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## Structural Controls of AuNR@mSiO<sub>2</sub>: Tuning of the SPR, and Manipulations of the Silica Shell Thickness and Structure

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Research interests on pursuits of desirable longitudinal surface plasmon resonance (LSPR) of gold nanorod (AuNR) and suitable silica coating structure are two important parts concerning mesoporous silica-coated gold nanorod (AuNR@mSiO<sub>2</sub>). This paper reports a simple approach to not only tailor the LSPR of AuNR but also simultaneously control the structure and thickness of silica shell after the silica coating process. Under an acidic condition, the use of O<sub>2</sub> for ends-selective etching of internal AuNR shows a good control over the aspect ratio of AuNR, thus enabling the controllable tuning of the LSPR of AuNR@mSiO<sub>2</sub>. Comparing to other strong oxidant such as aqua regia, O<sub>2</sub> provides more mild and gentle etching atmosphere, which offers the etched AuNRs with good uniformity and regularity. Results showed that the thermal treatment of AuNR@mSiO<sub>2</sub> solution before the initiation of etching reaction had important impacts on the silica shell structure. Thermal treatment in ethanol solution gave rise to empty and open mesopores shell, and the use of ethanol-water as solvent witnessed thinning change of the shell thickness, while the internal AuNR was basically unaffected in both cases. Both the opening and reduced thickness of mesoporous silica shell facilitate the etching of AuNR. In addition, the rigid-type of mesoporous silica framework exposed in ethanol solution led to generation of cavities-possessed, rattle-type and hollow AuNR@mSiO<sub>2</sub> as etching proceeded; However, in ethanol-water solution, the silica shell gained certain extent of fluidity, resulting in moving of silica to fill the cavities created by ends-etching of internal AuNR.

### 1. Introduction

In the past two decades, gold nanorod (AuNR) attracted increasing attentions from researchers as owing to the unique property of surface plasmon resonance (SPR) and the related great potential it showed in various fields.<sup>1-5</sup> The collective oscillation of conduction band electrons along the length and radius of AuNR give rise to two modes of surface plasmon resonance: the longitudinal SPR (LSPR) and transverse SPR, of which the strong localized electromagnetic fields generated on the surface of AuNR show resonances absorptions of incident light in particular wavelengths.<sup>1-3</sup> Location of LSPR wavelength is sensitive to the surrounding medium, and can be tuned from visible to near-infrared (NIR) region by increasing the aspect ratio (length/diameter) of AuNR; while, the transverse SPR wavelength is fixed at about 510 nm.

Techniques to tailor the aspect ratio of AuNR spurred

continuing interest for the advantages of different LSPR showed in various applications. LSPR in NIR widow exhibits great practical potentials in biomedicine and theranostics<sup>1-5</sup> for the minimum absorption of light in this region from living tissue.<sup>6</sup> The conversion from strong LSPR absorption of light to heat can cause temperature rise in surrounding environment of AuNR, providing the promising application in killing cancer cells.<sup>7-12</sup> The strong light-scattering property at LSPR wavelength could also make the AuNR excellent candidate for biomedical labelling and imaging.<sup>10-12</sup> For instance, AuNR conjugated with anti-bodies can specifically bond to cancer cells, thus enabling the imaging of these cells.<sup>7,13</sup> Additionally, the requirement of spectra overlaps between LSPR and different fluorophores for SPR-enhanced fluorescence indicated the significance of management of LSPR in wide ranges.<sup>14-16</sup> To date, studies have shown that AuNR with different aspect ratios could be produced during the synthesis by managing reaction parameters<sup>1-3</sup> including pH of growth solution, concentration of Ag<sup>+</sup>, and so on. As a complement to synthesis-controlled protocol, management of the aspect ratio after synthesis is also available. Recently, Kozek *et al.*<sup>17</sup> and Scarabelli *et al.*<sup>18</sup> respectively reported methods for controlling the aspect ratio through secondary growth of AuNR, in which deliberate managements of the parameters of growth solution

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like concentration of ascorbic acid or addition of additive were needed. Besides, the after-growth controlling can also be realized in an etching way. Rodriguez *et al.*<sup>19</sup> reported that in cooperation with cetyltrimethylammonium bromide (CTAB), the weak oxidant of Au<sup>3+</sup> could selectively etch the AuNR from the ends, which suggested an efficient way for shortening control of AuNR. Tsung and co-workers<sup>20</sup> then demonstrated that under an acidic condition, O<sub>2</sub> could also oxidize the CTAB-protected AuNR in a selective way, and a rise in temperature could accelerate this process. The years followed have seen oxidant such as Fe<sup>3+</sup>,<sup>21</sup> and H<sub>2</sub>O<sub>2</sub><sup>22</sup> could lead to the same selective etching of AuNR.

