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## Plasmon-Free SERS Self-monitoring of Catalysis Reaction on Au Nanoclusters/TiO<sub>2</sub> Photonic Microarray

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**Here, using (Au/TiO<sub>2</sub>)-catalyzed reduction of 4-nitrothiophenol as a probe reaction, catalysis/SERS bifunctional composite fabricated by uniformly dispersing catalysis-active Au nanoclusters (~2 nm) on SERS-active TiO<sub>2</sub> photonic microarray was successfully applied to the non-plasmonic SERS self-monitoring of catalytic reaction for the first time, which is superiorly sensitive and interference-free.**

Surface-enhanced Raman scattering (SERS) is a label-free and non-destructive analysis technique with fingerprint spectrum. When applied on monitoring a catalyzed reaction process, it can identify abundant surface/interface information including the surface structure, molecule bonding, configuration and orientation.<sup>1</sup> Exploring the molecular activation and chemical transformation processes on the surface of different catalysts is necessary to figure out the catalysis mechanism and finally guide the design of highly efficient catalyst system surface.<sup>2</sup> Coinage metals are well-known SERS-active substrate, so it is desirable that Au or Ag-catalyzed reactions can be self-monitored by SERS spectra. However, this idea has been unfortunately restricted by the incompatibility between SERS (particle size > 20 nm) and catalysis (particle size < 10 nm) activities.<sup>3</sup>

The combination of SERS-active plasmonic metal substrate and catalysis-active metal nanoparticles has been commonly used to achieve the SERS monitoring of a catalysis reaction.<sup>3a,4</sup> However, the photo- or thermo-induced side reaction caused by laser irradiation in plasmonic system has posed a big obstacle to the monitoring of a real reaction process,<sup>5</sup> which may become more complicated in "hot spot" areas with strong local surface plasmon resonance (LSPR) effect. The side reaction can be avoided on very few plasmonic metal SERS

substrate.<sup>6</sup> This kind of interference can be reduced by decreasing the power density, using the wavelength far from the LSPR region or introducing a thin inert shell between SERS-active substrate and catalysis-active nanoparticles (NPs).<sup>5a,7</sup> Different from the electro-magnetic enhancement by coinage metals, SERS signals observed from semiconductors such as TiO<sub>2</sub> and ZnO is due to chemical enhancement,<sup>8</sup> which is expected to be more effective on avoiding the interference caused by plasmon. It is known that reactions catalyzed by semiconductor-supported metals have improved catalysis efficiency through the coordination between metal and semiconductor.<sup>9</sup> Therefore, it is desirable that the reaction on metal/semiconductor can be SERS self-monitored. However, SERS from semiconductor has been not successfully applied to monitor a catalysis reaction due to its low sensitivity. Fortunately, we have recently revealed that TiO<sub>2</sub> in the form of ordered photonic array shows highly SERS activity by improving the light-matter coupling effect,<sup>10</sup> which triggered us to study whether catalytic reactions on TiO<sub>2</sub> supported metal can be SERS self-monitored.

In this study, Au nanoclusters (NCs, ~2 nm) supported on TiO<sub>2</sub> photonic array (Au NCs/TiO<sub>2</sub> photonic array) has been fabricated and applied to the catalytic reduction of 4-NTP in NaBH<sub>4</sub> solution. A quick and direct reaction process from 4-NTP to 4-ATP was successfully self-monitored by Au NCs/TiO<sub>2</sub> photonic array with slow light region matching with the incident laser wavelength (785 nm). This reaction has been intensively studied by SERS but there still remain some ambiguous and hardly resolvable points. 4-NTP can be accordingly reduced to 4-ATP in a direct way or through the formation of intermediate 4, 4'-DMAB.<sup>4</sup> However, a side reaction from 4-ATP to 4, 4'-DMAB caused by laser irradiation has also been commonly observed.<sup>3a,4-5,5c,11</sup> The situation may become more entangled in a plasmonic system with LSPR-induced heating effect and widened plasmonic resonance peak, significantly interfering the understanding about the mechanism of original reaction. Here, the side reaction is completely eliminated on Au NCs/TiO<sub>2</sub> photonic array by using 785 nm laser far from the intrinsic absorption band of Au NCs

