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In-situ SHINERS study of the size and composition effect of Ptbased nanocatalysts in catalytic hydrogenation

Chen Wang,^[a] Xing Chen,^[a] Tian-Ming Chen,^[a] Jie Wei,^[a] Si-Na Qin,^[a] Ju-Fang Zheng,^{*[b]} Hua Zhang,^{*[a]} Zhong-Qun Tian,^[a] and Jian-Feng Li^{*[a],[c]}

Abstract: Understanding the structure-activity relationship of catalytic reactions at a molecular level still remains a great challenge. Herein, shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) is employed to in-situ study the catalytic hydrogenation of para-nitrothiophenol (pNTP) on Pt-based nanocatalysts with different size and composition. The nanocatalysts are assembled on pinhole-free shell-isolate nanoparticles (SHINs), which work as Raman amplifiers to enhance the Raman signals of species on the catalysts, allowing the in-situ monitoring of catalytic reactions carried out on the catalysts. Using this strategy, we find that the catalytic activity of the Pt nanocatalysts shows a volcanic trend with the Pt size, and that PtM (M = Ni or Cu) bimetallic nanocatalysts display much higher performance compared with Pt due to better activation of the nitro group. This work demonstrates that SHINERS is a promising technique for in-situ study of nanocatalysis thus can deepen the understanding of the behaviors of different catalysts.

In-situ study of catalytic reaction processes is essential for the fundamental understanding of reaction mechanism and the structure-activity relationship thus would promote the rational design of efficient catalysts.^[1] The development of various characterization techniques has led to the rapid growth of this field. For example, X-ray photoelectron spectroscopy(XPS)^[2] and scanning tunneling microscopy(STM)^[3] have been used for the *in-situ* characterization of the fine structure of catalysts under working conditions. With the help of these techniques, the influence of the size,^[4] morphology,^[5] and composition^[6] of nanocatalysts on the catalytic performance have been extensively investigated.^[7]

Recently, surface-enhanced Raman spectroscopy (SERS) has been employed to *in-situ* monitor the catalytic reactions.^[8] SERS has ultrahigh surface sensitivity due to the electromagnetic and chemical enhancement generated by the

[a]	C. Wang, X. Chen, T. M. Chen, J. Wei, S. N. Qin, Dr. H. Zhang, Prof.
	Z. Q. Tian, Prof. J. F. Li
	College of Materials, Fujian Key Laboratory of Advanced Materials,
	MOE Key Laboratory of Spectrochemical Analysis and
	Instrumentation, State Key Laboratory of Physical Chemistry of Solid
	Surfaces, <i>i</i> ChEM, College of Chemistry and Chemical Engineering,
	Xiamen University
	Xiamen 361005, China
	E-mail: Li@xmu.edu.cn; zhanghua@xmu.edu.cn
[b]	J. F. Zheng
	Key Laboratory of the Ministry of Education for Advanced Catalysis
	Materials, College of Chemistry and Life Sciences
	Zhejiang Normal University
	Jinhua 321004, China
	E-mail: jfzheng@zjnu.cn
[c]	Prof. J. F. Li
-	Shenzhen Research Institute of Xiamen University, Shenzhen 518000,
	China

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Au or Ag nanostructures,^[9] allowing *in situ* study the catalytic reactions carried out on their surfaces.^[10] The intermediate species and kinetics of the reaction, as well as the effect of the morphology and composition of the catalysts on them, can be studied in depth using *in-situ* SERS.^[11] However, only a few metals (gold, silver and copper, *etc.*) have strong SERS enhancement. Though a borrowing strategy has been developed to expand SERS to other transition metals.^[12] it still remains a great challenge to *in-situ* monitor reactions catalyzed by transition-metal nanocatalysts.