For practical applications of CTAB bilayers-capped AuNR, modification of the bilayers is often required because of its poor biocompatibility and difficulty in full functionalization.<sup>1,2,4</sup> As one of the solutions, silica shell coating that is almost transparent in SPR bands can not only overcome these defects, but also improve the stability of the structure.<sup>12,23</sup> Mesoporous silica coating of AuNR<sup>24</sup> (AuNR@mSiO<sub>2</sub>) further provides the shell with enlarged loading capacity, as well as enables exposure of AuNR to the surrounding medium. The controllable silica shell thickness also offers an opportunity to adjust the distance from environment to surface of AuNR, to which a majority of SPR-involved applications are closely related. For examples, isolated by an ultrathin silica shell, Au nanoparticles used for surface-enhanced Raman scattering was able to enhance the characteristic spectra of various molecules in a high quality, providing the technique with much higher detection sensitivity and vast application prospects.<sup>25</sup> For plasmon-enhanced fluorescence, the silica shell thickness required much fine control in order to obtain better enhancement effect.<sup>16</sup> So far, most of related approaches to manipulate the silica shell thickness were based on controlling the parameters of silica coating reaction. By increasing the concentration of precursors, such as tetraethylorthosilicate (TEOS) and CTAB, thicker silica shell can be produced.<sup>13, 16</sup> However, as far as we know, controlling the mesoporous silica shell thickness after coating is rarely reported.

The recent years have seen boom of mesoporous rattle-type and hollow silica nanostructures for drug delivery and other biomedical applications,<sup>26,27</sup> in which AuNR@mSiO<sub>2</sub> showed great advantages for the unique properties it possessed. For these applications, the priority is to obtain a good control over the morphology and structure of the core and external mesoporous silica. However, the etching synthesis of cavities-possessed and rattle-type AuNR@mSiO<sub>2</sub> by using strong oxidant, *i.e.* aqua regia,<sup>28</sup> showed not only difficulty in management, but also low ability to maintain the rod shape during the etching, leading to poor control over the LSPR. Accordingly, explore to controllably and selectively etch the AuNR of AuNR@mSiO<sub>2</sub> is of great value.

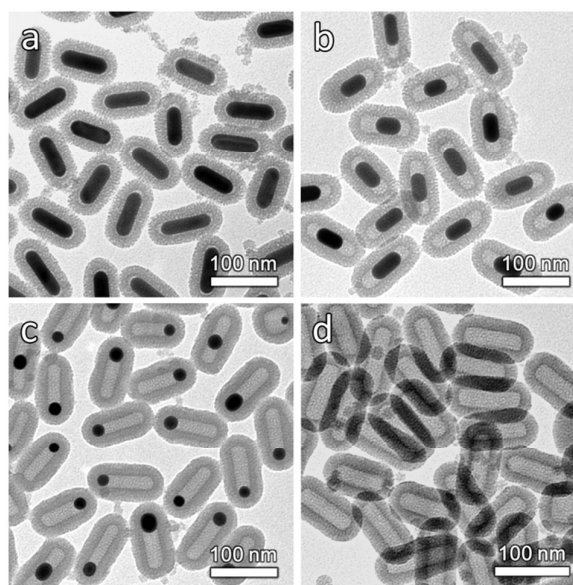
In this contribution, we reported a convenient step control method for manipulating the structure of AuNR@mSiO<sub>2</sub> "after

growth". With achievements of selective etching of internal AuNR by using mild oxidant of O<sub>2</sub>, and simultaneous managements of the structure and thickness of external mesoporous silica shell by deliberate control of experiment parameter of the etching reaction, well tunings of the LSPR and the silica coating structure of the AuNR@mSiO<sub>2</sub> have been realized.

## 2. Results and Discussion

### AuNR and AuNR@mSiO<sub>2</sub>

The UV-vis spectra and TEM images (see Electronic Supplementary Information, Fig. S1) show the significant characters of the prepared AuNRs and AuNR@mSiO<sub>2</sub>. The average length and diameter of prepared AuNRs are 92.8 ± 5.1 nm and 23.8 ± 1.6 nm, respectively, the aspect ratio is about 3.9, showing the LSPR wavelength (LSPW) at 806 nm (Fig. S1a,b). The narrow size distribution of these AuNRs, verified by the narrow full width of half maxima (fwhm, 113 nm) of the LSPR peak and also confirmed by TEM image (Fig. S1b), is beneficial for evaluating the effect of subsequent structural control experiment on AuNRs. After coated by mesoporous silica shell with average thickness of 17.3 ± 1.2 nm, the rise in local refractive index caused 14 nm of red shift of the LSPW (Fig. S1a,c).

