multiple reaction pathways in Suzuki–Miyaura coupling implies that the role of leached Pd must also be evaluated to fully understand the effect of NC shape on catalytic reactivity.

Cubic Pd NCs displaying {100} surface facets, octahedral NCs enclosed by {111} facets, and cuboctahedral NCs with 6 {100} and 8 {111} surface facets having a shape consistency of nearly 100 %, were prepared as illustrated in Scheme 1.[3c] The NCs were comparable in diameter (ca. 20 nm) and supported on activated carbon (see Supporting Information Figures S1–S3). The catalytic properties of the polyhedra were compared in the Suzuki–Miyaura coupling of 4-bromoanisole (**1**) and phenylboronic acid (**2**) in ethanol/H_2O (3:1), with K_2CO_3 as the base at room temperature, as depicted in Scheme 1.



Scheme 1. Model Suzuki–Miyaura reaction and Pd nanocrystal catalysts used in this study.

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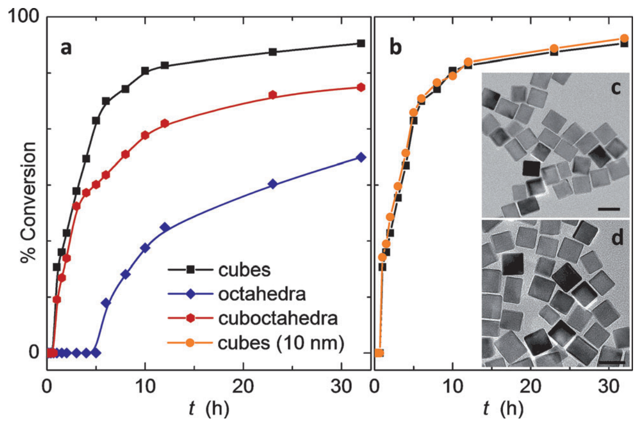

Figure 1. a) Structure sensitivity of Suzuki–Miyaura coupling of **1** and **2** over cubic, cuboctahedral, and octahedral Pd NCs. b) Reaction profile of 20 nm and 10 nm cubic NCs where the total surface Pd atoms were equivalent. c) TEM image of 10 nm and d) 20 nm cubic Pd NCs. Scale bar = 20 nm.

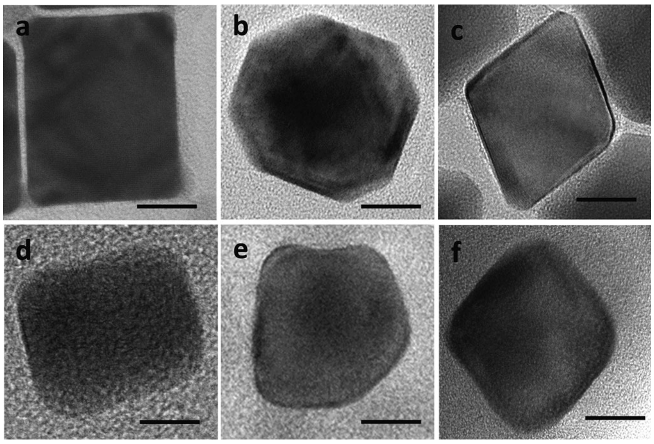

Figure 2. Pd NCs in the form of a) cubic b) cuboctahedral, c) octahedral before reaction, and d) cubic, e) cuboctahedral f) octahedral, after reaction. Scale bar = 10 nm.

Figure 1 illustrates the catalyzed reaction profile of 4-bromoanisole (**1**) with phenylboronic acid (**2**), showing that all of the nanoparticle polyhedra were active in generating the coupled product 4-methoxybiphenyl (**3**). A marked enhancement in the catalytic reactivity was observed for the cubic NCs. In the first 300 min, conversion with the cubic Pd NCs reached 76 %, while no conversion was observed for octahedral NCs over the same time period. The final yield of the coupled product (**3**) obtained with cubic NCs was 94 %, compared to 58 % for octahedral NCs. Cuboctahedral NCs displayed an initial reaction profile similar to the cubic NCs, but a decrease in reactivity was observed after 250 min, giving a final yield of 78 %. Previous reports suggest that reactivity is associated with edge and corner sites, either through surface reaction[11] or by leaching of these low-coordinated atoms.[12] Cubic NCs possess the least amount of surface and edge atoms compared to cuboctahedra and octahedral NCs (Table S1). After normalization to either the number of surface atoms or edge atoms, the reactivity trend in our system follows cube > cuboctahedra > octahedral NCs, suggesting that the shape-dependent reactivity is directly associated with the presence of the Pd{100} surface facet. To further investigate the facet effect on the coupling of **1** and **2**, we used 10 nm cubic NCs, which possess 0.4 % edge and corner atoms, compared to just 0.16 % for 20 nm cubes. The TEM inset in Figure 1 b shows the excellent reproducibility and length control of the cubic NCs synthesized in this study. When the concentration of Pd was adjusted, such that the total number of surface Pd atoms was equivalent, the reaction profiles for both the 10 nm and 20 nm cubes were almost identical, as shown in Figure 1 b. This observation suggests that the reactivity is not solely associated with the density of edge and corner site densities, but advocates a shape-dependent reactivity and a surface facet effect. Coupling of 4-iodoanisole showed the same reactivity trend with respect to the NC shape that is, cubic > cuboctahedra > octahedra (Figure S4).

