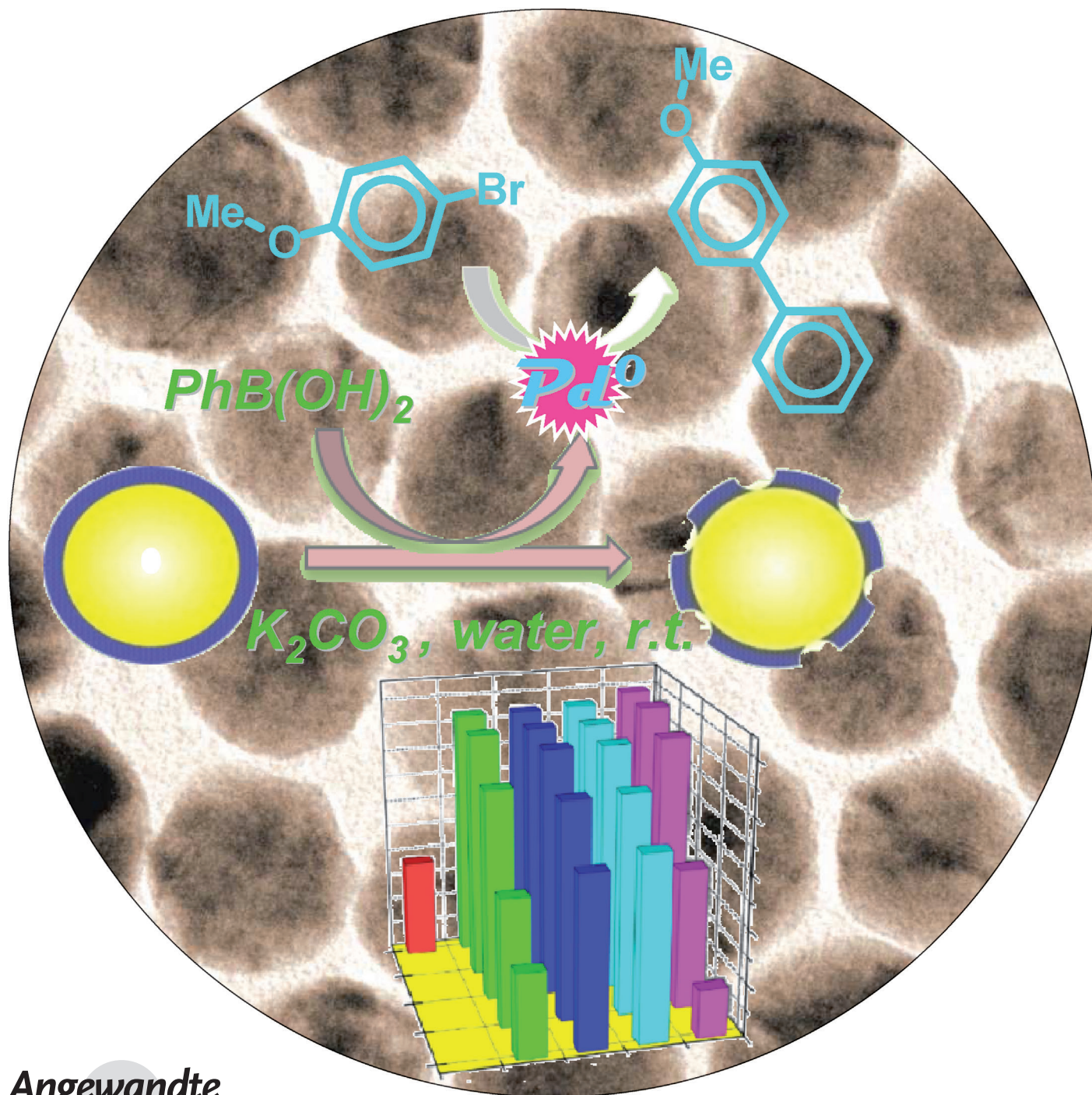


Au–Pd Core–Shell Nanoparticles Catalyze Suzuki–Miyaura Reactions in Water through Pd Leaching**