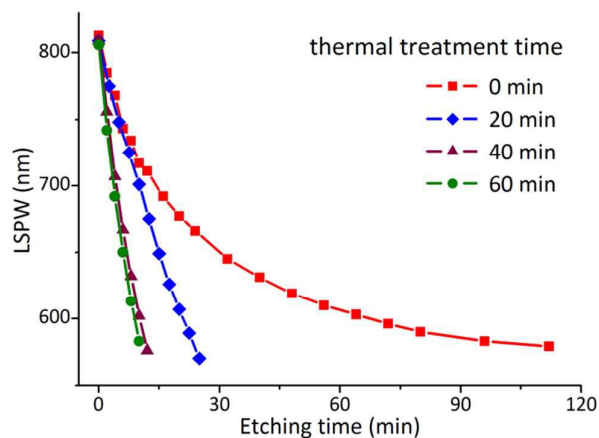


**Fig. 1** TEM images of AuNR@mSiO<sub>2</sub> acquired with different etching time in ethanol solution. The thermal treatment time was 20 min. The etching times were (a) 10, (b) 20, (c) 30, and (d) 45 min, respectively. Silica shell thicknesses in all these images were fixed at about 17 nm.

### Structural controls of AuNR@mSiO<sub>2</sub>

#### Structural control in ethanol solution

Fig. 1 shows typical TEM images of AuNR@mSiO<sub>2</sub> acquired during the etching of internal AuNR in ethanol solution. Thermal treatment of the solution was performed for 20 min before start of the etching. After addition of HCl, obvious etching of the ends of AuNR occurs, while the side is unaffected, supporting the happening of selective etching in this case. As this ends-etching proceeds, cavities-possessed AuNR@mSiO<sub>2</sub> is obtained (Fig. 1a, b). Note that the etched AuNRs remain in well size distribution. This observation suggests that the etchings in each silica-coated structure have similar reaction rate. Further etching of the rod results in formation of gold nanosphere inside the structure (Fig. 1c). Because the surface curvature of sphere shares the same value, the etching reaction turns to be non-selective in this case, resulting in the decreasing of gold nanosphere diameter. At this time, movable core appears since the silica shell can no longer keeps the core fixed in the centre of the structure, indicating the generation of rattle-type nanostructure. After the AuNR is completely dissolved, hollow silica structure is acquired, as shown in Fig. 1d. These etching-induced structural evolutions of AuNR@mSiO<sub>2</sub> suggest that the selective etching of AuNR can be realized in ethanol solution, and the mesoporous silica shell is rigid under this condition as well, which can be verified by the almost constant thickness of silica shell (~17 nm) throughout the etching.

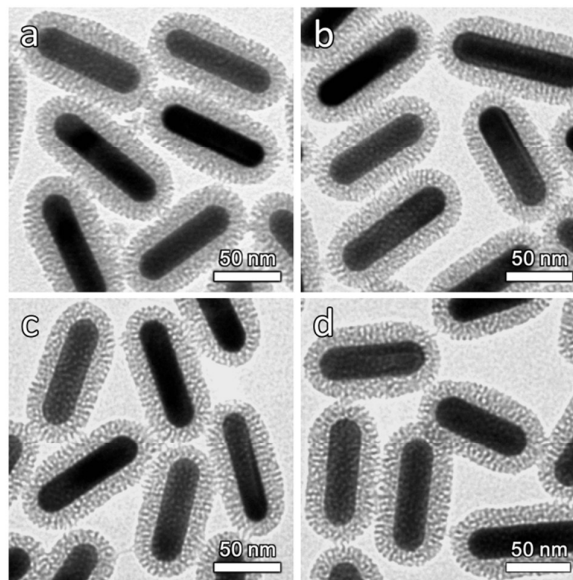


**Fig. 2** Influence of thermal treatment time on reaction rate of selective etching of AuNR in ethanol solution.

Fig. 2 reveals the influences of different time of thermal treatment (0, 20, 40, 60 min) in ethanol solution on the LSPW changes of AuNR@mSiO<sub>2</sub> during the etching. Because the decrease in aspect ratio of AuNR caused by selective etching can be identified by the blue shift of LSPW, this LSPW change is capable of reflecting the etching rate. Results showed in this

figure indicate that with increasing of thermal treatment time, the etching rate also increases. After 40 and 60 min of thermal treatment, the accelerated etching reaction can etch the gold core from rod shape to sphere in about 15 min, indicated by moving of LSPW to less than 600 nm. However, for 0 min of thermal treatment, similar level of etching is hardly to achieve, despite the etching time spent is more than 100 min.