TEM analysis of the catalysts after the reaction revealed that the average size of the NCs was maintained but a clear loss of the well-defined facets was observed with all polyhedra, as seen by comparison of Figure 2 a–c before the reaction, with Figure 2 d–f after reaction (also see Figures S5–S7). Reference samples stirred in EtOH/H_2O solvent showed no variations in morphology. Changes to NC morphology can indicate leaching, which was further assessed by inductively coupled plasma mass spectrometry (ICP-MS). Pd was detected in the filtrate of all polyhedra after the reaction, as summarized in Table 1.

Table 1: ICP-MS analysis of reaction filtrates.

Sample[a]	[Pd] [ppb]	Sample	[Pd] [ppb]
cubic^{Air}	1008	*cubes:*	–
cuboctahedra	663	K_2CO_3 + PhB(OH)$_2$	658
octahedra	324	$MeOC_6H_4Br$	69
cubic^{Ar}	96[b]	*octahedra:*	–
cuboctahedra^{Ar}	79[b]	K_2CO_3 + PhB(OH)$_2$	106
octahedra^{Ar}	81[b]	$MeOC_6H_4Br$	51

[a] Samples normalized to 5 wt % HCl. Average of 3 samples. [b] Catalyst degassed under vacuum before addition to reaction solution previously deoxygenated with Ar.

Pd concentrations in the reaction filtrate were higher for cubic NCs (1.08 ppm) compared to octahedral NCs (0.66 ppm), suggesting that the origin of the structure-dependent reactivity may be due to preferential leaching from the {100} surface. The presence of O_2 in the reaction has also been shown to result in greater Pd leaching compared to reactions in inert atmosphere.[13] ICP analysis (Table 1) shows that the presence of O_2 promotes Pd leaching and is influenced by the NC shape. In the presence of O_2, leached Pd concentrations correlate directly with catalytic activity, increasing from octahedral < cuboctahedra < cubic NCs. In control experiments without dissolved O_2 (deoxygenated with Ar), the amount of Pd in the filtrates was lower and similar for all polyhedra (ca. 80 ppb), implying Pd leaching is shape sensitive at least under aerobic conditions. Additional ICP analysis of the NCs was undertaken to identify the primary species responsible for leaching and also to determine if a specific reagent gave rise to preferential leaching on a particular surface facet.

Much debate concerns the nature of the species responsible for leaching Pd. Oxidative addition of the aryl halide is often reported to be the primary mechanism for leaching,[14] while other studies demonstrate the boronic acid and base to be responsible.[7a,15] Under our reaction system, the use of ICP analysis identified the base and boronic acid as the primary leaching reagents, however the aryl bromide also contributed to a lesser degree. Significantly, the base and boronic acid induced greater leaching from the cubic NCs compared to octahedral NCs, suggesting the {100} surface is more susceptible to leaching than {111} surfaces.