Ping-Ping Fang, Anny Jutand,* Zhong-Qun Tian,* and Christian Amatore*



Zero-valent palladium catalysts synthesized in the absence of suitable ligands lead to the uncontrolled formation of palladium nanoparticles (NPs) or palladium black.^[1] Palladium NPs are prone to catalyze reactions (e.g. Heck^[1,2] and Suzuki–Miyaura^[2–5] reactions) though it is debated if the catalysis stems from the NPs themselves, in other words heterogeneous catalysis,^[2,3b,4] or results from traces of Pd leaching into solution and acting homogeneously.^[1,2,5] There is a priori support for both possibilities. NPs essentially differ from bulk metal; the metal centers are highly activated as a result of, for example, surface tension and incomplete reticulation shells, so they may have a specific reactivity bridging the gap between homogeneous and heterogeneous catalysis. Conversely, low ligated palladium centers^[6] or clusters possibly formed by leaching^[1,2,5] may act as particularly effective homogeneous catalysts even at nearly undetectable amounts.^[6a]

Discriminating experimentally between the two pathways is highly challenging because of possible dynamic exchanges linking different types of palladium species in solution and NPs acting as reservoirs.^[1,5] This weakens the significance of claims based on NP size exclusion or on filtered solutions after exposition to NPs.^[1d,5a] Moreover, the two pathways may be intertwined since leaching may be catalyzed by one or several steps of the catalytic cycle. For example, it has been argued that the oxidative addition of aryl halides to Pd surface atoms favors their extraction,^[1d,5a] yielding ArPdX moieties that react homogeneously to ultimately deliver the final product and low-ligated Pd⁰ centers which can either further react^[1,5] or redeposit^[5b] onto surfaces including NPs. Hence the relative proportion of the heterogeneous and homogeneous pathways may well depend not only on the NPs themselves but also on the very reaction catalyzed. This explains why previous attempts have not been able to provide clear-cut general answers.

Herein, we use an unprecedented strategy relying on the use of core–shell NPs (Au@Pd) in which a shell of one or several palladium(0) monolayer(s) (MLs) is precisely wrapped around a gold(0) nanocore (Figure 1a). The presence of the gold core allows a precise assessment of the status of the

Pd surface after a catalytic reaction by surface-enhanced Raman spectroscopy (SERS) or by cyclic voltammetry (CV). The high sensitivity of both methods is sufficient to characterize any palladium leaching or NP surface reorganization. The catalytic properties of these NPs were tested on the Suzuki–Miyaura cross-coupling of 4-bromoanisole (**1**) with phenylboronic acid (**2**) in water with the base K₂CO₃ (**3**), at room temperature [Eq. (1), Figure 1b).

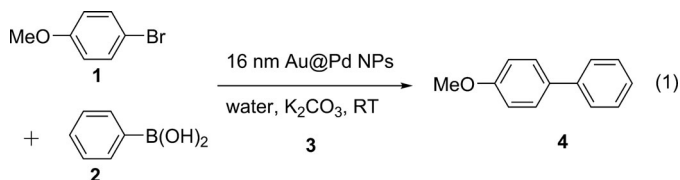


Figure 1b shows that Au@Pd NPs are efficient catalysts since 4-bromoanisole, a sluggish reagent in oxidative addition reactions,^[7] reacts readily in water at room temperature providing **4** with an average yield of 95 % in roughly 4 h. An optimum conversion rate was observed for NPs with two to five monolayers of Pd (Figure 1b and Table S1 in the Supporting Information). Interestingly, no induction period was detected since the conversion proceeded in all cases (ML = 1–10) according to an extremely reproducible single-exponential kinetic law (see Figure S1 in the Supporting Information).^[8]

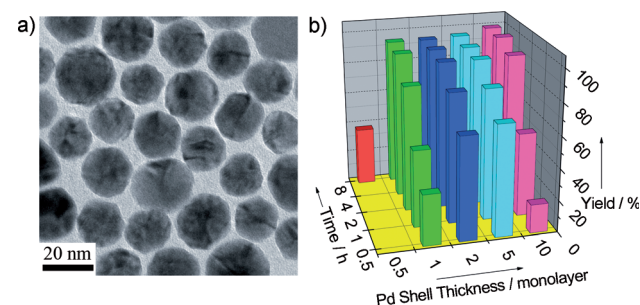


Figure 1. a) Transmission electron microscopy (TEM) image of 16 nm Au@Pd NPs with two monolayers of Pd. b) Plot of the yields versus the Pd shell thickness as a function of reaction time for the cross-coupling of 4-bromoanisole (**1**; 0.5 mmol) with phenylboronic acid (**2**; 0.75 mmol) in 66 mL of degassed water/K₂CO₃ (1.5 mmol) at room temperature [Eq. (1)]. See Table S1 in the Supporting Information for *t*_{1/2} and reproducibility, and Figure S1 for kinetic treatment.