How does the thermal treatment influence the etching reaction? Characterization of the AuNR@mSiO<sub>2</sub> acquired after the thermal treatment by TEM (Fig. 3) reveals that as the thermal treatment time increases, without obvious variation in AuNR, evident change appears in micro-structure of the silica shell, of which the mesopores become increasingly empty and open, especially for those adjacent to the surface of AuNR. It is generally accepted that the role of CTAB molecules in the bulk solution is to serve as organic templates for the formation of mesopores in silica-coating process. Following this process, the acquired silica structure was usually treated by acidified and hot alcohols for removing the CTAB templates and generating empty mesopores.<sup>29-31</sup> Data showed in Fig. 3 clearly reveal that the similar observation is obtained in our experiment for the template removal. The distinct mesoporous structure acquired after this treatment also suggests the silica framework is stable under this condition. Because the empty and open mesoporous structure favours the transportation of reactants such as O<sub>2</sub>, H<sup>+</sup>, and so on, the acceleration of etching reaction with increasing time of thermal treatment can be reasonably acquired.

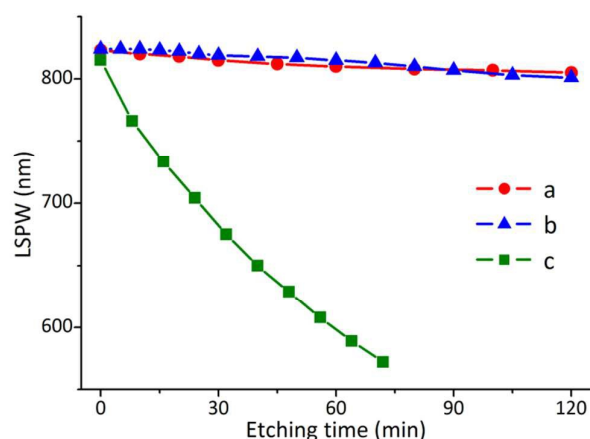


**Fig. 3** TEM images of AuNR@mSiO<sub>2</sub> after different thermal treatment time in ethanol solution: (a) 0 min, (b) 20 min, (c) 40 min, and (d) 60 min. The mesopores in silica shell became increasingly empty and open as thermal treatment time increased.



The number of washing and centrifugation for the as-prepared AuNR@mSiO<sub>2</sub> is also a very important factor to be considered for the proceeding of subsequent etching of AuNRs. If centrifugation was performed only once, the AuNR@mSiO<sub>2</sub> can be etched promptly as demonstrated in Fig. 1. By contrast, two or more rounds of centrifugation and washing of the as-prepared AuNR@mSiO<sub>2</sub> would lead to the failure of etching the AuNR by O<sub>2</sub>, which has been shown in Fig. 4a.

According to the previous report,<sup>19</sup> using weak oxidant for oxidation of gold nanoparticle required adsorption of CTAB micelle or bilayer structure on the surface of nanoparticle. The high curvature at the ends of AuNR causes obvious defects formed in the CTAB-capping bilayers, enabling the entry of oxidant and then incorporation with CTAB molecule, thus selective etching occurs at these sites. If the bilayer structure of CTAB is destroyed, etching of AuNR will be failed. Previous work has also revealed that the AuNR@mSiO<sub>2</sub> solution acquired after once centrifugation was positively charged because of the residual CTAB.<sup>24</sup> It can be inferred that because of the existence of small amount of CTAB in this solution, CTAB bilayers are maintained during the thermal treatment and etching process, thus successful etching of AuNR can be achieved by using O<sub>2</sub>. At this point, our experimental results are a little different from the oxygen-etching of "bare" AuNR,<sup>20</sup> in which the reaction was carried out in aqueous solution with relatively high concentration of CTAB (0.1 M). The underlying reason of these observations may be that the silica shell coating is able to not only improve the stability of AuNR,<sup>12,23</sup> but also provide the CTAB bilayers with certain extent of protections to the thermal treatment and even to the ethanol solvent, because CTAB bilayers can survive in the ethanol solution with very low concentration of CTAB.



