A single-particle SERS system enabling real-time and \textit{in situ} observation of Au-catalyzed reactions has been developed. Both the catalytic activity and the SERS effect are coupled into a single bi-functional 3D superstructure comprising Au nanosatellites self-assembled onto a shell-insulated Ag microflower core, which eliminates the interference from photocatalysis.

Much effort has recently been devoted to the study of metallic nanoparticle (NP) catalyzed reactions driven by its potential applications in diverse areas, as well as its fundamental importance in elucidating reaction mechanisms and evaluating the catalyst performance at the nanoscopic level.\textsuperscript{1–4} Among others, the employment of surface enhanced Raman scattering (SERS) as a versatile tool for \textit{in situ} characterization of reaction processes is especially attractive because of its high sensitivity, surface-selectivity and water transparency.\textsuperscript{5–7} Many distinct strategies have been reported to fabricate bifunctional (integration of catalytic and SERS activities) nanostructures, such as Au/Pt core/shell nanorods, Au/Au core/satellite NPs, and polycrylonitrile (PAN)/Ag-M (M = Au or Pd) nanofibers.\textsuperscript{8–13} While these well-dispersed nanoscale colloids have shown success to characterize the reaction process \textit{in situ}, it is hard to strike a good balance between high catalytic efficiency and SERS activity in individual NPs. The lack of sufficient SERS enhancement for individual particles would severely limit the temporal resolution of the assay, and thereby the elucidation of the reaction pathway. A recent study by Xie et al. showed that gold and silver nanoparticle monomers are non-SERS-active.\textsuperscript{14} Thus, the formation of NP clusters is frequently adopted to generate sensitive SERS interfaces in the fabrication of bi-functional platforms.\textsuperscript{15} This can lead to interference from the enhanced plasmon fields among the closely spaced neighboring NPs.\textsuperscript{16} Furthermore, the direct use of colloidal NPs as SERS media is still challenging due to their intrinsic thermodynamic instability, especially under harsh reaction conditions. In this context, a multifunctional single-particle platform would be highly advantageous for real-time tracing of reaction processes due to the improved plasmon-enhancing effect and stability.

Indeed, with the continuous progress in the synthesis of metallic micro/nanostructures, single-particle SERS system combining high sensitivity with much improved spatial resolution has attracted increasing attention in plasmonics and development of biological assays.\textsuperscript{17} It has been reported that the highly roughened surface of individual noble metallic particles, especially those made of silver, with irregular nanoscale protrusions and crevices can provide an unexpected plasmonic activity.\textsuperscript{18} Based on this property, single-particle SERS has been used as a promising tool for the investigation of surface plasmon-driven photocatalytic reactions.\textsuperscript{19–21} For example, Kang and co-workers demonstrated the laser wavelength- and power-dependent reduction of 4-nitrothiophenol (4-NTP) on the surface of single Ag particles.\textsuperscript{19} In spite of this, directly probing chemical reaction processes using single-particle SERS has not been achieved mainly because it is difficult to avoid the unwanted side reactions caused by the SERS substrate itself. In this work, we demonstrate the \textit{in situ} observation of chemical reactions catalyzed by Au NPs based on a single-particle SERS system which is ideal for probing chemical events at the particle surface without interference from the physical and chemical properties of neighboring particles. The approach relies on the rational preparation of hierarchical 3D superstructures (roughened surface) integrating a flower-like Ag microsphere and abundant catalytically active Au NPs. The SERS-active Ag core is isolated by an ultrathin silica shell to protect from a direct contact with the chemicals relating to the reaction. The dual function of such a single-particle platform was investigated for the reduction of 4-NTP to the corresponding aniline derivative 4-aminothiophenol (4-ATP) by recording the time dependent fingerprint signals of the reactants and products through SERS.
Scheme 1 depicts the synthesis of bifunctional Ag/Au 3D superstructures for single-particle SERS monitoring of Au nanosatellite-catalyzed chemical reactions in real time. Briefly, Ag microspheres were first prepared through a modified acid-directed wet-chemistry route. The SERS-active Ag particles were modified with (3-aminopropyl)trimethoxysilane (APTMS), followed by incubation with sodium silicate to form a thin layer of silica encapsulating the inner core. The obtained shell-isolated Ag microspheres were then reacted with (3-mercapto-propyl)-trimethoxysilane (MPTMS) to functionalize their surface with mercapto groups. Catalytically active Au NPs were subsequently mixed with the thiol-functionalized Ag particles and covalently attached on the particle surface via S–Au interaction (see experimental details in the ESI†).