ICP analysis identified O_2 as a promoter of leaching and this observation led us to explore the impact of O_2 on the catalytic activity and to determine if the leached Pd contributed to the catalytic activity in the reaction. The influence of adsorbed O_2 and the role of dissolved O_2 during the reaction were investigated by comparing the reactivity of the NCs immobilized (Imb) and reacted (Rx) under air or Ar. The reaction profiles are compared in Figure 3a and show that the Air^{Imb}-Air^{Rx} catalysts exhibited the fastest reaction, giving a 96% conversion after 28 h. The Air^{Imb}-Ar^{Rx} catalysts displayed similar initial profiles but the reaction became progressively slower as it progressed, resulting in a final yield of 62%. This finding confirms that dissolved O_2 promotes catalytic activity, which in turn contributes to greater leaching as determined by ICP. The Ar^{Imb}-Air^{Rx} catalytic system displayed an induction period nearly 4 times longer than that of Air^{Imb}-Air^{Rx}, with the yield decreasing to 50%, indicating that the presence of chemisorbed O_2, as well as dissolved O_2 is beneficial for catalytic activity. Finally and quite remarkably, the Ar^{Imb}-Ar^{Rx} catalytic system did not show any conversion after 28 h. Leaching concentrations also correlated with reactivity, with the filtrates under the Air^{Imb}-Air^{Rx} having the highest Pd concentrations, while low amounts of Pd were detected in the filtered solutions of the Ar^{Imb}-Ar^{Rx} samples (Table S2). Reaction profiles using 4-iodoanisole also displayed the same reactivity trend (Figure S8).

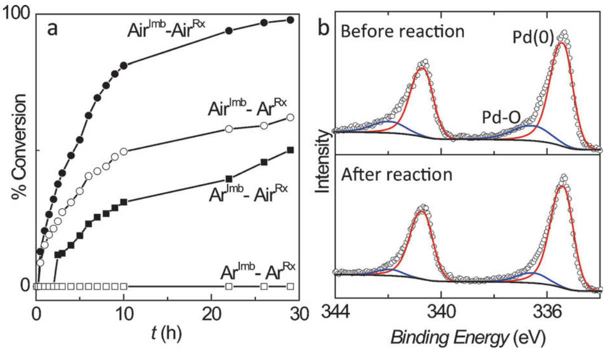

Figure 3. a) Reaction profile of cubic Pd NCs immobilized and reacted under aerboic and inert conditions. b) XPS analysis of cubic NCs before and after reaction.

The beneficial effect of O_2 has been reported for Suzuki–Miyaura coupling using in situ generated Pd nanoparticles although its role in the mechanism was not identified.[16] Reaction of O_2 with arylboronic acids has been shown to generate peroxopalladium species.[17] XPS analysis was used to probe changes in the surface chemistry of the catalysts. Figure 3b displays the Pd 3d core level spectra of cubic NCs before and after the reaction, showing the presence of a doublet at a binding energy (BE) of 335.4 eV (340.6 eV), which can be assigned to metallic Pd^0.[18] An additional shoulder peak at a BE of 336.4 eV was also present in the spectra for all polyhedrons. The presence of surface oxide species is typically reported at a BE $\approx$ 1 eV higher than Pd^0, while bulk oxides are observed at BE > 1.5 eV, thus the peak at 336.4 eV is assigned to the presence of surface Pd-O species.[19] NCs immobilized under Ar also displayed a contribution of Pd-O in the Pd 3d spectrum, as the NC synthesis is performed in air, where the presence of O_2 is important for oxidative etching and shape control of the particles.[20] The Pd 3d spectra of cubic NCs after the reaction in air displayed a decrease in the peak intensity associated with surface Pd-O. NCs immobilized and reacted under Ar, showed negligible changes to the Pd 3d spectra (Figure S9), confirming that O_2 plays a key role in the removal of surface species, as illustrated in Figure 4. O_2 adsorption on Pd surfaces is a spontaneous process but is influenced by the crystal orientation of the surface. Molecular adsorption and activation of O_2 is preferential on Pd{100} surface facets compared to {111} facets due a lower activation energy.[21] The presence of chemisorbed O_2 may facilitate the adsorption of phenyl borates which are subsequently more readily removed from the surface.[22] This scenario is also consistent with ICP analysis indicating boronic acid as a primary species responsible for Pd leaching.

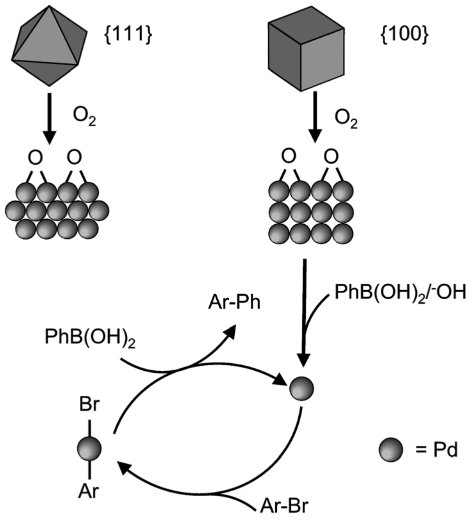

Figure 4. Mechanism of O_2-promoted leaching on Pd NCs.