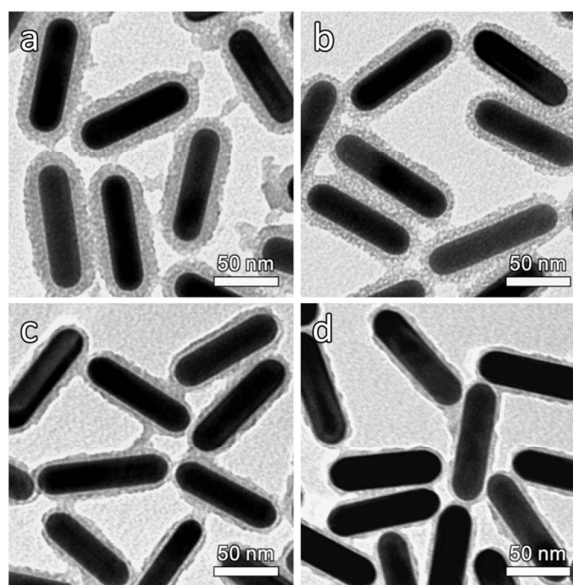
**Fig. 4** Influence of CTAB on the etching of AuNR@mSiO<sub>2</sub> in ethanol solution. Thermal treatment time was 40 min. The as-prepared AuNR@mSiO<sub>2</sub> solution was centrifuged twice then re-dispersed in ethanol. (a) AuNR@mSiO<sub>2</sub> solution  $\rightarrow \Delta \rightarrow +\text{HCl}$ ;

(b) AuNR@mSiO<sub>2</sub> solution  $\rightarrow \Delta \rightarrow +\text{HCl} \rightarrow +\text{CTAB}$ ; (c) AuNR@mSiO<sub>2</sub> solution + CTAB  $\rightarrow \Delta \rightarrow +\text{HCl}$ .

In order to further verify the role of CTAB on the protection of CTAB bilayer structure, additional CTAB was added to the AuNR@mSiO<sub>2</sub> solution that was acquired after two times centrifugation to reach a concentration of 2.0 mM. After thermal treatment and addition of HCl, the etching of AuNRs recovered (Fig. 4c). However, if CTAB was added after the thermal treatment and the addition of HCl, no further etching was observed (Fig. 4b). This indicates the CTAB bilayer structure is difficult to re-form under the heated and acidified condition, even when additional CTAB is used.

#### Structural control of AuNR@mSiO<sub>2</sub> in ethanol-water solution

In experiment using ethanol-water as solvent, the thermal treatment exhibited the same acceleration of etching reaction (Fig. S2). However, comparing to ethanol solution, the ethanol-water system showed different structural change of AuNR@mSiO<sub>2</sub>.

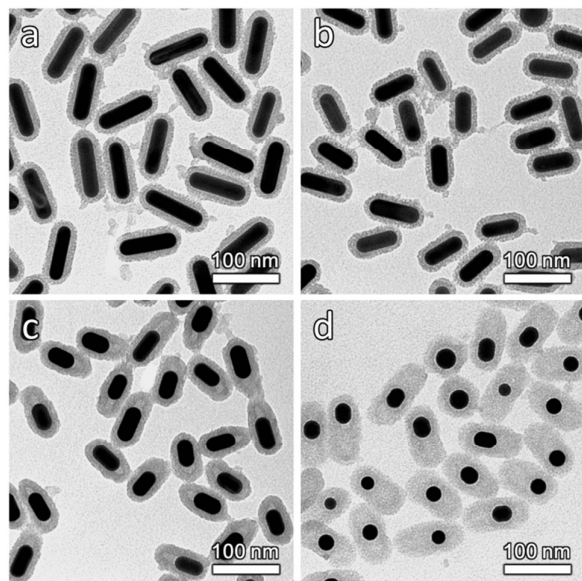


**Fig. 5** TEM images of AuNR@mSiO<sub>2</sub> acquired after different thermal treatment time in ethanol-water solution. Thermal treatment time and silica shell thickness were: (a) 0 min, 12.7 ± 1.0 nm, (b) 30 min, 8.1 ± 0.9 nm, (c) 60 min, 6.0 ± 0.8 nm, and (d) 90 min, 3.8 ± 0.5 nm, respectively.

TEM images of AuNR@mSiO<sub>2</sub> acquired after different time of thermal treatment in ethanol-water solution are showed in Fig. 5. They reveal that silica shell thickness decreases homogeneously as the thermal treatment time increases, while no evident change is observed on the internal AuNR. The

decrease of shell thickness from original value of 17.3 nm to 12.7 nm (Fig. 5a) is caused by 10 min of temperature rising process before the start of thermal treatment time. 60 min of thermal treatment results in silica shell thickness about half to that of 0 min ( $\sim 6.0$  nm, Fig. 5c). As far as we know, it is the first time manipulation of silica shell thickness of AuNR@mSiO<sub>2</sub> has been achieved in subtractive way. Therefore, it is reasonable that the acceleration of etching reaction in this case is resulted from the thinning of shell thickness that benefits the materials transference between the internal core and the bulk solution.

