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In-situ Monitoring of Palladacycle-Mediated Carbonylation by Surface-Enhanced Raman Spectroscopy

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Palladium-catalyzed carbonylation has emerged as one of the most potential approaches for the synthesis of carbonyl-containing molecules, however, the understanding remains challenging in many reactions partly because of lacking robust monitoring methods. Herein, we reported a novel surface-enhanced Raman spectroscopy (SERS) based strategy for the in-situ monitoring of palladacycle-mediated carbonylation. The nanoplatforms integrated with SERS activity and reaction mediability were constructed through assembling new synthesized palladacycles (PCs) on the surface of gold nanoparticles. It was shown that, when carbon monoxide (CO) was introduced to the nanoplatform-contained system as a C1 source, palladacycle-mediated carbonylation was initiated, and the SERS spectra of the nanoplatforms changed concomitantly. With this SERS spectrum variation, the reaction mechanism could be investigated facilely, and the corresponding reaction was found to follow a pseudo-first-order kinetic rate law based on the relationship between the relatively ratiometric peak intensities of I_{1319}/I_{1338} and the reaction time. Therefore, using the proposed SERS approach, the carbonylation process could be directly monitored in situ without tedious pretreatment.

The palladium-catalyzed carbonylation has become one of the most powerful methods for the synthesis of carbonyl-containing molecules because (i) it is very efficient in carbonylative synthesis, which increases the carbon number simultaneously, and (ii) carbon monoxide (CO) can be served as a costless and easily available C1 source.[1–5] This important carbonylation approach has been studied in laboratory scope but also used in industry scale. However, the mechanism study remains challenging in many aspects.[6,7] Currently, there are a series of analytical techniques suitable for investigating catalytical reactions, such as UV-vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), electrospray ionization mass spectrometry (ESI-MS), etc.[7–10] However, despite these techniques contribute to realize the mechanism of palladium-catalyzed carbonylations, they still suffer from limited sensitivity, slow response, strong inference from water, or incapability to probe reactions in an in-situ manner.[11,12]

Surface-enhanced Raman scattering (SERS) has emerged as a powerful spectroscopy technique that can provide molecular vibrational fingerprint information of the analytes.[13,14] Compared with other techniques, SERS has many significant advantages such as high sensitivity, rapid response, easy operation, in-situ detection, and little interfere from water.[15] These advantages make SERS highly competitive to meet almost all needs for the label-free in-situ monitoring of the reaction processes. Recently, SERS monitoring of catalytical reactions has been successfully performed by using plasmonic nanomaterials combined with catalytical activity.[11,12,16–18] For instance, direct SERS observation of catalytic hydrodechlorination of dichloroethene in water was accomplished using core-shell bimetallic structures.[16] In addition, SERS monitoring of catalytic hydrogenation of 4-nitrothiophenol was further studied by constructing bifunctional raspberry-like Au/Pt/Au core/shell particles,[18] 3D superstructures with small gold satellites assembled onto a large shell-isolated gold core,[12] and Au nanorods grown with alloy horns.[11] These achievements revealed exciting prospects of SERS for studying some catalytic reactions locally, however, these approaches are hard to be directly utilized for the in-situ SERS monitoring of palladium-catalyzed carbonylation. Therefore, in this work, as a proof-of-concept, a SERS-based approach was explored for the in-situ monitoring of palladacycle-mediated carbonylation using CO for C1 source. Palladacycles (PCs) were designed and synthesized, then they were functionalized on the surface of gold nanoparticles (Au NPs) to form a nanoplatform (AuNPs/PCs). It can be expected that, once CO bonding to the nanoplatform, palladacycle-mediated carbonylation will take place and SERS spectrum of the nanoplatform will change correspondingly. With the