To overcome this limitation, our group developed a universal spectroscopic technique named shell-isolated nanoparticleenhanced Raman spectroscopy (SHINERS).^[13] In this technique, the Au core works as the Raman signal amplifier and is coated with an ultrathin but pinhole-free silica shell to isolate the interference of the Au core. SHINERS overcomes the long-standing limitations of SERS in materials and morphologies, so it has been widely used in electrochemistry, materials science, life science, energy storage and conversion, *etc.*^[14]

In this work, SHINERS has been used to *in-situ* study the size and composition effect of Pt-based nanocatalysts towards catalytic hydrogenation. The nanocatalysts are uniformly self-assembled around the shell-isolated nanoparticles (SHINs) through electrostatic interaction to form SHINERS-satellite nanocomposites. Using such nanocomposites, the influence of the size and composition of the platinum nanocatalyst on the hydrogenation of *para*-nitrothiophenol (pNTP) to *para*-aminothiophenol (pATP) are investigated by *in-situ* SHINERS. This work demonstrates that the SHINERS-satellite strategy can be a general strategy for various catalytic reactions.



Figure 1. (a) Schematic illustration of the SHINERS-satellite nanocomposite and its application in the *in-situ* study of the hydrogenation of pNTP. (b) TEM image of the Pt-SHIN nanocomposite. (c) Comparison of the Raman signals of pNTP adsorbed on the Pt-SHIN nanocomposites and silica supported Pt nanoparticles.

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The schematic illustration of the SHINERS-satellite strategy is shown in Figure 1a. The nanocatalysts are uniformly selfassembled around the SHIN, which consists of Au cores and pinhole-free silica shells. The fabrication of the SHINERSsatellite nanocomoposite is achieved through a charge-induced self-assemble method,^[15] in which the surface of the nanocatalysts are modified by NOBF₄ to be positivity charged while the SHIN is negtively charged. Figure 1b shows TEM image of the as-prepared Pt-SHIN nanocomposites. The size of the Au cores is ~120 nm, while the thickness of the silica shell is ~2 nm. Pt nanoparticles with a mean diameter of ~3.7 nm are uniformly assembled on the surface of the Au@SiO₂ SHINs. Since the nanocatalysts are directly located within the electromagnetic field enhancement range of the SHINs, the Raman signal on the nanocatalysts surface can be greatly enhanced. This can be verified through the comparison of the Raman signals of pNTP adsorbed on the Pt-SHIN nanocomposites and Pt nanoparticles supported on silica. As dispalyed in Figure 1c, strong Raman signals of pNTP can be clearly observed for the Pt-SHIN nanocomposites, while such signals completely disappear for the silica supported Pt nanoparticles.

The SHINERS-satellite nanocomposite is used to study the size and composition effect of Pt-based nanocatalysts in the hydrogenation of pNTP to pATP. To achieve this goal, the nanocatalysts with different size and composition were first prepared. The Pt nanocatalysts with a size of ~3.7 nm was first prepared (Figure 2a and Figure S1a) and used as the seed for the growth of Pt nanoparticles with larger sizes. Figures 2b-d and Figures S1b-d display the TEM imanges and correponding size distributions of Pt nanoparticles with larger sizes, which clearly exhibit that homogeneous Pt nanoparticles with mean sizes of ~5.0 nm, ~6.8 nm, and ~8.0 nm are successfully prepared via such a seed-mediated growth method. Furthermore, we also prepared PtCu and PtNi nanocatalysts to investigate the composition effect on the hydrogenation of pNTP. Figures 2e and 2f show that PtCu and PtNi bimetallic nanoparticles with near-spherical morphology are obtained.



Figure 2. TEM images of Pt nanocatalysts and the corresponding size histograms of (a) \sim 3.7 nm, (b) \sim 5.0 nm, (c) \sim 6.8 nm, (d) \sim 8.0 nm. Scale bar, 20 nm. (e)TEM image of PtCu bimetallic nanocatalyst. Scale bar, 50 nm. (f) PtNi bimetallic nanocatalyst. Scale bar, 20 nm.

