



Single-Atom Catalysis Hot Paper

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Probing Single-Atom Catalysts and Catalytic Reaction Processes by Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy

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Abstract: Developing advanced characterization techniques for single-atom catalysts (SACs) is of great significance to identify their structural and catalytic properties. Raman spectroscopy can provide molecular structure information, and thus, the technique is a promising tool for catalysis. However, its application in SACs remains a great challenge because of its low sensitivity. We develop a highly sensitive strategy that achieves the characterization of the structure of SACs and in situ monitoring of the catalytic reaction processes on them by shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) for the first time. Using the strategy, Pd SACs on different supports were identified by Raman spectroscopy and the nucleation process of Pd species from single atoms to nanoparticles was revealed. Moreover, the catalytic reaction processes of the hydrogenation of nitro compounds on Pd SACs were monitored in situ, and molecular insights were obtained to uncover the unique catalytic properties of SACs. This work provides a new spectroscopic tool for the in situ study of SACs, especially at solid-liquid interfaces.

Single-atom catalysts (SACs) with unique electronic properties and maximum atom utilization have become a new frontier in the field of heterogeneous catalysis and have attracted widespread attention.^[1] The unsaturated coordination environment of single atoms (SAs) has been proved by theory and experiment to be beneficial for various reactions including CO oxidation,^[2] water-gas shift reaction,^[3] oxidation of alcohols,^[4] chemoselective hydrogenation,^[5] and so on.^[6] To reveal the reaction mechanism of the smallest catalytic unit in catalytic processes, it is necessary to develop in situ experimental technologies for the identification of single-atom structure and real-time monitoring of reaction processes.^[7]

Recently, various in situ technologies have been applied for exploring the reaction mechanism, such as Fourier trans-

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form infrared spectroscopy (FTIR), ambient pressure X-ray photoelectron spectroscopy (AP-XPS), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), X-ray absorption spectroscopy (XAS).^[8] These in situ measurements play a key role in improvement of our understanding of the catalytic reaction.^[9] Nevertheless, we still lack a simple, economical, and efficient technique to identify SACs, and even study the reaction processes on SACs in situ.^[7a,10] As a molecular vibration spectroscopy, Raman spectroscopy can provide fingerprint information of substances,^[11] and shows great advantages in the study at solid-liquid interfaces and the detection of species at low-wavenumber regions, such as oxygen species and hydroxy. However, normal Raman can only monitor the structure information of the bulk catalyst owing to the low sensitivity, impeding the application of Raman spectroscopy on SACs. Surfaceenhanced Raman spectroscopy (SERS) possesses extremely high sensitivity and can provide a variety of structural information of trace species on the catalyst surface.^[12] However, only a few metals such as Au, Ag, and Cu with nanostructured surfaces can generate strong Raman signal enhancement.^[13] Limited by this condition, it is difficult to directly apply SERS to SACs due to the demand of metal oxide or other materials as the support to stabilize single atoms.

Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) has been developed as a new generation of spectroscopy, focusing on higher sensitivity and wider universality.^[14] In SHINERS, Au nanoparticles (NPs) with Raman enhancement effect are evenly coated by ultra-thin shells to form shell isolation nanoparticles (SHINs).^[15] The extremely strong electromagnetic field between SHINs can greatly enhance Raman signals.^[16] The shells in SHINERS not only isolate the influence of Au core, but also serve as the support to stabilize single atoms, making SHINERS a promising tool to study catalytic reaction over SACs. However, to date, implementing SHINERS to investigate the single atoms on the surface of metal oxides is urgently desired but remains challenging.