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variation of SERS spectra, the transformation of PCs can be tracked, thereby the in-situ monitoring of the carbonylation reaction can be accomplished (Figure 1). Further experimental details are provided in the Supporting Information.
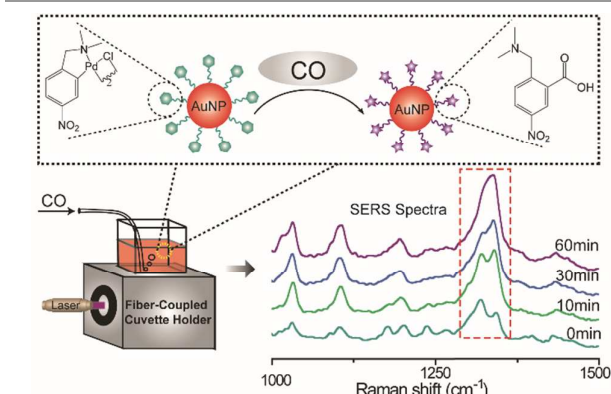

Fig. 1 Schematic illustration of the in-situ monitoring of palladacycle-mediated carbonylation with SERS.

PCs, synthesized by cyclometalation with Na_2PdCl_4 from N,N-Dimethyl-4-nitrobenzylamine and subsequent transformation to chloride dimers,[19,20] were confirmed by ^1H NMR, ^{13}C NMR and Mass spectrometry (Figure S1-S3). The prepared AuNPs were then incubated with the PCs solution to fabricate SERS nanoplatforms. Transmission electron microscopy (TEM) characterization of the fabricated SERS nanoplatforms shows that they are spherical with a diameter of approximately 60 nm (Figure 2A), which is consistent with the result obtained by the UV-vis spectroscopy (Figure S4).[21] As AuNPs with similar size are efficient for Raman enhancement at the near-infrared excitations which could avoid the photolysis of compound,[22] the nanoplatform may have a good SERS activity without destroying responsive information of the reaction process. Further SERS tests demonstrate that both simple AuNPs and saturated PCs solution barely have Raman response, whereas AuNPs/PCs washed with ultrapure water show an obvious SERS spectrum (Figure 2B). This may mean that PCs molecules were successfully functionalized on AuNPs since SERS is a surface selective technique. Moreover, there is a red-shift in the plasmon resonance Rayleigh scattering spectra of AuNPs after the introduction of PCs, further implying that PCs could be on the surface of AuNPs.[23] (Figure S5).

In addition, the SERS spectra of nanoplatforms did not change over 12 hours. The profile of the spectra of AuNPs/PCs almost remain the same, and the intensities at individual peaks like 875 cm^{-1} and 1319 cm^{-1} also remained approximately constant (Figure 2C and 2D). This illustrates the good SERS stability of AuNPs/PCs without obvious chemical changes, which can ensure that the spectral variation only comes from the reaction between PCs and CO. Taken together, SERS-active nanoplatforms with good stability were successfully established, which will be in favour of the in-situ monitoring of carbonylation reaction.
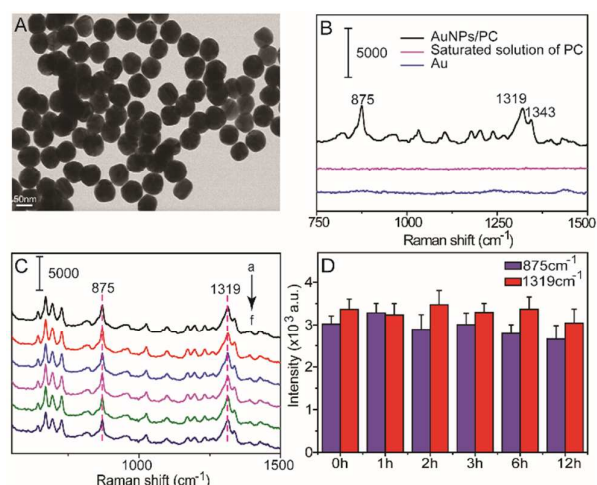

Fig. 2 (A) Typical TEM image of AuNPs/PCs. (B) Raman response of AuNPs/PCs, AuNPs and saturated PCs solution. (C) Raman spectra of AuNPs/PCs stored over different hours under ambient conditions: (a) 0h; (b) 1h; (c) 2h; (d) 3h; (e) 6h; (f) 12h. (D) Plots of SERS intensities versus storage time based on the band at 875 cm^{-1} and 1319 cm^{-1}. Each data point represents the average value from three SERS spectra. Error bars show the standard deviations.

