Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Direct SERS tracking of a chemical reaction at a single 13 nm gold nanoparticle

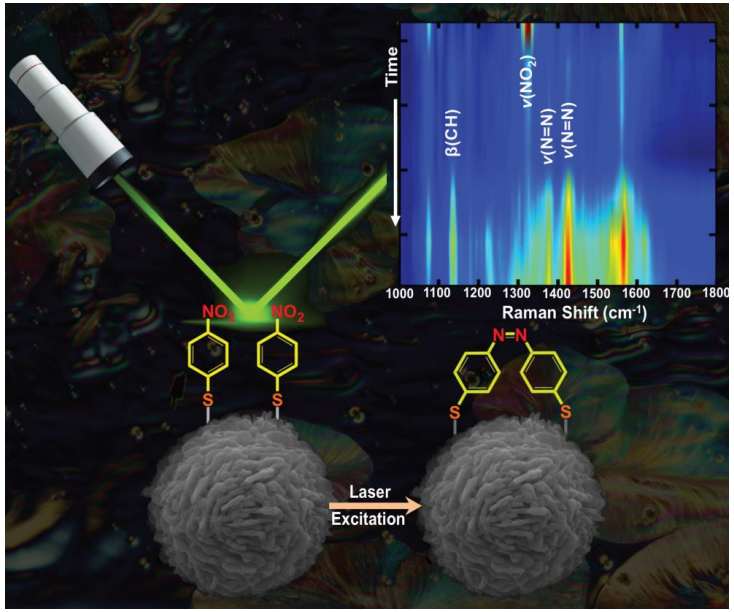
Kun Zhang, Yujie Liu, Yuning Wang, Jingjing Zhao and Baohong Liu

Department of Chemistry, Shanghai Stomatological Hospital, State Key Lab of Molecular Engineering of Polymers, and Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai 200433, China

Chem. Sci., 2019, 10, 1741–1745 | 1741

Tripti Ahuja
13/07/19

Background work



ChemComm

RSCPublishing

COMMUNICATION

View Article Online
View Journal | View Issue

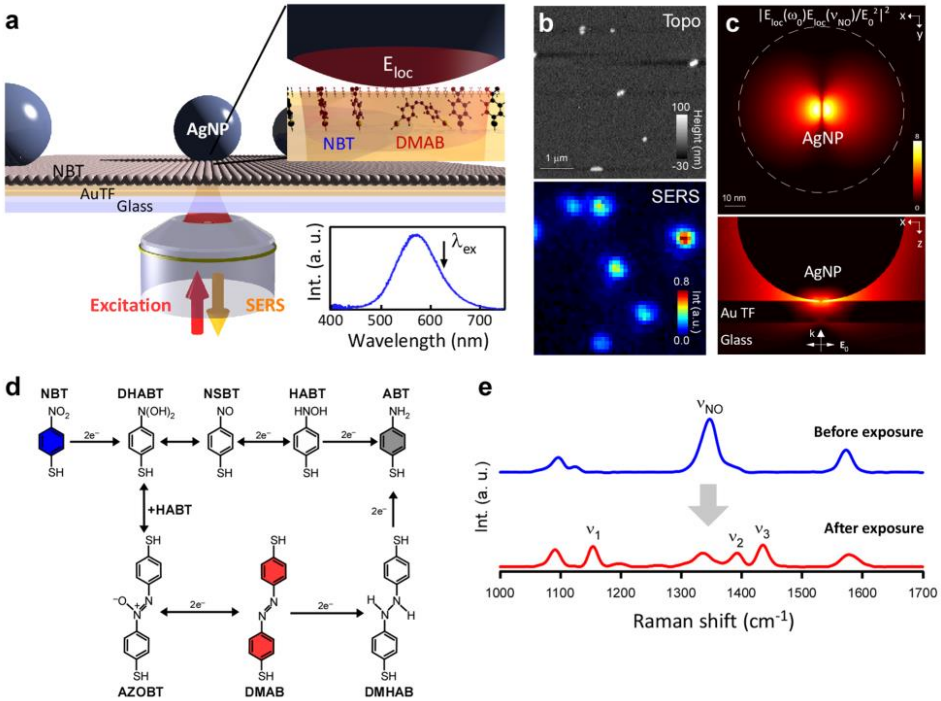
Laser wavelength- and power-dependent plasmon-driven chemical reactions monitored using single particle surface enhanced Raman spectroscopy†