In summary, we find that the shape sensitivity in Suzuki–Miyaura coupling originates from a homogenous reaction pathway. Leaching from the NCs is not solely attributed to the loss of low-coordination edge and corner atoms, but to the nature of the surface facets. The catalytically active Pd species are generated by leaching of the surface oxide and this leaching mechanism is shape-sensitive. Preferential adsorption of O_2 on Pd {100} compared to Pd {111} surfaces induces greater Pd leaching and consequently enhanced reactivity when using cubic NCs compared to octahedral NCs. These insights will help in the rational design of catalysts and reaction conditions for cross-couplings and other important transformations.

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[1] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; b) G. A. Molander, N. Ellis, *Acc. Chem. Res.* **2007**, *40*, 275–286; c) G. C. Fu, *Acc. Chem. Res.* **2008**, *41*, 1555–1564; d) F.-S. Han, *Chem. Soc. Rev.* **2013**, *42*, 5270–5298; e) S. R. Chemler, D. Trauner, S. J. Danishefsky, *Angew. Chem.* **2001**, *113*, 4676–4701; *Angew. Chem. Int. Ed.* **2001**, *40*, 4544–4568.

[2] a) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133–173; b) M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet, F.-X. Felpin, *Adv. Synth. Catal.* **2010**, *352*, 33–79; c) Y. Xiong, B. J. Wiley, Y. Xia, *Angew. Chem.* **2007**, *119*, 7291–7293; *Angew. Chem. Int. Ed.* **2007**, *46*, 7157–7159; d) H. Zhang, M. S. Jin, Y. J. Xiong, B. Lim, Y. N. Xia, *Acc. Chem. Res.* **2013**, *46*, 1783–1794; e) D. Astruc, F. Lu, J. R. Aranzaes, *Angew. Chem.* **2005**, *117*, 8062–8083; *Angew. Chem. Int. Ed.* **2005**, *44*, 7852–7872.

[3] a) M. Crespo-Quesada, A. Yarulin, M. Jin, Y. Xia, L. Kiwi-Minsker, *J. Am. Chem. Soc.* **2011**, *133*, 12787–12794; b) K. M. Bratlie, H. Lee, K. Komvopoulos, P. Yang, G. A. Somorjai, *Nano Lett.* **2007**, *7*, 3097–3101; c) M. Jin, H. Zhang, Z. Xie, Y. Xia, *Energy Environ. Sci.* **2012**, *5*, 6352–6357; d) C. M. Sánchez-Sánchez, J. Solla-Gullón, F. J. Vidal-Iglesías, A. Aldaz, V. Montiel, E. Herrero, *J. Am. Chem. Soc.* **2010**, *132*, 5622–5624.

[4] a) R. Narayanan, M. A. El-Sayed, *Langmuir* **2005**, *21*, 2027–2033; b) R. Narayanan, M. A. El-Sayed, *J. Phys. Chem. B* **2005**, *109*, 12663–12676.

[5] a) F. Wang, C. Li, L.-D. Sun, H. Wu, T. Ming, J. Wang, J. C. Yu, C.-H. Yan, *J. Am. Chem. Soc.* **2011**, *133*, 1106–1111; b) X. Huang, Y. Li, Y. Chen, E. Zhou, Y. Xu, H. Zhou, X. Duan, Y. Huang, *Angew. Chem.* **2013**, *125*, 2580–2584; *Angew. Chem. Int. Ed.* **2013**, *52*, 2520–2524; c) A. Mohanty, N. Garg, R. Jin, *Angew. Chem.* **2010**, *122*, 5082–5086; *Angew. Chem. Int. Ed.* **2010**, *49*, 4962–4966.

[6] J. Xu, A. R. Wilson, A. R. Rathmell, J. Howe, M. Chi, B. J. Wiley, *ACS Nano* **2011**, *5*, 6119–6127.

[7] a) P.-P. Fang, A. Jutand, Z.-Q. Tian, C. Amatore, *Angew. Chem.* **2011**, *123*, 12392–12396; *Angew. Chem. Int. Ed.* **2011**, *50*, 12184–12188; b) M. B. Thathagar, J. E. ten Elshof, G. Rothenberg, *Angew. Chem.* **2006**, *118*, 2952–2956; *Angew. Chem. Int. Ed.* **2006**, *45*, 2886–2890.