We further investigated the feasibility of the prepared AuNPs/PCs for the in-situ SERS monitoring of palladacycle-mediated carbonylation. In order to carry out the reaction, AuNPs/PCs were dispersed into the deionized water that was saturated with CO by means of continuous introduction of 5% CO/N_2 gas. The kinetic in-situ monitoring of the carbonylation process was then performed by directly collecting the SERS spectrum from the SERS nanoplatform of AuNPs/PCs at different reaction times (Figure 3A). The monitoring was stopped when no significant difference could be found between adjacent spectra. From the experimentally measured spectra and the corresponding density functional theory (DFT) calculation (Table S1), the analysis of the reaction process can be achieved facilely. Originally, SERS spectrum of PCs on the surface of the AuNPs was observed. The Raman bands at 1177 cm^{-1}, 1202 cm^{-1} and 1236 cm^{-1} could be attributed to the in-plane bending of phenyl C-H, the stretching of phenyl ring and the stretching of C-N-Pd, respectively.[24-27] Moreover, the band observed at 1319 cm^{-1} may be assigned to the stretching vibration of C-N and C-H,[28] the peak at 1343 cm^{-1} may arise from the C-Pd bond. As the reaction progressing, the peak at 1236 cm^{-1} decreased gradually, while the peak at 1343 cm^{-1} shifted to 1338 cm^{-1} and became gradually stronger. Furthermore, the peak at 1202 cm^{-1} shifted to 1196 cm^{-1} where the peak at 1177 cm^{-1} seems to be covered. The bands at 1196 cm^{-1} and 1338 cm^{-1} may be related to the group of –COOH,[29] which agreed with the result obtained from DFT calculation (Table S1). This could be regarded as a result of the depalladation and the formation of carbonylation product of carboxyl-contained 4-nitro-N,N-dimethylbenzylamine which has stronger SERS responsiveness.
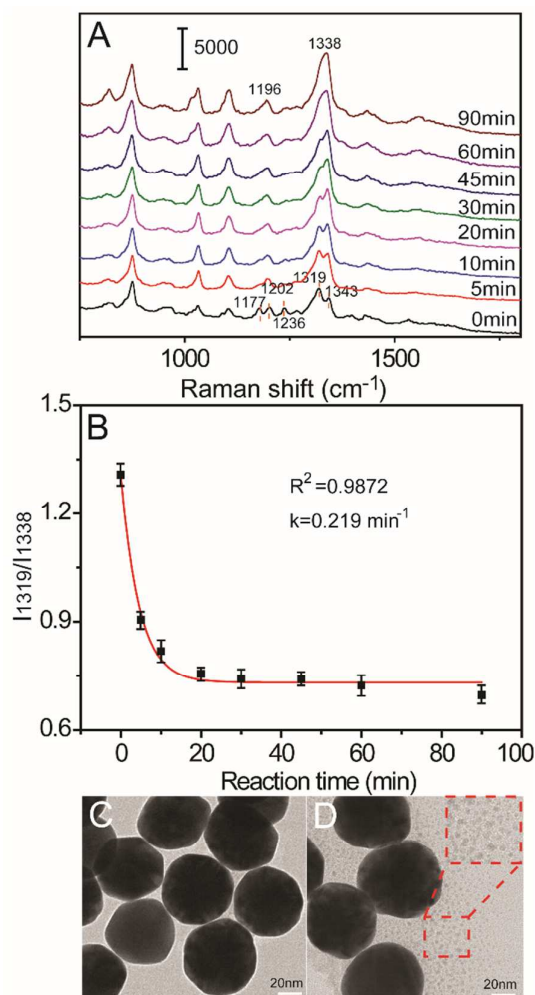
Fig. 3 In-situ SERS monitoring of palladacycle-mediated carbonylation using CO for C1 source. (A) SERS spectra collected from the AuNPs/PCs in the presence of CO at different reaction time. (B) Plots of ratiometric peak intensities versus reaction time based on I_{1319}/I_{1338}. (C) and (D) Typical TEM images of AuNPs/PCs before and after reaction with CO, respectively. Each data point represents the average value from three SERS spectra. Error bars show the standard deviations.