Leilei Kang,[a] Ping Xu,*[ab] Bin Zhang,[a] Hsinhan Tsai,[b] Xijiang Han*[a] and Hsing-Lin Wang*[b]

Cite this: *Chem. Commun.*, 2013, **49**, 3389

Received 29th January 2013,
Accepted 13th February 2013

DOI: 10.1039/c3cc40732b



J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

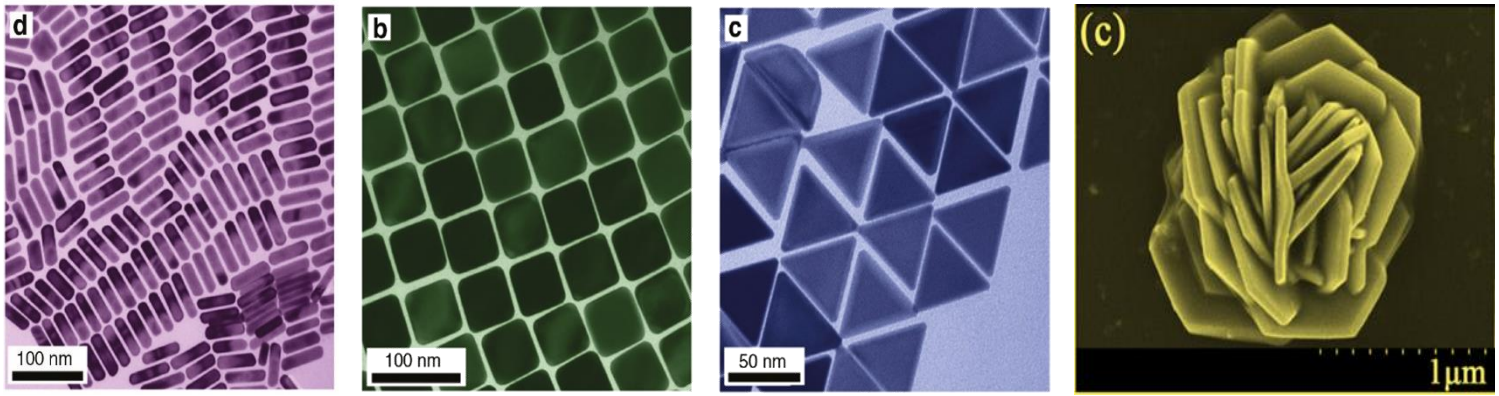
Metal-Catalyzed Chemical Reaction of Single Molecules Directly Probed by Vibrational Spectroscopy

Han-Kyu Choi, Won-Hwa Park, Chan-Gyu Park, Hyun-Hang Shin, Kang Sup Lee, and Zee Hwan Kim*

Department of Chemistry, Seoul National University, Seoul 08826, Korea

Relevance to lab…

❖ Anisotropic nanomaterials such as cubes, triangles and spheres, structural heterogeneity and chemical reactions can be looked at a single particle level using existing DFM assisted SERS technique.



❖ Ag@PET NPs can be dimerized with other anisotropic NPs for fabrication of nanostructures with better functionality.

❖ Electrospray droplet science can also be integrated with single particle SERS to shed more light on droplet distribution and plasmonics.

In this paper…

✓ Direct SERS observation of the chemical transformation catalyzed by a single 13 nm S-GNP in aqueous solution.

✓ Well-isolated S-GNP-molecule-L-GNP dimer nanostructures with three components in the molecular layer were designed.