The transmission electron microscopy (TEM) image in Fig. 1a shows that the as-prepared Ag microspheres are highly uniform and monodispersed with an average size of 3.1 ± 0.3 μm (Fig. S1, ESI†). The thickness of the silica shell coating around the Ag particle is about 2.5 nm (see Fig. 1b and S2, ESI†), which is very favorable for effective transfer of the strong electromagnetic field from the Ag core to the shell surface. This thin layer of silica can be further evidenced by performing scanning TEM (STEM) measurements (Fig. 1c). The intensities of Si and O signals are far less than that of Ag in the STEM images acquired and treated under the same conditions and, indicating that the amount of silica on the Ag surface is very small. The superimposed STEM image of the particle using the Ag, Si, and O signals shows that the silver surface is entirely covered by the inert silica shell (Fig. 1d). Although SiO₂-isolated Au (or Ag) NPs have been reported in the literature, to the best of our knowledge, this is the first example to facilely generate micrometer-sized metallic particles with an ultrathin and even layer of silica coating around their surface. It is also worth noting that the ultrathin and fully enclosed shell of silica around the Ag core plays crucial roles both in fabricating the superstructures and in elucidating the reaction mechanism. First, the thiol-terminated silica surface acts as a template for the Au NPs anchoring. Second, the silica shell prevents the Ag particle surface from a contact with the molecules involved in the reaction process. The elemental composition from the energy dispersive spectroscopy (EDS) measurement also reveals that the silica layer is successfully formed at the Ag surface (Fig. 1e).

After incubating with the thiol-functionalized Ag microspheres and removing the excess Au NPs, the plasmonic 3D superstructures were obtained. The scanning electron microscopy (SEM) image in Fig. 1f vividly shows the morphology of the single Ag/Au core/satellite particle. From the STEM images in Fig. 1g, it is also clearly observed that the small Au catalysts are evenly distributed on the surface of the silica-isolated Ag core. The hierarchical flower-like architecture is composed of Ag nanosheets, creating a nanoscale surface roughness. Very large abundant Au NPs are self-assembled on the particle surface as active dust (Fig. S3 and S4a, ESI†). The magnified SEM pictures demonstrate the local details of the microspheres (Fig. S4b–d, ESI†), where no obvious difference could be observed in the Au NP coverage from one microsphere to another.

The catalytic activity of the as-prepared 3D superstructures was first characterized with UV-vis spectroscopy by monitoring the conversion of 4-NTP to 4-ATP in solution. 4-NTP possesses a characteristic absorption band at around 410 nm, the intensity of which hardly changes with the addition of NaBH₄ only (Fig. S5, ESI†). Upon introduction of such Ag/Au superstructure particles into the mixed solution, the band intensity of 4-NTP decreased gradually, accompanied by the appearance of a new band at around 280 nm, indicating the reduction of 4-
NTP to 4-ATP (see Fig. 2a). A relatively long induction time can be observed at the first 150 s, which may be ascribed to the diffusion of the reactant molecules to the catalyst surface and the reconstruction of the catalyst nanoparticle surface during this period. Complete reduction was achieved within 6 min, as visually reflected by the color changes of the reaction media from yellow to colorless (data not shown). Since a large excess of NaBH4 relative to 4-NTP was employed in the experiment, the kinetics of the catalytic process could be treated as a pseudo-first order reaction. Fig. 2b shows the plot of the logarithm of the relative absorbance at 410 nm (ln(At/A0)) as a function of the reaction time. A reaction rate constant of 8.59 × 10−3 s−1 could thus be readily derived from the slope of the linear fitting response curve.

Having demonstrated the highly catalytic activity of such Ag/Au superstructures, we next investigated whether these plasmonic microspheres could be used as single-particle SERS sensors to probe chemical reactions occurring at the catalyst surface. Due to the specific features of the roughened surface and a good match between the particle size and the laser facula diameter, an individual superstructure can be facilely spotted under a Raman confocal microscope, allowing us to observe the reaction from a single particle surface without interference from the surrounding environment (e.g., surface plasmon field of neighboring particles), which is normally present on a flat substrate. The reduction of 4-NTP by NaBH4 was employed as a prototypical reaction to facilitate the study. After incubation with the Ag/Au assemblies to form a dense self-assembled monolayer (SAM) of 4-NTP molecules on the surface of the Au satellites, the microspheres were rinsed with ethanol and dispersed on a glass slide for SERS measurement. The conversion of 4-NTP to its corresponding aniline derivative was tracked by recording the time dependent SERS spectra of chemical species involved in the reaction (Fig. 3a). As can be seen from Fig. 3b, the SERS spectrum of 4-NTP exhibits two intense characteristic bands centered at 1334 cm−1 and 1567 cm−1, attributed to O–N–O symmetric stretching, and the phenyl-ring stretching modes, respectively. The result is consistent with the former study using a concept of shell isolated nanoparticle-enhanced Raman scattering, further confirming the complete encapsulation of the Ag core by the silica shell. In order to confirm that the observed SERS effect is mainly due to the silver core instead of the small gold nanoparticles, we conducted a control experiment by recording the SERS spectra of a molecular monolayer of 4-NTP adsorbed on the surface of a closely-packed assembly of the Au catalysts (Fig. S6, ESI†). It is found that the average spectral intensity was ten times less than that recorded from the single Ag/Au superstructure. Upon initiating the reaction with introduction of the NaBH4 aqueous solution (50 mM), the peak intensities of nitro groups gradually decreased with concomitant emergence of a new band centered at 1592 cm−1 due to the phenyl ring mode of 4-ATP. The whole reaction was complete within 220 s, as indicated by the complete disappearance of 4-NTP associated Raman bands. Moreover, the time evolution of SERS spectra of 4-NTP and its reduction product 4-ATP.