It is widely accepted that dissolution and regrowth of mesoporous silica can be catalysed by hydroxide ions in aqueous solution,<sup>26,27,32</sup> and a rise in temperature can accelerate these processes.<sup>33</sup> This suggests that the homogeneous dissolution of silica in hot ethanol-water solution in our experiment should be responsible for the decreasing of the silica shell thickness. Note that this homogeneous dissolution of silica shell from external surface distinguishes from what were shown in previous studies, in which the dissolution reaction randomly occurred inside the mesoporous silica structure.<sup>32,33</sup> This may partly because of the use of mixed solution of ethanol and water, in which the ethanol can stabilize the silica framework like what happened in pure ethanol solution.



**Fig. 6** TEM images of etching of AuNR@mSiO<sub>2</sub> in ethanol-water solution after 0 min of thermal treatment. The etching times and the silica shell thicknesses at side of AuNRs were (a) 0 min,  $12.7 \pm 1.0$  nm, (b) 40 min,  $11.2 \pm 1.0$  nm, (c) 100 min,  $11.8 \pm 0.9$  nm, and (d) 136 min,  $15.1 \pm 1.4$  nm, respectively.

Fig. 6 and S3 show TEM images of etching of AuNR@mSiO<sub>2</sub> in ethanol-water solution after 0 min and 30 min of thermal

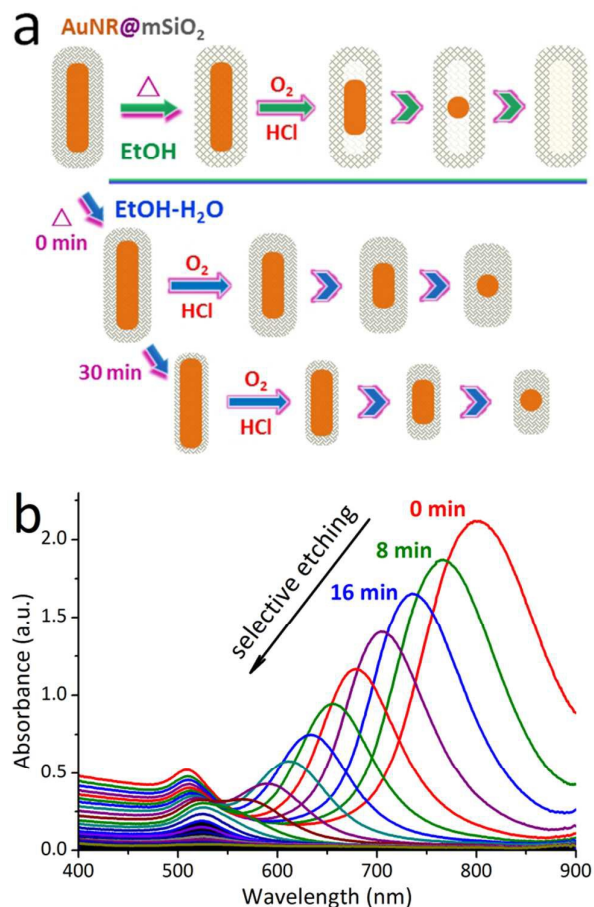
treatment, respectively. The only measurable difference between the initial AuNR@mSiO<sub>2</sub> is silica shell thickness ( $\sim 12$  nm in Fig. 6a and  $\sim 8$  nm in Fig. S3a). After addition of HCl to initiate the selective etching reaction, shape-adaptive silica shell-coated AuNRs were observed throughout the etching. This observation is in line with those reported previously in literatures<sup>32,33</sup> that both dissolution and regrowth processes occur inside the silica shell under this condition, providing the shell with certain fluidity, but without causing severe destruction of mesoporous silica framework. Recently, the similar “elastic” silica coating structure was reported by Lin and co-workers.<sup>34</sup> Their experiment suggested that using pure water as solvent could also obtain shape-adaptive silica coating of gold nanoparticle.