✓ Molecular layer include, a reactive molecule as the reaction substrate (4-NTP), an inert molecule as a Raman standard (2-NT), and a linker molecule (HDT) to form the GNP dimers.

✓ A promising model reaction of hydrogenation of 4-nitrothiophenol (4-NTP) in the presence of sodium borohydride was shown for SERS characterization and catalytic performance.

✓ Reaction kinetics of the redox reaction was quantified through dynamic spectral information.

✓ Compared the catalytic activity between different GNPs.

✓ Demonstrated the heterogeneity in reactivity of individual S-GNPs.

Results and discussion

Preparation and characterization of bifunctional GNP dimers

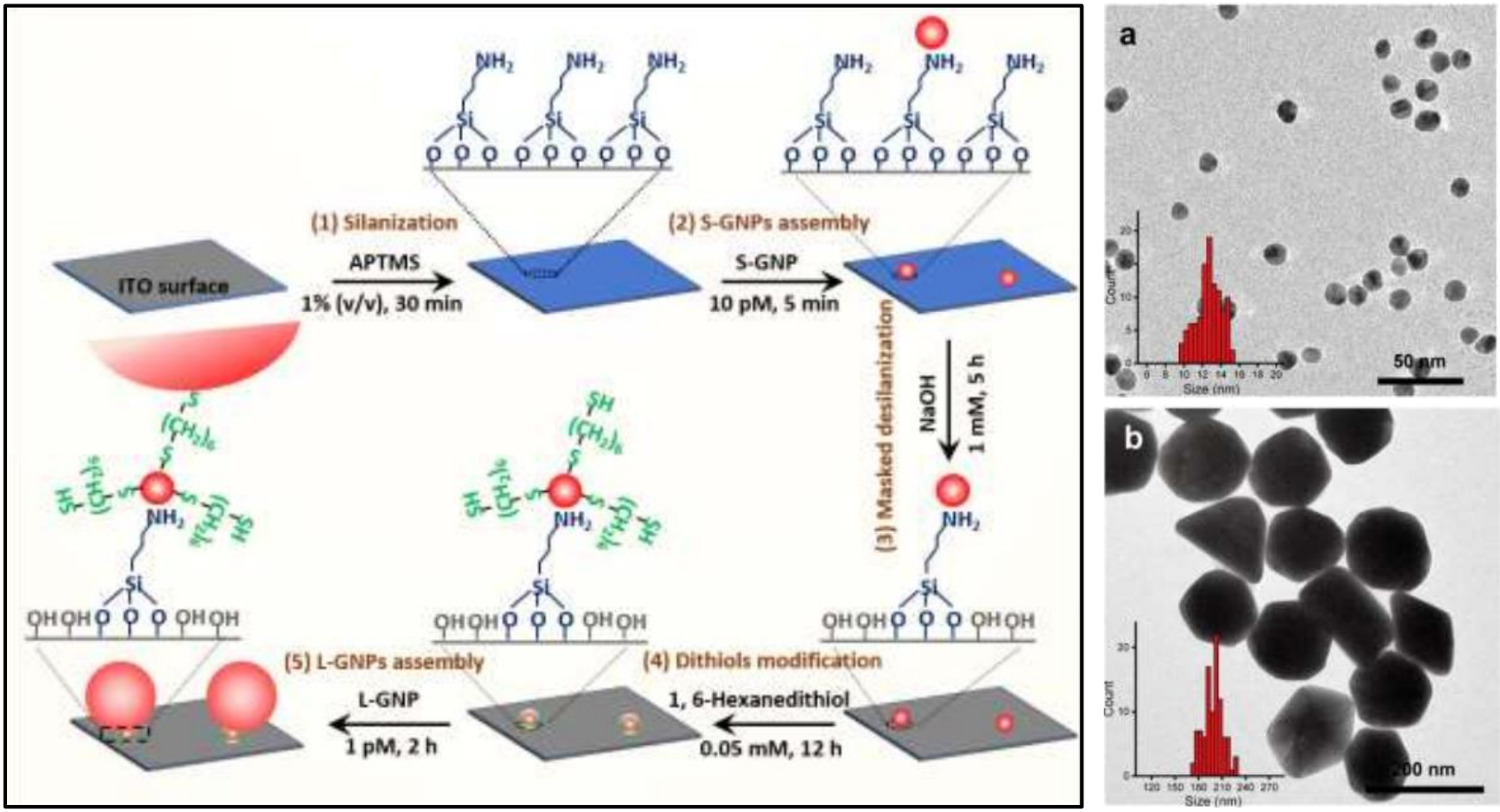


Figure 1. Schematic illustration for stepwise dimer assembly using masked desilanization. Representative TEM images of (a) the S-GNPs and (b) L-GNPs dried on a carbon film coated Cu-based grid. The average sizes for the S-GNPs and L-GNPs were found to be 12.8 ± 2.5 nm and 198.6 ± 12.4 nm.