After each run the Au@Pd NPs were collected by centrifugation, cleaned (see the Supporting Information), and analyzed by CV and SERS to assess their surface status. CV is extremely sensitive: a small peak is observed at approximately 0.35 V vs. SCE only when gold atoms are exposed to the electrolyte^[9] (compare the green trace (pure gold NPs) and black trace (Au@Pd NPs purposely synthesized with pinholes) with the blue trace (Au@Pd NPs before reaction) (Figure 2a). Hence, the observation of this peak for Au@Pd NPs after a catalytic run (red trace in Figure 2a) is direct evidence for Pd leaching during the reaction.

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[**] This work was supported by CNRS, ENS, and UPMC (UMR 8640 and LIA XiamENS) in France and the Major International Collaborative Research Project of NSFC (no. 20620130427) in China. P.P.F. acknowledges the Chinese Scholarship Council for support during her stay in Paris.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201103465>.

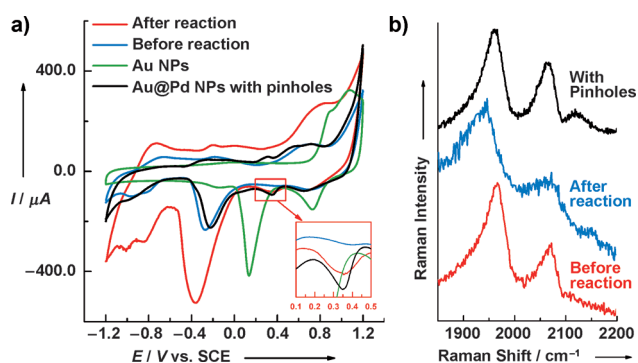


Figure 2. a) CV of Au NPs (green), Au@Pd NPs purposely synthesized with Au pinholes (black), and Au@Pd NPs with one monolayer of Pd in aqueous 0.1 M NaClO₄ before (blue) and after (red) reaction. The potential range of main interest is expanded in the inset (note that the position of the CV peak at 0.35 V vs. SCE varies slightly as a function of the exposed Au surface area and structure). b) SERS spectra of adsorbed CO on Au@Pd NPs purposely synthesized with pinholes (black) and Au@Pd NPs with one monolayer of Pd before (red) and after (blue) reaction.

Though CV alone was sufficient to prove that leaching occurred during catalytic runs, we used SERS to confirm the surface alteration of the Au@Pd NPs after reactions. For this purpose we relied on the characteristic SERS bands of adsorbed CO which are very sensitive to the nature of the metal surface.^[10] The bands around 1960 and 2070 cm⁻¹ (Figure 2b, red) characterize bridging and linearly bonded CO on Pd, respectively.^[11] Whenever pinholes expose Au, a peak above 2100 cm⁻¹ must appear (Figure 2b, black).^[10] The SERS spectrum recorded after catalytic runs consistently displayed a small peak above 2100 cm⁻¹ (S/N > 3) confirming that Pd atoms leached away from Au@Pd NPs during the reactions (Figure 2b, blue).^[12]

Therefore, both electrochemistry and SERS indicated unambiguously that a Pd fraction leached away from the Au@Pd NPs surface during catalytic reactions, while Au@Pd NPs surface was perfectly stable in the absence of reagents **1** and **2** or of the base **3**. It was thus of interest to determine which species (or which combination) provoked such Pd leaching and quantify it by inductively coupled plasma mass spectrometry (ICPMS) (Table 1).