The depalladation phenomenon can also be observed in TEM images, which demonstrates that black palladium is generated after the carbonylation reaction (Figure 3C and 3D). In order to further verify the SERS monitoring result of the carbonylation process using the nanoplatforms, the PCs and its product after reacting with CO were characterized by UV-vis spectra and high-performance liquid chromatography/mass spectrometry (HPLC/MS) (Figure S6 and S7). The UV-visible spectra show that UV-Vis peaks of PC solution shift after the introduction of CO, indicating the formation of new products. Further HPLC/MS characterization demonstrates that the molecular ion of the product is m/z 225.0870, implying a molecular formula of $C_{10}H_{12}O_4N_2$ with a group of –COOH (error<0.1 ppm). The abundant daughter ion at m/z 181.0970 (calculate for $C_9H_{12}O_2N_2$, error=4.9 ppm) could be assigned to be the

diagnostic fragment. The difference between 225.0870 (m/z) and 181.0970 (m/z) matches well with the molecular ion of –COOH (m/z 44.9977). This means that the reaction product was approved to be 2-carboxyl-4-nitro-N,N-dimethylbenzylamine (CNDBA), which is well agreeable with the finding of -COOH by the proposed SERS strategy. Moreover, this reaction took place in water, a potentially transformative environment to safer and greener synthetic chemistry, rather than in organic solvents. Thus the compound with -COOH was the dominating carbonylation product in aqueous solution instead of the product of 2-methyl isoindolin-1-one or dealkylative amide as previous report[1], which may be on account of the hydrolysis reaction happened to the latter as soon as it was formed.

In addition, to obtain the kinetic information of the carbonylation using the developed nanoplatforms, the ratiometric peak intensities of I_{1319}/I_{1338} were correlated quantitatively with the reaction time (Figure 3B). It can be found that the relationship between I_{1319}/I_{1338} and reaction time follows an exponential function changing law. The reaction rate constant k can be determined by the pseudo-first-order rate equation (1).[17,30]

$$\ln(I_t/I_0) = -kt \tag{1}$$

Here I_t is ratiometric peak intensities of I_{1319}/I_{1338} at time t, I_0 is the ratiometric peak intensities of I_{1319}/I_{1338} at time 0, and k is the obtained pseudo-first-order rate constant for the reaction. In this way, The pseudo-first-order rate constant for the palladacycle-mediated carbonylation could be determined as k=0.219 min^{-1}.

In conclusion, we have demonstrated a novel SERS-based strategy for the in-situ monitoring of palladacycle-mediated carbonylation through rationally designing and preparing nanoplatforms of AuNPs/PCs. The nanoplatforms integrated with SERS activity and reaction mediability enabled the direct in-situ investigation of the mechanism of the palladacycle-mediated carbonylation process by observing SERS spectrum variation. Moreover, the kinetic parameter of the reaction could also be obtained on basis of the relationship between the relatively ratiometric peak intensities and the reaction time. Therefore, the proposed SERS method demonstrated great promise for studying the mechanism of the palladacycles-catalyzed/or -mediated reaction in situ and noninvasively.

Acknowledgements

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