

Coherent acoustic phonon vibration of hexagonal Pd nanosheets and Ag/Pd/Ag sandwich nanoplates

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[Introduction] Pd and its hybrid nanostructures have attracted attention over the last decade owing to their unique catalytic and plasmonic properties. The electron and phonon properties directly govern conversion efficiencies in applications by using these nanostructures as energy collectors and photocatalysts. We report the dynamic processes of electron-phonon scattering and coherent acoustic phonon vibration of hexagonal Pd nanosheets and Ag/Pd/Ag sandwich nanoplates by transient absorption spectroscopy. Our results represent an understanding of electron and phonon kinetics of Pd and its hybrid nanostructures, including the spatially confined electron scattering and the transformation of phonon vibrational mode.

[Experimental] Hexagonal ultrathin Pd nanosheets and Ag/Pd/Ag sandwich nanoplates were synthesized following the procedures reported in the literatures.^{1,2} Pd nanosheets were prepared in an aqueous solution of Palladium(II) acetylacetonate by using carbon monoxide as both reducing agent and surface-confining agent. Ag/Pd/Ag nanoplates were achieved by epitaxial growth of Ag shells, reduced from AgNO₃ with methanal solution, on both sides of Pd nanosheets. Eleven sandwich nanoplates were prepared and named as Ag/Pd/Ag A ~ K with increasing the Ag contents. Transient absorption spectroscopy was performed with 800 or 400 nm excitation and detected in near-IR or visible region, corresponding to the LSPR of the samples. Numerical calculations were conducted for the simulations of LSPR and structural mechanics.

[Results and discussion] TEM images of hexagonal ultrathin Pd nanosheets and two typical Ag/Pd/Ag sandwich nanoplates are shown in Figures 1a-c. The schematics for the three kinds of samples are plotted in Figure 1d. Edge length and thickness of Pd nanosheets were estimated to be 27.3 ± 3.0 and 1.8 ± 0.3 nm. With

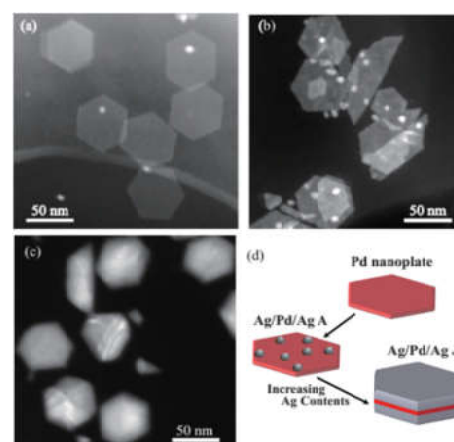


Figure 1 TEM images of Pd nanosheets (a) and Ag/Pd/Ag sandwich nanoplates with two different Ag contents labeled as Ag/Pd/Ag A (b) and Ag/Pd/Ag J (c). Schematics of the three nanostructures (d).

adding a little amount of Ag source into Pd nanosheet solution, Ag ions were reduced and Ag nanospheres were formed on the surfaces of Pd nanosheets, which cannot form a complete Ag shell as shown in Figure 1b for Ag/Pd/Ag A. With more increasing the Ag content, continuous Ag shells were formed on Pd nanosheets as shown in Figure 1c for Ag/Pd/Ag J. The edge lengths of all the nanoplates were similar to that of Pd nanosheets while the thicknesses became larger with increasing Ag contents, which were determined by inductively coupled plasma mass spectroscopy.

As shown in Figure 2a, electron-phonon coupling constant of Pd nanosheets $G_{\text{Pd-nanosheet}}$ ($8.7 \times 10^{17} \text{ Wm}^{-3}\text{K}^{-1}$) became larger as compared to the bulk G_{Pd} ($5.0 \times 10^{17} \text{ Wm}^{-3}\text{K}^{-1}$), which results from spatially confined electron scattering.³ Effective G_{eff} of

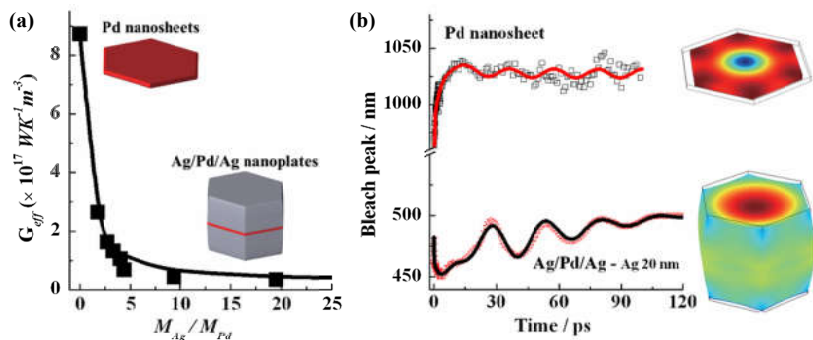


Fig. 2 Dependence of effective electron-phonon coupling constant G_{eff} on the molar ratio of Ag and Pd from the experimental data and the calculated results (a), and dynamics of the bleach peak in TA spectra of Pd nanosheets and Ag/Pd/Ag J sandwich nanoplates with ~ 20 nm Ag shell thickness (b)

Ag/Pd/Ag nanoplates reduces with increasing Ag shell thickness, finally approaching to the bulk G_{Ag} ($0.25 \times 10^{17} \text{ Wm}^{-3}\text{K}^{-1}$).⁴ The contribution of each component to the G_{eff} was explained with a reduced density of state near Fermi level in Pd nanosheets owing to the quantum confinement effect associated with their 1.8 nm ultrathin thickness. The dynamics of bleach peak of Pd nanosheets and Ag/Pd/Ag nanoplates were obtained by Gaussian fitting to the TA spectra. The results for Pd nanosheets and Ag/Pd/Ag J are shown in Figure 2b. Combined with the numerical calculations of structural mechanics, coherent acoustic phonon vibration of ultrathin Pd nanosheets was assigned to a fundamental breathing mode, similar to the vibration of benzene molecule. The period increases with increasing Ag shell thickness. For Ag/Pd/Ag nanoplates with 20 nm Ag shell thickness, the vibrational mode was ascribed to a quasi-extensional mode. The results show the mode transformation of the coherent acoustic phonon vibration with the geometric variation of Pd nanosheets and Ag/Pd/Ag nanoplates.

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