In analyzing the results in Table 1 one must note that during the synthesis of Au@Pd NPs a 25 % excess of H₂PdCl₄ was used to ensure perfect Pd coatings.^[13a] A fraction of this excess remained in solution after the synthesis corresponding to the (11 ± 3) % listed in entry 1.^[13b] This value compares also extremely well with the figures obtained after exposure of the NPs to **2** alone (entry 2) or to **1** alone (data not shown). Conversely, K₂CO₃ alone (entry 3) provoked an additional 15–20 % Pd leaching and this increased up to 45–50 % for the combination K₂CO₃ + **2** (entry 4) indicating a synergy between the two species. No similar synergy was observed for the combination K₂CO₃ + **1** (entry 5 vs. 3) or in the presence of all reagents (entry 6 vs 4). Finally, even though it was impossible to determine if the detected palladium atoms corresponded to single centers, or to clusters, it was absolutely

Table 1: Average quantities and weight percent of Pd atoms detected by ICPMS in the supernatant liquid after exposure of Au@Pd NPs (two monolayers of Pd) to different reagents in water for 24 h (concentrations of reagents were identical to those listed in Figure 1 b).

Entry	Reagent	Amount of Pd leached [%] ^[a]	[ppm]
1	none (control, see text)	11 ± 3	1.10
2	2	8 ± 3	0.80
3	K ₂ CO ₃	27 ± 5	2.67
4	K ₂ CO ₃ + 2	59 ± 10	5.98
5	K ₂ CO ₃ + 1	25 ± 5	2.51
6 ^[b]	K ₂ CO ₃ + 2 + 1	58 ± 10	5.86

[a] Percentages refer to the total amount of H₂PdCl₄ used during NPs synthesis; standard deviations are based on three runs with three different NPs batches. [b] Compare Table 3 for NPs with different numbers of monolayers.

clear that no Au@Pd NPs were present in the supernatants (see Section S2 in the Supporting Information).

CV, SERS, and ICPMS concurred in establishing that Pd leaching occurred during each catalytic run. However, this did not provide a clue about the origin (homogeneous or heterogeneous) of the efficient catalysis observed (Figure 1b). Therefore, a series of sequential reactivity study was developed to pinpoint the main origin of the efficient catalysis. In each series, two identical catalytic runs were first performed through reacting **1** (0.5 mmol), **2** (0.75 mmol), and K₂CO₃ (1.5 mmol) with freshly prepared Au@Pd NPs (0.01 equiv Pd; 16 nm Au core with two monolayers of Pd) in 66 mL of water. The two solutions afforded quantitative conversion after 24 hrs and were then labeled **A1**.

In one of the flasks the reaction mixture **A1** was reloaded with **1** (0.5 mmol), **2** (0.5 mmol), and K₂CO₃ (0.5 mmol) to compensate for the reagents consumed during the first run, and the solution reacted a second time for 24 h. A (88 ± 5) % yield of **4** was then obtained (Table 2, run **A2**). The content **A1** of the second flask was separated into two parts by centrifugation to give **B1**, consisting of the isolated NPs, and **C1**, the supernatant liquid. **C1** was analyzed beforehand by UV/Vis spectroscopy^[14] and ICPMS to ensure that no gold-containing moieties were present (see Figure S2 in the Supporting Information) though Pd-centered species were present (Table 1). A solution of 66 mL of water containing **1** (0.5 mmol), **2** (0.75 mmol), and K₂CO₃ (1.5 mmol) was added to **B1**. **C1** was reloaded with **1** (0.5 mmol), **2** (0.5 mmol), and K₂CO₃ (0.5 mmol) to compensate for the reagents consumed during the first catalytic run. Both **B1** and **C1** were left to react for 24 h.

Table 2: Yield of **4** after a second run based on solutions **A1**, **B1**, **C1** extracted after a first run (see text).

Run	System (added quantities in mmol)	Yield [%] ^[a]
A2	A1 + 1 (0.5) + 2 (0.5) + 3 (0.5)	88 ± 5
B2	B1 + 1 (0.5) + 2 (0.75) + 3 (1.5) + 66 mL H ₂ O	51 ± 10
C2	C1 + 1 (0.5) + 2 (0.5) + 3 (0.5)	88 ± 5

[a] Standard deviations are based on three runs involving three different batches of NPs.

Table 2 shows that **A2** (the whole solution) and **C2** (the supernatant without Au@Pd NPs) gave identical yields (88 %) of **4**, while the isolated NPs (**B2**), though active, led to poorer results (51 % yield). This indicates unambiguously that the main catalytic Pd species consisted of solution complexes/clusters formed by the combined action of PhB(OH)₂ and K₂CO₃ on the NPs (Table 1). The lower reactivity observed for **B2** (Table 2) may stem either from additional slow Pd leaching or possibly a slower reaction catalyzed by the NPs surface,^[4] though the latter is doubtful since one would then expect that **C1** (supernatant only) would be less efficient than **A1** (NPs and supernatant), which contradicts the observations.