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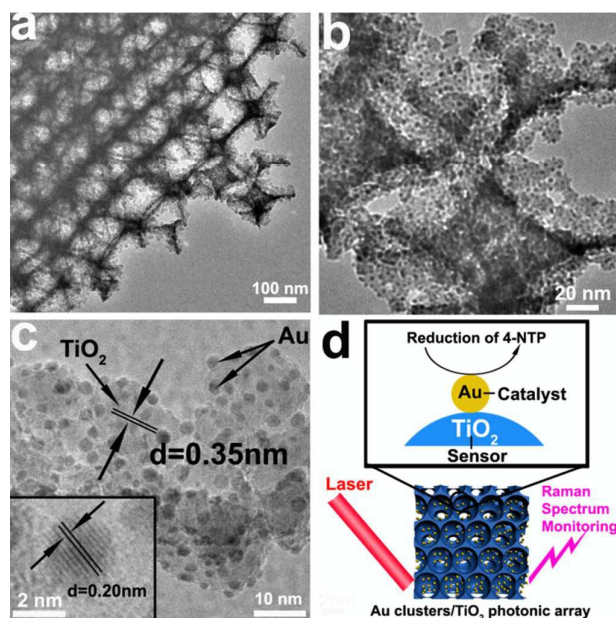


Fig. 1 TEM (a and b) and HRTEM (c) images of Au NCs/TiO<sub>2</sub> photonic array. The inset is the magnification of a Au NC. (d) Schematic diagram of Au NCs/TiO<sub>2</sub> photonic microarray.

and TiO<sub>2</sub>, resulting in the successful plasmon-free SERS self-monitoring of the real reduction process. In contrast, the side reaction cannot be avoided by Au NCs deposited on plasmonic Au NPs (Au NCs/Au NPs) under the same laser irradiation, leaving an ambiguous reduction process of 4-NTP on Au NCs/Au NPs.

TiO<sub>2</sub> inverse opal photonic microarray was prepared through impregnation-calcination procedure using closely packed polystyrene (PS) microarray as the hard template. Au NCs were first prepared using L-glutathione containing amide and mercapto groups as the ligand, and then loaded on TiO<sub>2</sub> microarray through impregnation. Transmission electronic microscopy (TEM) images indicate TiO<sub>2</sub> inverse opal has a 3D-interconnected macroporous structure (Fig. 1a) and high-density Au NCs are deposited on the macroporous framework (Fig. 1b). High-resolution TEM (HRTEM) image shows Au NCs are highly dispersed and have uniform size of about 2 nm (Fig. 1c). Two kinds of lattice fringes with spacing of 0.35 nm and 0.20 nm are observed, corresponding to the (101) plane of anatase TiO<sub>2</sub> and (200) plane of Au (inset in Fig. 1c), respectively. Fig. 1d presents a schematic model for this Au/TiO<sub>2</sub> composite to further illustrate the uniform combination of Au NCs and TiO<sub>2</sub> photonic microarray, which are responsible for the roles of catalysis and SERS detection, respectively.

Raman spectra of 4-NTP adsorbed on different substrates were first analyzed under the irradiation of 785 nm laser, which is far from the absorption edge of both Au NCs (~500 nm) and TiO<sub>2</sub> (~380 nm) to avoid the possible photocatalytic effect (Fig. S2). Two control experiments were carried out by using Au NCs and a commercial TiO<sub>2</sub> nanoparticle (P25) as the SERS substrates. Raman spectrum collected on Au NCs does

not show any peak (Fig. 2a), indicating the negligible plasmon resonance effect of Au NCs. Some signals can be observed from P25 but the intensity is extremely low. In comparison, 4-NTP on TiO<sub>2</sub> photonic array presents well-resolved Raman signals with a high peak at 1342 cm<sup>-1</sup>, which ascribed to the stretching mode of -NO<sub>2</sub>.<sup>3a</sup> SEM image indicates TiO<sub>2</sub> microarray has a highly interconnected and ordered macroporous structure with the pore size of ~350 nm (Fig. 2b). Based on our previous report, this pore size is chosen to achieve the highest detection sensitivity by maximizing the light-matter coupling effect.<sup>10</sup> As verified by UV-Vis reflectance spectrum, the macroporous microarray actually possesses a slow-light region near 785 nm (Fig. 2c). Similar to that on TiO<sub>2</sub>, the Raman signals observed from Au NCs/TiO<sub>2</sub> photonic array still preserve the high intensity, indicating the deposition of Au does not decrease the SERS-enhancing effect of ordered array. Moreover, it is noted that the peak attributed to -NO<sub>2</sub> is split into two peaks at 1342 cm<sup>-1</sup> and 1332 cm<sup>-1</sup>, where the latter new peak at 1332 cm<sup>-1</sup> should be ascribed to the -NO<sub>2</sub> stretching of 4-NTP adsorbed on Au.