The Pt nanoparticles with different sizes are then assembled on SHINs and used in the hydrogenation of pNTP. The Pt-SHIN nanocomposites with pNTP were deposited on a silicon wafer, which was then put in a home-made Raman cell for the in situ SHINERS study. Figures 3a-d display the in-situ SHINERS spectra of the hydrogenation of pNTP on Pt nanocatalysts with a size of 3.7, 5.0, 6.8, and 8.0 nm, respectively. In the Raman spectra, the band at 1331 cm⁻¹ is assigned to the -NO₂ stretching vibration of pNTP, and the band at 1571 cm⁻¹ and 1586 cm⁻¹ are C-C stretching vibration of the benzene ring of pNTP and pATP, respectively.^{[8],[16]} Such assignments are also confirmed by the Raman spectra of bulk pNTP and pATP (Figure S2). From the result, we can see that as time goes on, the band at 1571 cm⁻¹ gradually decreases while the band at 1586 cm⁻¹ increases for all the catalysts (as shown Figure S3a, such a trend can also be observed for 3.7 nm Pt when the reaction time is prolonged to 1400 s). Further control experiments performed under Ar atmosphere show that the C-C stretching vibration of the benzene ring of pNTP remain almost unchanged (Figure S3b). Such results indicate that pNTP can be hydrogenated to pATP under the catalysis of Pt nanoparticles. Furthermore, no Raman peaks for p,p'-dimercaptoazobenzene (DMAB) (at ~1140, 1390 and 1435 cm⁻¹) are observed, suggesting that the silica shell can isolate the influence of the Au cores on the reaction.[16]

The SHINERS spectra of Pt nanoparticles with different sizes clearly show that the reaction rate of pNTP hydrogenation is strongly dependent on the Pt size. As the Pt size increases form 3.7 nm to 8.0 nm, the conversion diplays a volcanic trend, and 6.8 nm Pt nanocatalysts exhibits the best catalytic performance (Figure S4). Such results imply that the hydrogenation of pNTP is a structure sensitive reaction. As pNTP is adsorbed on Pt via the Pt-S bond, the nitro group would be far away from the Pt surface, if the Pt size is too small, thus cannot participate in the hydrogenation reaction. On the other hand, Pt with too large size are well coordinated thus cannot efficiently activate hydrogen.



Figure 3. In-situ SHINERS spectra of the hydrogenation of pNTP on Pt-SHIN nanocomposites with different Pt size. (a) 3.7 nm. (b) 5.0 nm. (c) 6.8 nm. (d) 8.0 nm. Reaction conditions: 25 °C and H₂ at a flow rate of 10 mL/min.

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Figure 4. In-situ SHINERS spectra of the hydrogenation of pNTP under using (a) Pt-SHIN, (b) PtCu-SHIN, and (c) PtNi-SHIN, respectively. (d) The corresponding conversion of pNTP as a function of reaction time. (e) The O-N-O stretching vibration band of the pNTP absorbed Pt, PtCu and PtNi.

Bimetallic nanocatalysts usually tend to have better catalytic activity compared with pure metals.^[17] Therefore, we have also fabricated PtCu-SHINs and PtNi-SHINs nanocomposites, and further investigated the catalytic performance of the bimetallic nanocatalysts towards the hydrogenation of pNTP. As shown in Figure S5, both PtCu and PtNi nanoparticles are successfully attached on the surface of SHINs, forming homogeneous SHINERS-satellite nanocomposites. The time-resolved SHINERS spectra of Pt, PtCu, and PtNi nanocatalysts for hydrogenation of pNTP are displayed in Figures 4a-c. The bimetallic nanocatalysts show much higher activity than that of Pt. The hydrogenation of pNTP to pATP on the bimetallic nanocatalysts almost completes in 100 s (the activity of PtNi is slightly higher than that of PtCu), while the conversion for Pt is less than 20% (Figure 4d).