Herein, we achieve the characterization of SACs and in situ study of catalytic processes on SACs using Raman spectroscopy for the first time through the construction of Au-core TiO₂-shell SACs-satellite (SHINERS-SACs-satellite) nano-composite. Atomic layer deposition (ALD) is employed to coat a very thin layer of TiO₂ or Al₂O₃ on the surface of Au NPs with strong Raman enhancement capability. Atomically dispersed Pd is then deposited on the shell surface of SHINs (Figure 1 a,b). The Pd nucleation process from single atoms to NPs is identified by SHINERS using

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Figure 1. Illustration of the a) synthesis and b) Raman enhancement of SHINERS-SACs-satellite nanocomposites. c) TEM image of Au@TiO₂ SHINs. d) TEM images and e) element maps of a single particle of SHINERS-NPs-satellite structures.

phenyl isocyanide (PIC) as a probe molecule. Moreover, the hydrogenation of nitro compounds on Pd SACs is monitored in situ using SHINERS. Compared with Pd NPs, SACs significantly affect the interactions between the nitro group and the active sites thus change the catalytic performance.

The SHINs were prepared by an improved ALD method to coat uniform shells on Au NPs (Supporting Information, Figures S1 and S2). As shown in Figure 1c and Figure S3, TiO_2 and Al_2O_3 are evenly and completely coated on the surface of Au, respectively. Figure S4 shows the high-resolution TEM (HRTEM) image of Au@TiO2. The lattice spacing of 0.35 nm corresponds to the (111) plane of TiO₂. Then, single-atom Pd was deposited on the surface of SHINs by a wet-chemical method using NaBH₄ as the reduction agent and $[Pd(NH_3)_4](NO_3)_2$ as the Pd precursor, respectively. By adjusting the amount of NaBH₄ and $[Pd(NH_3)_4](NO_3)_2$, atomically dispersed Pd or particles can be loaded on the surface of SHINs. Figure 1d clearly shows the core-shellsatellite architecture of a single particle of Au-core TiO₂-shell Pd-NPs-satellite (SHINERS-NPs-satellite) structures, which is further demonstrated by the element maps in Figure 1 e and the HRTEM image in Figure S5.

The existence of the large Au core in the SHINERS-SACs-satellite nanocomposites greatly influences the characterization results of the single-atom structure by aberrationcorrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and XAS. Therefore, to sufficiently characterize the atomic-level dispersed Pd, we prepared Pd single atoms on titanium dioxide (Pd₁-TiO₂) by the same method. Typical TEM images clearly illustrate that Pd NPs did not exist in the as-synthesized Pd_1 -TiO₂ (Figure S6a). Further elemental mapping analysis confirms that Pd species are evenly dispersed in TiO₂ (Figure S6b).

We further performed the HAADF-STEM measurements for Pd_1 -TiO₂ to verify the single-atom Pd. As shown in Figure S6c, individual Pd atoms, which were observed as bright spots, were uniformly dispersed on the surface of TiO₂. Moreover, the electronic and coordination structures of Pd₁-TiO₂ were determined by X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) profiles. As shown in Figure 2a, the energy absorption edge profile of Pd K-edge for Pd1-TiO2 is close to PdO, indicating that the valence of Pd in Pd₁-TiO₂ is ca. +2. Figure 2b shows the Fourier transform of k3-weighted EXAFS in the R-space of Pd1-TiO2. According to the reference spectra of PdO and Pd foil, the signals at 1.53 Å and 2.49 Å are attributed to Pd-O and Pd-Pd coordination, respectively. Figure 2b clearly demonstrates that only Pd-O but no Pd-Pd coordination exists in Pd₁-TiO₂. The signals in 2.55 Å may be attributed to Pd-Ti coordination. This implies there exists a strong metal support interaction between Pd and $\text{TiO}_2.^{[17]}$ Therefore, it can be concluded that Pd is atomically dispersed in Pd₁-TiO₂.



Figure 2. a) Pd K-edge XANES and b) EXAFS spectra in the R-space of Pd₁-TiO₂, Pd foil, and PdO.