The reduction of 4-NTP adopts NaBH<sub>4</sub> as the reducing agent. 4-NTP was first adsorbed on Au NCs/TiO<sub>2</sub> photonic array and then immersed into NaBH<sub>4</sub> solution for different times. The reaction process was monitored by SERS under the irradiation of 785 nm laser, where the characteristic peaks of 4-NTP and 4-ATP are marked by black square and pink triangle (Fig. 3c), respectively. The small peak at 1332 cm<sup>-1</sup> quickly disappears in the first one minute, indicating 4-NTP molecules adsorbed on Au surface are firstly reduced. In the next six minutes, the peaks around 1342 cm<sup>-1</sup> and 1114 cm<sup>-1</sup> gradually fade away, along with a shift of the peak at 1575 cm<sup>-1</sup> to 1585 cm<sup>-1</sup>, indicating 4-NTP molecules are completely reduced to 4-ATP.<sup>3a</sup>

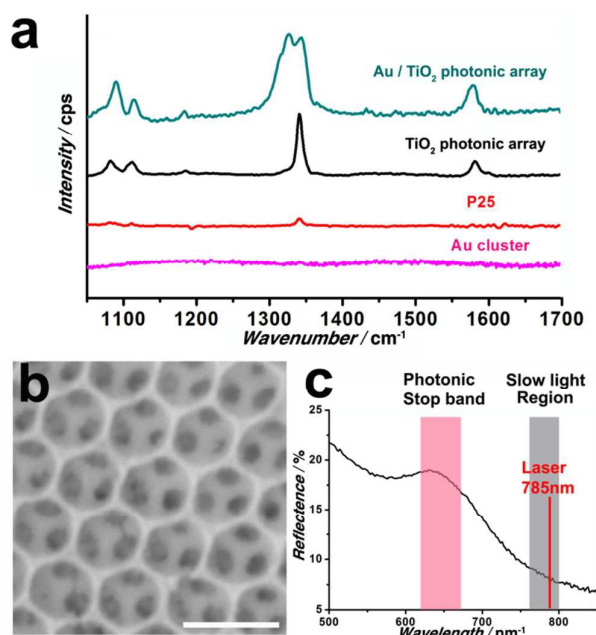


Fig. 2 (a) Raman spectra of 4-NTP adsorbed on different substrates, (b) SEM image of TiO<sub>2</sub> photonic array. The scale bar is 500 nm and (c) UV-Vis reflectance spectrum of TiO<sub>2</sub> photonic array.

To rule out the possible catalysis by  $\text{TiO}_2$ ,  $\text{TiO}_2$  photonic array without Au NCs was also used to monitor the reaction (Fig.S3), and the result indicates  $\text{TiO}_2$  has no catalytic activity to the reaction. Given that Au NCs are the only active sites, and 4-NTP molecules are adsorbed on both Au NCs and  $\text{TiO}_2$  surface. We consider that 4-NTP molecules on  $\text{TiO}_2$  surface can diffuse to the neighbor Au NCs and are reduced there.<sup>6b</sup> Because of the ultrahigh dispersion of Au NCs, the complete reduction is finally achieved. Moreover, Au NCs dispersed on  $\text{TiO}_2$  microarray shows good stability during catalysis since no particle growth is observed from the TEM image, while strong agglomeration occurs between non-loaded Au NCs (Fig. S4). To further reveal the reliability of the self-monitoring performance, Au NCs/Au NPs (Fig. 3b) fabricated by depositing Au NCs (~2 nm) on Au NPs (~20 nm) is also used for the plasmonic SERS monitoring of 4-NTP reduction, which however shows characteristic peaks of 4, 4'-DMAB (blue sphere) at 1145, 1391 and 1438  $\text{cm}^{-1}$  besides the signal of 4-ATP (Fig. 3d).<sup>11a</sup>

The generally accepted reduction mechanism of the nitroaromatic compounds is Haber scheme, in which two routes (direct route and condensation route) are proposed. In direct route, nitro group of 4-NTP is reduced into nitroso, hydroxylamine, and amino groups successively. In condensation route, an azobenzene compound is generated as an intermediate from the condensation of a nitroso compound and a hydroxylamine compound, and it is finally reduced into two amino compounds.<sup>9b, 12</sup> Therefore, 4, 4'-DMAB may be an intermediate product from the reduction of 4-NTP to 4-ATP, and it is possible that the absence of 4, 4'-DMAB signals on Au NCs/ $\text{TiO}_2$  is attributed to the complete reduction of 4-NTP on Au NCs/ $\text{TiO}_2$  photonic array. The concentration of 4, 4'-DMAB

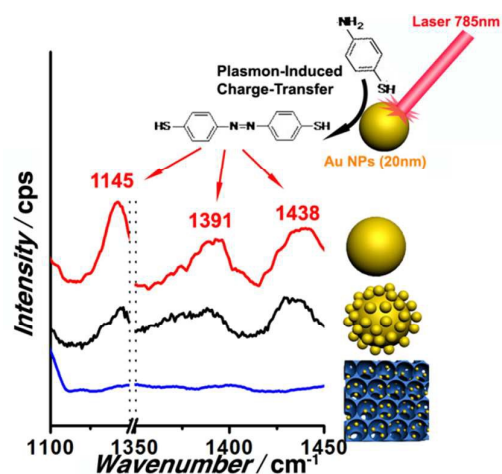


Fig. 4 Raman spectra collected from 4-ATP adsorbed on different substrates. Inset above is the scheme for laser-induced formation of 4, 4'-DMAB from 4-ATP on Au NPs.