![Fig. 2](image_url) (a) Time-dependent absorption spectra showing the reduction of 4-NTP in the presence of Ag/Au 3D superstructures. (b) Logarithm of the relative absorbance (ln(At/A0)) at 410 nm as a function of the reaction time.

![Fig. 3](image_url) (a) Schematic diagram showing the reduction of 4-NTP to 4-ATP on the Au NP surface probed by single-particle SERS. Conditions: laser wavelength of 638 nm, laser power of ~0.24 mW, objective of 10× (N.A. = 0.24), integration time of 10 s for single spectrum with no accumulation. (b and c) Time-dependent SERS spectra showing the reduction progress of 4-NTP. (d) SERS intensities at 1567 cm−1 (4-NTP) and at 1592 cm−1 (4-ATP) as a function of reaction time.
The inert and fully enclosed silica shell prevents the molecules on the catalysts thus get enhanced Raman signals enhanced by a single isolated particle. Due to strong enough to protect the SAM from falling off the Au surface, the intensities of the two modes measured during the reactions were compared directly. And the relative concentration of each component in the mixed SAM was facely represented with the corrected intensity of the corresponding Raman mode, as demonstrated in Fig. 3d.

The spectral information acquired during the kinetic monitoring process can also help in elucidating the reaction mechanisms. Although the 4-NTP reduction to 4-ATP has been frequently chosen as a prototypical reaction in many studies such as metal-catalyzed hydrogenation and surface plasmon-induced reduction, there still remains ongoing debate about the underlying mechanism of the conversion process. For example, it is reported that the 4-NTP can undergo surface plasmon-induced dimerization to generate 4,4′-dimercaptoazobenzene (4,4′-DMAB) at the surface of metallic nanostructures, especially for Ag-based structures. In the present work, we did not observe the formation of azobenzenes as shown in the SERS spectra of Fig. 3b, suggesting that 4-NTP was converted directly to 4-ATP. In order to study the role of the inert silica shell which protected the Ag against the environment, a control experiment was carried out by synthesizing Ag/Au superstructures without isolating the thin silica layer. After formation of a SAM of 4-NTP on the metallic surface, SERS spectra were acquired under the same experimental conditions as described above. In this case, vibrational modes of 4,4′-DMAB at 1387 cm⁻¹ and 1428 cm⁻¹ were clearly observed possibly due to a plasmon-driven metal-to-molecule charge transfer mechanism (Fig. S7, ESIF). This result is consistent with previous studies in which 4-NTP is directly exposed to a bare Au/Ag surface with strong plasmonic activity. Therefore, it is concluded that the ultrathin layer of silica plays a critical role in the elimination of unwanted photocatalytic side reactions by preventing the direct interaction between the SERS-active Ag core and the reaction system.

In conclusion, we report a single-particle SERS system as an outstanding opportunity for in situ monitoring of Au-catalyzed reactions based on 3D plasmonic superstructures comprising a silica shell-isolated Ag microsphere core and plenty of catalytically active Au satellites assembled on the shell surface. The microscaled flower-like silver cores (~3.1 μm) with a hierarchical structure and roughened surface act as promising scaffolds for real-time reaction observation by recording time-dependent Raman signals enhanced by a single isolated particle. Due to an ultrathin thiol-terminated silica-shell spacer (~2.5 nm) coating on the Ag surface, the Au NP catalysts could be trapped within the local electromagnetic field of the SERS-active core through the Au-S bonding interaction, and the molecules on the catalysts thus get efficient Raman enhancement. The inert and fully enclosed silica shell prevents the direct contact between the SERS substrate and chemicals involved in the catalytic process, which effectively avoids interference from the photocatalytic side reaction. As a result, the catalyst performance and the reaction mechanism can be investigated in a real-time manner via such a single-particle based SERS platform. The present study provides a complementary means toward fabricating multifunctional plasmonic platforms and understanding the chemical reactions catalyzed by metallic nanoparticles.

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