Results and discussion

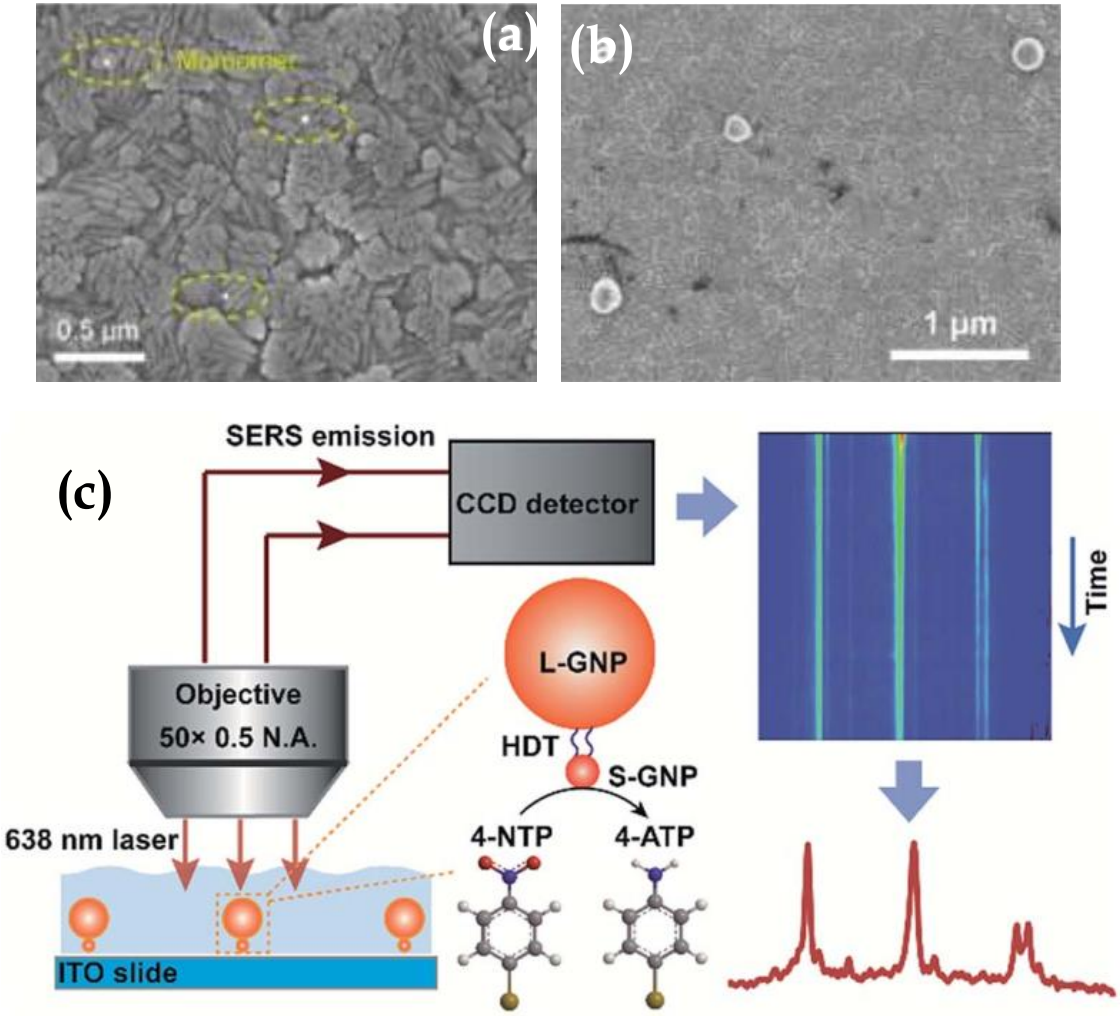


Figure 2. Representative SEM images showing the distribution of the (a) S-GNPs, and (b) GNP assemblies, on the surface of the ITO slide. (c) Illustration of *in-situ* SERS tracking of catalytic reactions at single 13 nm GNPs. Spatially isolated dimers, each of which consists of a single L- and S-GNP bridged by 1,6-hexanedithiol (HDT), are electrostatically immobilized on the indium tin oxide (ITO) glass surface. 4-Nitrothiophenol (4-NTP) is chemically reduced to 4-aminothiophenol (4-ATP) under the catalysis of a single 13 nm S-GNP.