Due to the low sensitivity of normal Raman spectroscopy, it is extremely challenging, if not impossible, to employ it to investigate SACs. Fortunately, in the SHINERS-SACs-satellite nanocomposites, the Raman signals from the single-atom sites can be efficiently amplified by the SHINs, allowing the Raman studies of SACs. Thus, we further characterize the SACs by SHINERS using PIC as a probe molecule. PIC can be adsorbed on the surface of Pd via Pd-C≡N interactions by adopting top or bridge configurations.^[18] In the case of atomically dispersed Pd, only top adsorption can be observed in Raman spectra.^[19] Otherwise, when Pd exists in the form of NPs, the adsorption of PIC is dominated by bridge adsorption. Thus, it is feasible to determine Pd SAs and Pd NPs by monitoring the vibration frequency of the N≡C bond of PIC.

Figure 3 a displays the SHINERS spectra of PIC adsorbed on Pd SACs and NPs. The Raman peaks at 1001 and 1590 cm⁻¹ are assigned to the in-plane ring deformation vibration and C=C stretching vibration of the benzene ring in PIC, indicating PIC can be adsorbed on both Pd SAs and NPs. As for the Pd NPs, the peaks at 2028 and 2130 cm⁻¹ are ascribed to N=C adsorbed on Pd surface with bridge ($v_{N=C(Pd)-bridge}$) and top ($v_{N=C(Pd)-atop}$) configurations, respec-



Figure 3. a) SHINERS spectra of PIC adsorbed on Pd SAs and NPs. b) Illustration of Raman studies of the growth of Pd species from SAs to NPs. SHINERS spectra during the growth of Pd on c) $Au@TiO_2$ and d) $Au@Al_2O_3$ SHINs.

tively. In the case of SACs, only the peak at higher wavenumber is observed, meaning that the PIC molecules are adsorbed on single-atom Pd with the top configuration. These results demonstrate that single-atom catalysts can be identified by constructing a SHINERS-SACs-satellite structure with Raman spectroscopy.

Furthermore, the nucleation and growth process of Pd on TiO₂ from SAs to NPs are monitored using SHINERS (Figure 3b; for further detail, see the Supporting Information). As shown in Figure 3c, with the increase of the reaction time, the structure of Pd changes significantly. When the Pd nucleation proceeds for 2.5 min, only the Raman band at 2129 cm⁻¹, which is attributed to the linear adsorption of PIC on Pd, can be observed, indicating the formation of Pd SAs. The bridge PIC at 2028 cm⁻¹ gradually appears when the nucleation proceeds for 15 min, implying the co-existence of Pd NPs and Pd SAs. With the further increase of the nucleation time, the intensity of the bridge PIC peak gradually increases whereas the intensity of atop PIC decreases. These results illustrate that Pd SAs are first formed during the synthesis, but they would further grow to Pd NPs with increasing reaction time. Moreover, redshift of the PIC Raman band is observed with the growth of Pd NPs, which may result from stronger $d-\pi^*$ backdonation between PIC and Pd.^[18c]

As Pd SAs are stabilized by the oxide support, the properties of the oxide would strongly affect the structure of Pd species during the synthesis. Therefore, we also investigate the growth of Pd on Al_2O_3 , which is a widely used inert support that has much weaker interactions with Pd compared to TiO₂. As shown in Figure 3 d, similarly to that on TiO₂, only

the linearly adsorbed PIC at 2120 cm^{-1} can be observed before 2.5 min, meaning that Pd can also form SAs on the Al₂O₃ shell. The slight shift of the N=C Raman band compared to that in Pd₁-TiO₂ implies that the interactions of Pd with Al₂O₃ is different from that with TiO₂. However, the bridge PIC peak at 2014 cm⁻¹ appears at 5 min and progressively rises, demonstrating the growth of Pd SAs to NPs. Notably, the time of the formation of Pd NPs on Al₂O₃ is less than 5 min, which is much lower than that on TiO₂ (≈ 15 min). These results confirm that TiO₂ is a better support to stabilize Pd SAs compared to Al₂O₃. The improved stability results from the strong-metal support interaction (SMSI).^[20] In comparison, the inert surface properties of Al₂O₃ make it has a much weaker binding ability with metal atoms.^[21]