can increase with the decrease of the reductant amount if 4-NTP is reduced to 4-ATP through the intermediate of 4, 4'-DMAB. However, no signal of 4, 4'-DMAB is observed with the decrease of the  $\text{NaBH}_4$  amount (Fig. S7), indicating 4, 4'-DMAB is not an intermediate product catalytically formed by Au NCs/ $\text{TiO}_2$ .

To acquire the accurate reason for the observation of different reduction products from Au NCs/ $\text{TiO}_2$  and Au NCs/Au NPs, the Raman spectra of 4-ATP are respectively recorded on Au NCs/ $\text{TiO}_2$  photonic array (Fig. 4, blue line), Au NCs/Au NPs (Fig. 4, black line) and Au NPs (Fig. 4, red line), assuming that 4-NTP molecules are completely reduced into 4-ATP. Signals attributed to 4, 4'-DMAB are clearly observed on Au NPs and Au NCs/Au NPs but are absent on Au NCs/ $\text{TiO}_2$  photonic array. The results demonstrate 4-ATP can be transformed to 4, 4'-DMAB under laser illumination in the presence of Au NPs, and the transformation may be caused by plasmon-induced charge transfer under the laser irradiation<sup>3a</sup>, because 4-ATP/Au NPs composite shows absorption at 785 nm (Fig. S8). In comparison, no photo-chemical side reaction is caused by Au NCs/ $\text{TiO}_2$  photonic array, indicating its reliability on self-revealing the catalytic kinetics. Therefore, our plasmon-free SERS substrate provides a good solution to the problem caused by plasmon-involved photochemical reaction, where the actual reduction process of 4-NTP is difficult to be distinguished in the presence of interference reaction from 4-ATP to 4, 4'-DMAB. To the best of our knowledge, this is the first successful demonstration of the plasmon-free SERS on  $\text{TiO}_2$  substrate used for the self-monitoring of catalytic reaction process.

In conclusion, plasmon-free substrate with Au NCs uniformly distributed on  $\text{TiO}_2$  photonic microarray was used for SERS self-monitored reduction of 4-NTP. The photonic microarray with macroporous size of 350 nm possesses enhanced coupling effect with incident laser of 785 nm, thus providing strong and well-resolved Raman signals for the reaction monitoring. Compared with plasmonic Au NCs/Au NPs, a higher catalytic activity and 100% selectivity for 4-ATP can be real-time revealed on Au NCs/ $\text{TiO}_2$  photonic array substrate

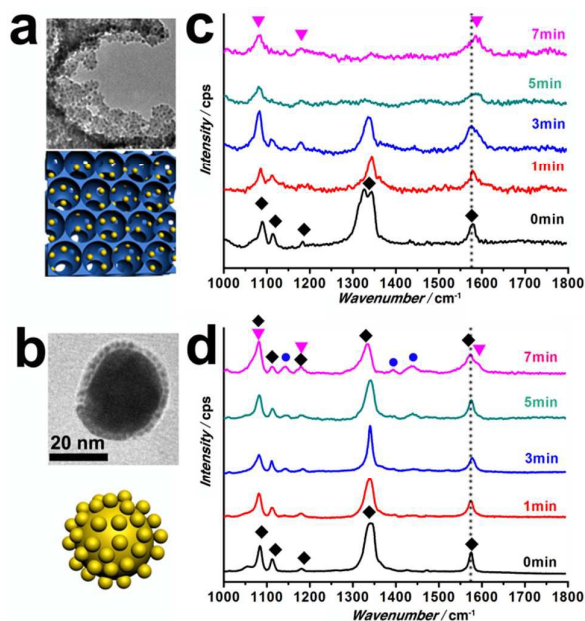


Fig. 3 TEM images and schemes of Au NCs/ $\text{TiO}_2$  photonic array (a) and Au clusters/Au NPs (b). Raman spectra for monitoring the reduction process of 4-NTP on Au NCs/ $\text{TiO}_2$  photonic array (c) and Au NCs/Au NPs (d). The characteristic peaks of 4-NTP, 4-ATP and 4, 4'-DMAB are respectively labelled by  $\blacklozenge$ ,  $\blacktriangledown$  and  $\bullet$ .



due to the effective screening of plasmon-involved photochemical side reaction from 4-ATP to 4, 4'-DMAB. We hope this study offer a useful reference for reaction monitoring by SERS on different semiconductor carriers.

## Notes and references

The authors declare no competing financial interest.

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