Results and discussion

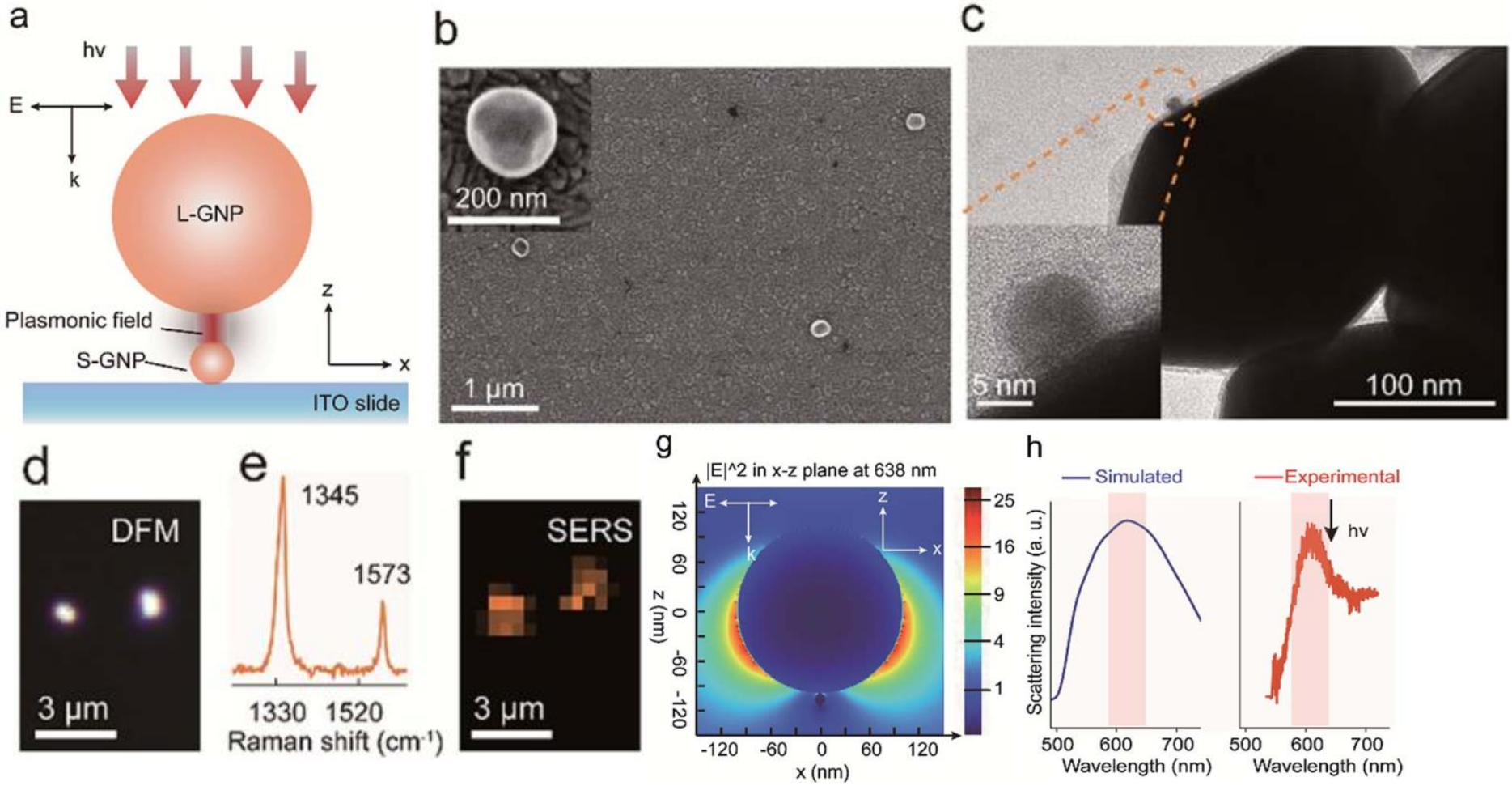


Figure 3. (a) Schematic diagram showing the configuration of a L-GNP/S-GNP dimer linked with 1,6-hexanedithiol. (b) SEM and (c) TEM images of the dispersed GNP dimers. The insets show a magnified view of a typical GNP dimer. (d) DFM image of two isolated GNP assemblies. (e) SERS spectrum of 4-NTP measured from an isolated GNP dimer. (f) SERS image of the same assemblies shown in (d), constructed by using the intensity of the 1345 cm^{-1} peak of 4-NTP in (e). (g) FDTD calculation showing the local electric field distribution of the GNP dimer at the X–Z plane. (h) Scattering spectrum of a single GNP dimer.