These results unambiguously established that the catalytic efficiency of the present NPs is due to Pd leaching which is triggered by the synergistic action of PhB(OH)₂ and K₂CO₃, and that the leached Pd species survive long enough in the reaction medium to allow a second catalytic cycle. The corresponding catalytic efficiencies are remarkable since the amounts of leached Pd species are in the ppm range (Tables 1 and 3).^[15]

However, Table 3 shows that there is no direct correlation between the Pd-leaching amounts and half-reaction times. This indicates that a significant proportion of the leached Pd atoms detected by ICPMS was not directly involved in the

Table 3: Variations of half-reaction times and amount of Pd leaching as quantified by ICPMS after one run for 24 h.

No. of Pd monolayers	1	2	5	10
Half-reaction time [h]	0.69	0.30	0.37	0.53
Pd in the supernatant [ppm]	0.911	5.23	16.3	27.1
Total initial Pd loading [ppm]	4.95	10.3	22.5	53.00
Leached amount [%] ^[a]	18 ± 5	51 ± 10	73 ± 15	51 ± 10

[a] Average of three independent runs involving three different batches of NPs. Percentages are given based on the initial loadings.

catalysis. One can invoke two arguments to rationalize this observation. First of all, one may consider that only a fraction of the released Pd atoms are in a chemical form prone to catalyze. Indeed, ICPMS differentiates neither between oxidation states (0, I, or II) nor between structures (complexes, clusters, or small Pd NPs) of the detected Pd. Hence one may envision that owing to the different reactivity of their Pd layers (see below) each type of NP generates different proportions of Pd species with diverse catalytic propensities. A second argument is based on the kinetic versus the thermodynamic situation. Table 3 represents the amount of leached Pd after 24 h exposure. Conversely, the absence of any induction period and the observation in each case of a single-exponential kinetic mode (that is, with no acceleration) imply that most of the active catalytic species were generated at the beginning of the reaction ($t < 10$ min). Hence, the catalytic species consist essentially of rapidly released Pd species while Table 3 reports the final situation (closer to thermodynamic conditions). Most presumably both phenomena concur, as they are both controlled by the specific reactivity of each Au@Pd NP type.

In this respect, it is interesting to note that for one monolayer of Pd, Shockley partial dislocations (SPDs) accompanied by the formation of stacking faults release the strain between the surface Pd layer and the Au core.^[16] This explains why single Pd monolayers on Au are relatively stable (only 18 % final leaching). This presumably also results in slow leaching kinetics hence in the largest $t_{1/2}$ values (Table 3). In NPs coated with much more Pd (> 2 nm or > 7 ML) stacking faults still exist but without SPDs,^[16] possibly because of Au diffusion into the Pd shell layers.^[16] Therefore, such large shells are expected to be relatively stable kinetically. Conversely, NPs with two to five monolayers of Pd suffer both mismatches and strain caused by the Au core which makes them rather unstable thermodynamically and most presumably also kinetically. For example, in other reactions, high-index-faceted Pd nanoshells exhibited higher catalytic activity than those with low-index facets.^[13]

In summary, Au@Pd NPs have been essential to prove the homogeneous origin of the high catalytic efficiency of palladium-based nanoparticles in Suzuki–Miyaura cross-coupling reactions in water at room temperature. These Au@Pd NPs enabled the use of SERS, CV, and ICPMS which all concurred to establish that the catalytic activity was primarily a result of Pd centers or clusters leaching away from the NPs in the presence of the reaction components. This leaching was mostly due to the synergistic action of the base and of the arylboronic acid and surprisingly not to oxidative addition by the aryl halide.^[17] In addition, this study showed that the reactivity of leached Pd species can be finely tuned by the number of Pd shells wrapped around the gold core. Though the presence of a gold core was essential in our study for SERS and electrochemical characterizations, Au may presumably be replaced by other metals, for example, Ag or Ni,^[18] to produce Pd-based NPs catalysts at a considerably reduced cost, and hence with wider applicability.

Received: May 19, 2011

Published online: September 26, 2011

Keywords: nanoparticles · electrochemistry · Suzuki–Miyaura reaction · Pd-leaching mechanism · SERS

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