The shape-adaptive silica coating of AuNR is featured as follows: in the process of etching reaction, silica capping at the ends of AuNR can gradually fill the cavities created by shortening of AuNR, leading to increase in silica shell thickness in those areas; however, verified by the constant thickness in the rest of areas, those locating at the side of AuNR are immovable as long as the core remains in rod shape (Fig. 6b,c and Fig. S3b,c). After the etching reaction turns to be non-selective, decrease in diameter of the gold nanosphere leads to a rise in the thickness of silica side wall (Fig. 6d and Fig. S3d). These phenomena are analogous to the evolution of cavities during etching of AuNR@mSiO<sub>2</sub> in ethanol solution. This shape-adaptive silica coating behaviour could be attributed to severe slowdown of dissolution of silica under the strong acidic condition, causing no significant change in the thickness of silica side wall; however, the effect of water remains inside the silica structure, thus enabling the filling behaviour.

#### Tuning the LSPR of AuNR@mSiO<sub>2</sub> by etching of internal AuNR.

Fig. 7a shows the schematic illustration of overall structural controls of AuNR@mSiO<sub>2</sub>. Because the silica shell is almost transparent in SPR spectra range, the difference between structure changes of AuNR@mSiO<sub>2</sub> in ethanol and ethanol-water solution only causes tiny variation of LSPR wavelength, which is almost negligible comparing to the significantly spectroscopic change resulted from the etching-caused decrease in aspect ratio of AuNR. Therefore, similar variations on AuNR@mSiO<sub>2</sub> UV-vis spectra can be obtained in both cases (Fig. 7b). The LSPW exhibits a gradual blue shift with increasing of etching time and the spectra acquired during the etching maintain the spectral features of AuNR in high quality, demonstrating a good control over the LSPR of AuNR@mSiO<sub>2</sub>. This controlled tuning of LSPR by selective etching is consistent with previously reported results.<sup>20-22</sup> However, those were acquired from management of AuNRs with absence of mesoporous silica coating. By contrast, our crucial observation clearly indicates that in spite of coated by mesoporous silica and under the alcoholic condition, selective etching of AuNR

using mild oxidant is still available. In particular, an expected structure of AuNR@mSiO<sub>2</sub> with a particular LSPW can be obtained at a certain time during the etching process by simply terminating the reaction.



**Fig. 7** (a) Summarized schematic illustration of structural controls of AuNR@mSiO<sub>2</sub>; (b) Typical UV-vis spectra of AuNR@mSiO<sub>2</sub> acquired during selective etching of AuNR.

## Conclusions

First, selective etching-control of the aspect ratio of internal AuNR of AuNR@mSiO<sub>2</sub> has been achieved by using mild oxidant of O<sub>2</sub>. By virtue of the mesoporous silica shell, the etching reaction could be carried out in solution with relatively low concentration of CTAB and even in ethanol solution. Second, further structural controls of the AuNR@mSiO<sub>2</sub> have also been realized through manipulating the etching experiment. In ethanol solution, because the mesoporous silica framework was rigid, thermal treatment of AuNR@mSiO<sub>2</sub> led to open porous structure, which resulted in acceleration of etching reaction. As etching of AuNR in this solution proceeded,

cavities-possessed, rattle-type, and hollow AuNR@mSiO<sub>2</sub> were obtained. In addition, when ethanol-water was used as solvent, thermal treatment of AuNR@mSiO<sub>2</sub> caused decrease in the silica shell thickness, which also led to speeding up of the etching reaction. This thinning change of silica shell showed potential in subtractive control of mesoporous silica shell thickness. The fluidity of silica shell in the ethanol-water solution, which was provided by water but was limited by ethanol, enabled shape-adaptive silica coating of the etched AuNR throughout the etching reaction. Third, the same to document reports that tuning of LSPR by using mild oxidant for selective etching of “bare” AuNRs, our result has shown that the mesoporous silica coating layers of all AuNR@mSiO<sub>2</sub> were effective for equally transporting the reactants, thus also enabled the structure for not only conducting the selective etching but also generating the etched AuNRs with high level of monodispersity. The use of mild oxidants of O<sub>2</sub> for the etching made the process easy of control, as well as was able to maintain the rod shape during the reaction. As a result, high performances of absorption spectra were kept throughout the etching. These features make the process a valuable technique for tuning of LSPR of AuNR@mSiO<sub>2</sub>.