Results and discussion

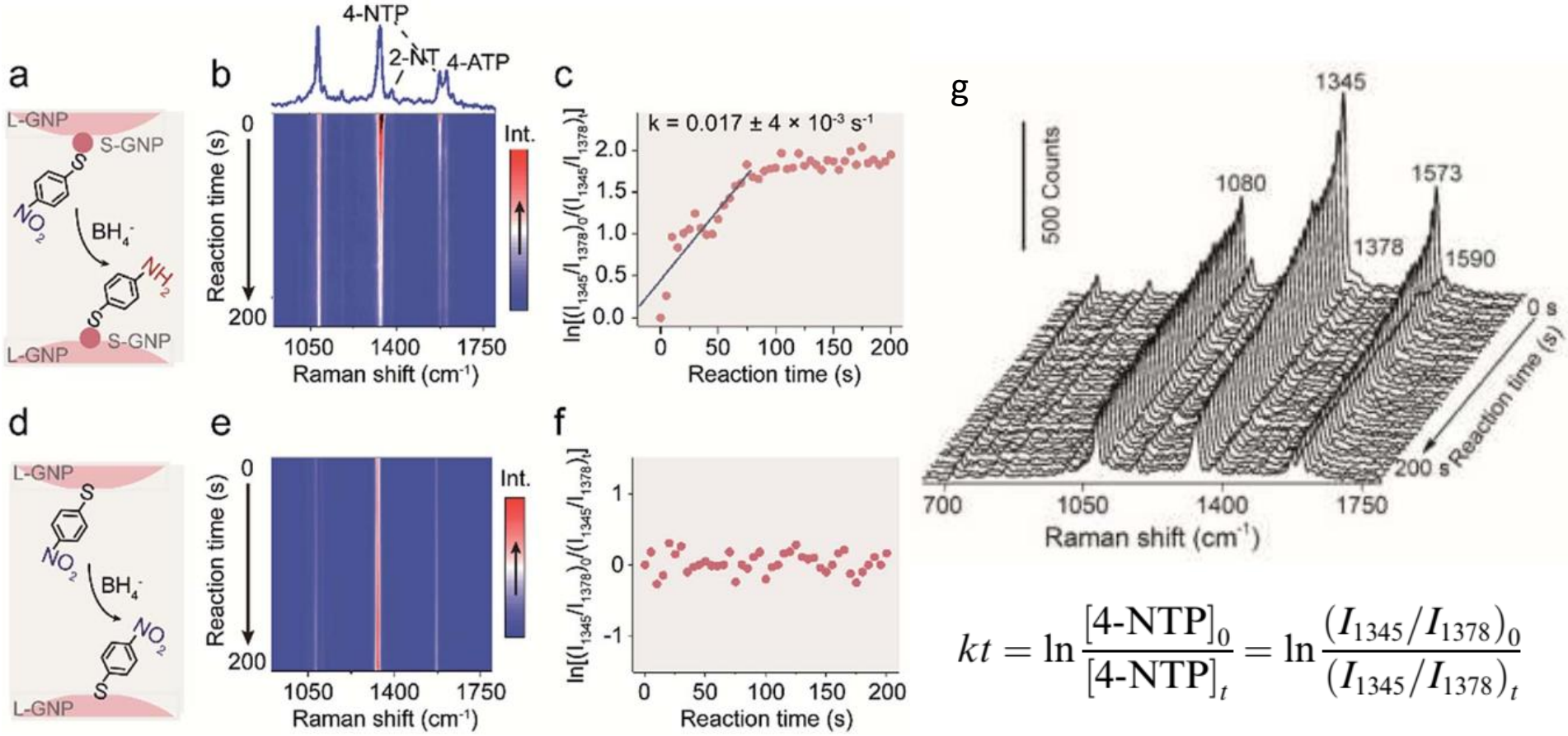


Figure 5. (a) Schematic illustration showing the S-GNP catalysed reduction of 4-NTP in the presence of borohydride. (b) Colour-coded intensity map of time-dependent single-NP SERS spectra after borohydride addition, with a range of Raman shifts between 900 cm^{-1} to 1800 cm^{-1} for a 1 s integration time, taken every 5 s at 638 nm. (c) Plot of ln[(I1345/I1378)0/(I1345/I1378)t] versus time for the determination of the rate constants for the reduction process with spectra shown in (b). (d) Schematic illustration and (e) colour-coded intensity map of time dependent single-NP SERS spectra without borohydride addition. (f) Plot of ln[(I1345/I1378)0/(I1345/I1378)t] versus time. (g) Time dependent SERS spectra depicting the catalytic conversion of 4-NTP to 4-ATP at single 13 nm S-GNP.