To reveal the reason for the higher activity of the bimetallic nanocatalysts compared the Pt, the adsorption of pNTP on these catalysts were carefully studied. As shown in Figure 4e, the O-N-O stretching vibration band of the pNTP absorbed the bimetallic nanocatalysts display a significant red shift compared with the pure Pt nanocatalyst, indicates the strengthen of the O-N-O bond of pNTP on these catalysts follows the order of Pt>PtCu>PtNi. This indicates that the superior performance of the bimetallic nanocatalysts may result from the surface electronic structure changes after introducing Cu or Ni,^[18] which promotes the activation of the $-NO_2$ group in the pNTP and weakens the strength of the N-O bond.

In summary, Pt and bimetallic Pt nanocatalysts are assembled on SHINs through electrostatic interactions to form the SHINERS-satellite nanocomposite, thus allowing the in-situ monitoring the reaction processes occurring on the catalysts. Using such nanocomposites, the size effect of Pt nanocatalysts on the hydrogenation of pNTP has been studied. As the size increases, the catalytic activity first increases then decreases, leading to an optimized size of ~6.8 nm. The reaction kinetics of PtCu and PtNi bimetallic nanocatalysts have also been in-situ investigated using SHIENRS and compared with the pure Pt nanocatalyst. It is found that the bimetallic nanocatalysts display much higher activity than that of Pt. According to the SHINERS study, such an improvement should result from the more efficient activation of the -NO2 group on the bimetallic nanocatalysts. This work not only uncover the kinetics of the hydrogenation of pNTP on Pt-based nanocatalysts with different size and composition. but also extends the SHINERS for the in-situ study on various catalysts.

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Experimental Section

Synthesis of SHINs

The SHINs were synthesis according to the previous work done by our group.^[13] Briefly, 120 nm Au nanoparticles were first prepared with a seed-mediated growth method (see Supporting information for details). Then, 0.4 mL of 1 mM fresh (3-aminopropyl) trimethoxysilane (APTMS) and 3.2 mL 0.54 wt% sodium silicate were added to 120 nm Au nanoparticles sequentially. The mixed solution was stirred at room temperature for 15 min and then heated to 90 °C to coat the silica shell on the Au nanoparticles.

Synthesis and self-assembly of Pt-based nanoparticles on SHINs

Pt, PtCu, and PtNi nanoparticles were first prepared (see Supporting information for details). The as-prepared nanoparticles were washed twice with ethanol, then dispersed in a 0.1 M NOBF4/acetonitrile solution to modify the surface to be positively charge. Then the nanoparticles were added to SHINs that are dispersed in acetonitrile, and ultrasonicated for 30 min. After that, the mixture solution was centrifuged. The supernatant was removed and the precipitate was dropped on a silicon wafer for further Raman measurement.

In-situ Raman study

The as-prepared silicon wafer was soaked in a 10 mM pNTP/ethanol solution for 30 min, allowing pNTP to be adsorbed on the Pt-based nanoparticles. The silicon wafer was then washed with clean ethanol for at least 3 times to remove the physically adsorbed pNTP, and dried at room temperature. The treated silicon wafer was put into a home-made Raman cell for *in-situ* study. First, the gas in the pipeline was purged with Ar, then H₂ is introduced to start the hydrogenation reaction, while the Raman signals were recorded in real time. The conversion of pNTP is calculated according to the change of the Raman intensity of pNTP (the Raman band at 1331 cm⁻¹). The Raman experiments were carried out by using the Jobin-Yvon Horiba Xplora confocal Raman system with an objective that has a numerical aperture of 0.55. The laser power is ~ 1.5 mW, and the laser was defocused ~25 µm.

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Keywords: SHINERS • in-situ study • catalytic hydrogenation • platinum-based nanocatalysts • size and composition effect

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Shell-isolated nanoparticles enhanced Raman spectroscopy (SHINERS) has been employed to reveal the size and composition effect of Pt-based nanocatalysts towards the hydrogenation of pNTP.



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