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As mentioned above, in situ monitoring of the reaction process on SACs is of significant importance but still very challenging. Considering the strong Raman enhancement effect in the SHINERS-SACs-satellite nanocomposites, we then employ them to monitor the hydrogenation of *para*nitrothiophenol (pNTP) to *para*-aminothiophenol (pATP) directly in situ (Figure 4a). The Raman peaks at 1337 and 1570 cm⁻¹ are attributed to the symmetric nitro stretching vibration and the characteristic vibration of the benzene ring of pNTP, respectively, and the peak at 1586 cm⁻¹ are assigned to the characteristic vibration of the benzene ring of pATP. With the increase of the hydrogenation reaction time, the Raman peak of the nitro group of pNTP decreases rapidly,



Figure 4. a) Diagram and in situ SHINERS spectra of the hydrogenation of pNTP over Pd SACs under H₂ at 80 °C. b) Time-dependent intensity of the Raman band of pNTP at \approx 1337 cm⁻¹ during the hydrogenation of pNTP on Pd SACs at different temperatures. c) Arrhenius plot and the apparent activation energy for the hydrogenation of pNTP over Pd SACs and NPs. d) In situ SHINERS spectra and a depiction of pNTP adsorbed on Pd SACs and NPs.

while the vibration peak of the benzene ring gradually shifts from 1570 to 1586 cm⁻¹. This change indicates that pNTP is effectively reduced to pATP.

To quantitatively evaluate the catalytic kinetics, pNTP hydrogenation on Pd SACs has been studied in situ by SHINERS at different temperatures. Figure 4b shows the plot of the normalized Raman peak intensity of -NO2 at 1337 cm⁻¹ as a function of reaction time. It clearly demonstrates that the hydrogenation of pNTP on Pd follows the first-order kinetics, and the rate constant increases with the reaction temperature. According to the Arrhenius plots in Figure 4c, the reaction rates for Pd NPs are higher than that for Pd SACs at all tested temperatures, while the apparent activation energy is slightly smaller than that for Pd SACs. To reveal the fundamental reason of this difference, we further compare the Raman spectra of pNTP adsorbed on Pd SACs and NPs (Figure 4d). It is found that the Raman band of the symmetric stretching vibration of -NO₂ for pNTP adsorbed on Pd NPs redshifts by $\approx 5\ \text{cm}^{-1}$ compared with that on Pd SACs. The redshift of the -NO₂ Raman band indicates the O-N=O bond is weaker on Pd NPs thus is apt to be hydrogenated. This can be explained by the different geometric effects of Pd SACs and NPs. As shown in the inset of Figure 4d, pNTP is adsorbed on Pd SACs via the Pd–S bond, making the -NO₂ group away from the catalyst surface, thus weakening the interactions between pNTP and the catalyst. However, in Pd NPs, the -NO₂ group can be effectively activated by nearby Pd atoms, leading to a weaker O-N=O bond and better hydrogenation performance.

In summary, a highly sensitive Raman strategy has been developed to characterize the structure of SACs and to monitor the reaction process on them in situ through constructing the SHINERS-SACs-satellite nanocomposites. Pd SAs are deposited on the surfaces of Au shell-isolated NPs with TiO₂ or Al₂O₃ shells. The oxide shells can stabilize the Pd SAs, while the Au cores can greatly amplify the Raman signals. The obtained Pd SAs are confirmed by aberrationcorrected HAADF-STEM and XAS. Using such a strategy, the nucleation process of Pd species from single atoms to NPs is identified by Raman spectroscopy. Moreover, the reaction process and kinetics of the hydrogenation of nitro compounds on Pd SACs are monitored in situ. Compared with Pd NPs, SACs significantly affect the interactions between the nitro group and the active sites thus change the catalytic performance. This work illustrates that SHINERS can be developed as a new technique for the in situ characterization and study of SACs.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: catalytic hydrogenation · in situ spectroscopy · nanoparticles · SHINERS · single atoms

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