Results and discussion

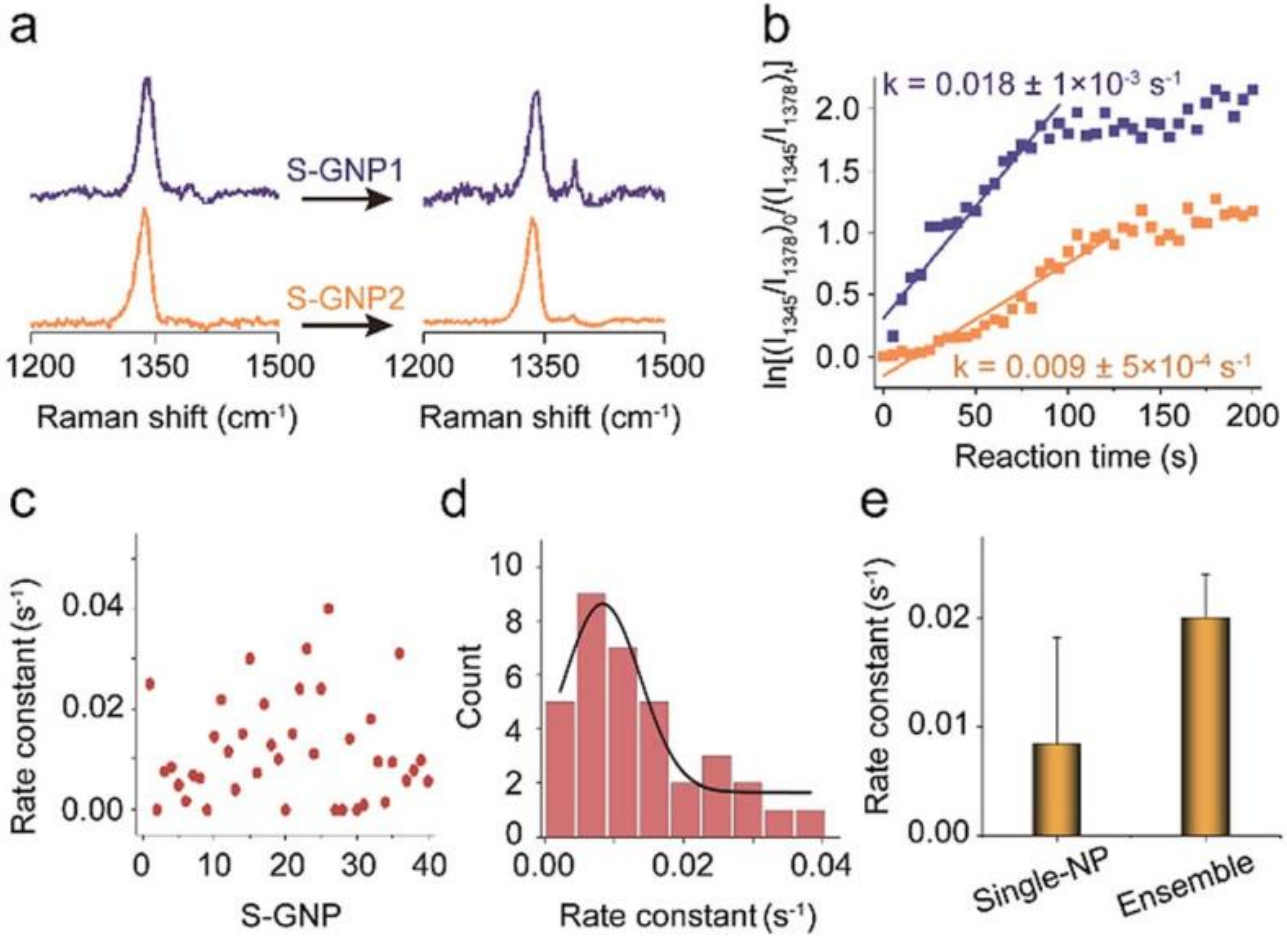


Figure 5. (a) SERS spectra corresponding to two different catalysts discussed in the main text, S-GNP1 and S-GNP2, before (0 s) and 60 s after the addition of borohydride for a 1 s integration time, taken every 5 s at 638 nm. (b) Plot of ln[(I1345/I1378)0/(I1345/I1378)t] versus time for the determination of the rate constants for the reduction process with the S-GNPs shown in (a). (c) Rate constants obtained from 40 S-GNPs and (d) their statistical distribution. (e) Comparison between the average rate constant obtained from the single nanoparticle measurement with that from the ensemble measurement by assembling the densely packed S-GNPs on the amino functionalized Si wafer.

Conclusions

✓ Direct SERS observation of surface catalytic reactions at single 13 nm S-GNPs in aqueous solution.

✓ S-GNP were bridged with L-GNP using HDT (weak Raman scattering molecule).

✓ Integrated SERS and catalytic activities into a single GNP dimer nano-assembly.

✓ In-situ tracking of the redox process.

✓ Quantifying the apparent rate constants for different nanocatalysts.

✓ Analyzing the average catalytic kinetics of multiple S-GNPs.

✓ Comparing single particle kinetics with the ensemble measurements.

✓ Revealing a large particle-to-particle variability in the catalytic property, using SERS trajectories and measured rate constants and attributed to the structural heterogeneity.

THANK YOU