[8] a) J. J. Davis, K. S. Coleman, K. L. Busuttil, C. B. Bagshaw, *J. Am. Chem. Soc.* **2005**, *127*, 13082–13083; b) J. J. Davis, C. B. Bagshaw, K. L. Busuttil, Y. Hanyu, K. S. Coleman, *J. Am. Chem. Soc.* **2006**, *128*, 14135–14141.

[9] a) P. J. Ellis, I. J. S. Fairlamb, S. F. J. Hackett, K. Wilson, A. F. Lee, *Angew. Chem.* **2010**, *122*, 1864–1868; *Angew. Chem. Int. Ed.* **2010**, *49*, 1820–1824.

[10] L. Shao, B. Zhang, W. Zhang, S. Y. Hong, R. Schlçgl, D. S. Su, *Angew. Chem.* **2013**, *125*, 2168–2171; *Angew. Chem. Int. Ed.* **2013**, *52*, 2114–2117.

[11] a) J. Le Bars, U. Specht, J. S. Bradley, D. G. Blackmond, *Langmuir* **1999**, *15*, 7621–7625; b) Y. Li, E. Boone, M. A. El-Sayed, *Langmuir* **2002**, *18*, 4921–4925.

[12] H. Ramezani-Dakhel, P. A. Mirau, R. R. Naik, M. R. Knecht, H. Heinz, *Phys. Chem. Chem. Phys.* **2013**, *15*, 5488–5492.

[13] R. G. Heidenreich, E. G. E. Krauter, J. Pietsch, K. Kohler, *J. Mol. Catal. A* **2002**, *182*, 499–509.

[14] a) Y. Y. Ji, S. Jain, R. J. Davis, *J. Phys. Chem. B* **2005**, *109*, 17232–17238; b) Z. Niu, Q. Peng, Z. Zhuang, W. He, Y. Li, *Chem. Eur. J.* **2012**, *18*, 9813–9817; c) A. K. Diallo, C. Ornelas, L. Salmon, J. R. Aranzaes, D. Astruc, *Angew. Chem.* **2007**, *119*, 8798–8802; *Angew. Chem. Int. Ed.* **2007**, *46*, 8644–8648.

[15] S. S. Soomro, F. L. Ansari, K. Chatziapostolou, K. Koehler, *J. Catal.* **2010**, *273*, 138–146.

[16] W. Han, C. Liu, Z. Jin, *Adv. Synth. Catal.* **2008**, *350*, 501–508.

[17] C. Adamo, C. Amatore, I. Ciofini, A. Jutand, H. Lakmini, *J. Am. Chem. Soc.* **2006**, *128*, 6829–6836.

[18] G. Collins, M. Blomker, M. Osiak, J. D. Holmes, M. Bredol, C. O'Dwyer, *Chem. Mater.* **2013**, *25*, 4312–4320.

[19] a) G. Ketteler, D. F. Ogletree, H. Bluhm, H. J. Liu, E. L. D. Hebenstreit, M. Salmeron, *J. Am. Chem. Soc.* **2005**, *127*, 18269–18273; b) E. Lundgren, G. Kresse, C. Klein, M. Borg, J. N. Andersen, M. De Santis, Y. Gauthier, C. Konvicka, M. Schmid, P. Varga, *Phys. Rev. Lett.* **2002**, *88*, 246103.

[20] a) Y. J. Xiong, J. M. McLellan, Y. D. Yin, Y. N. Xia, *Angew. Chem.* **2007**, *119*, 804–808; *Angew. Chem. Int. Ed.* **2007**, *46*, 790–794; b) Y. J. Xiong, J. Y. Chen, B. Wiley, Y. N. Xia, S. Aloni, Y. D. Yin, *J. Am. Chem. Soc.* **2005**, *127*, 7332–7333; c) M. C. Liu, Y. Q. Zheng, L. Zhang, L. J. Guo, Y. N. Xia, *J. Am. Chem. Soc.* **2013**, *135*, 11752–11755.

[21] R. Long, K. Mao, X. Ye, W. Yan, Y. Huang, J. Wang, Y. Fu, X. Wang, X. Wu, Y. Xie, Y. Xiong, *J. Am. Chem. Soc.* **2013**, *135*, 3200–3207.

[22] H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi, T. Tsukuda, *Langmuir* **2004**, *20*, 11293–11296.