## Experimental

### Materials

Cetyltrimethylammonium bromide (CTAB, ≥ 99.0%), hydrogen tetrachloroaurate tetrahydrate (HAuCl<sub>4</sub>·4H<sub>2</sub>O, 99.9%), L-ascorbic acid (≥ 99.7%), silver nitrate (AgNO<sub>3</sub>, ≥ 99.8%), sodium borohydride (NaBH<sub>4</sub>, ≥ 96%) were purchased from Sinopharm Chemical Reagent Co., Ltd; tetraethylorthosilicate (98%), sodium oleate (98.0%) were purchased from Aladdin Industrial Corporation. Hydrochloric acid (HCl, 37 wt.% in water), sodium hydroxide (NaOH), ethanol, methanol were purchased from Nanjing Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. Deionized water obtained from a Milli-Q Reference system was used in all experiments. All glassware was washed with aqua regia before use.

### Syntheses of AuNRs and AuNR@mSiO<sub>2</sub>

#### Synthesis of AuNRs

AuNRs were synthesized according to the previous report.<sup>35</sup> Seed solution was prepared as followed: 0.5 mL of 10 mM HAuCl<sub>4</sub>·4H<sub>2</sub>O and 0.73 g of CTAB were added into a flask containing 18.5 mL of water. The experiment temperature was kept at 30 °C. After stirring for 15 min, 1.0 mL of NaBH<sub>4</sub> solution prepared by dissolving 0.0091 g of NaBH<sub>4</sub> in 20 mL of ice cold water was injected to the solution under vigorous stirring. 2 min later, stirring was stopped and a brownish



yellow solution was acquired. The solution was kept undisturbed for at least 30 min before use.

For AuNR preparation, 7.0 g of CTAB and 1.234 g of sodium oleate were dissolved in 470 mL of water. The mixture was heated to 60 °C and stirred for at least 30 min. After cooled to 30 °C, 14.4 mL of 5.0 mM AgNO<sub>3</sub> was added under gentle stirring, then the mixture was kept undisturbed for 15 min. To this solution, 25 mL of 10 mM HAuCl<sub>4</sub> was added and followed by stirring for at least 30 min to obtain a colourless solution. Then 1.5 mL of HCl was added, and 15 min of stirring was performed. After that, 0.8 mL of 0.1 M ascorbic acid was added under vigorous stirring. 1 min later, 0.4 mL of seed solution was injected and another 1 min of stirring was needed. The mixture was left undisturbed at 30 °C for at least 12 h for growth of AuNRs.

#### Synthesis of AuNR@mSiO<sub>2</sub>

Method reported by Gorelikov<sup>24</sup> was employed for the mesoporous silica coating of AuNR with modification. In a typical process, 100 mL of the as-prepared AuNRs solution was centrifuged at 6000 rpm for 10 min, the supernatant was discarded and the sediment was dispersed in 25 mL of water, then the solution was centrifuged again. The acquired sediment was re-dispersed in 50 mL of 1.0 mM CTAB solution. Note that in order to maintain the integrity of CTAB bilayers on the AuNR no ultra-sonication of the solution was performed throughout this process, since the CTAB bilayer structure capped at the ends of AuNR is susceptible to solution condition of low CTAB concentration.<sup>11</sup> The temperature of the solution was kept at 30 °C. Under gentle stirring, 0.5 mL of 0.1 M NaOH was added to the solution to acquire pH of about 10.2. 30 min later, three 0.2 mL injections of 10% TEOS in methanol was added to the solution at interval of 30 min, then stirred for overnight. Finally, the prepared AuNR@mSiO<sub>2</sub> solution was centrifuged at 6500 rpm for 15 min. Supernatant was discarded and sediment was re-dispersed in ethanol or ethanol-water (1 : 1 in volume ratio) solution. It should be emphasized that centrifugation was performed only once, and no further washing and centrifugation of the acquired sediment were carried out.

#### Structural controls of AuNR@mSiO<sub>2</sub>

The method<sup>20</sup> of using O<sub>2</sub> for oxidizing AuNR was improved for the structural control of AuNR@mSiO<sub>2</sub> in our experiment. Certain volume of the re-dispersed AuNR@mSiO<sub>2</sub> was transferred to a three-necked flask under a condenser and continuous stirring and bubbling with O<sub>2</sub>. Thermal treatment of the solution before the etching was performed at 75 °C. Before the treatment time started to count, 10 min was needed for temperature rising. After a certain period of thermal treatment, certain amount of HCl, to acquire

concentration of 0.5 M, was injected to the solution to initiate the etching reaction.

#### Characterization

Transmission electron microscopy (TEM) images were acquired on Hitachi H-7650 microscope at 80 kV. Typically, solution was drop-casted on a carbon-coated copper grid, and then left for drying at room temperature. For solution acquired from structural control experiment, cooling, centrifugation and washing with ethanol was performed before the sample preparation. UV-vis spectra were taken using Shimadzu UV-2450 spectrophotometer.

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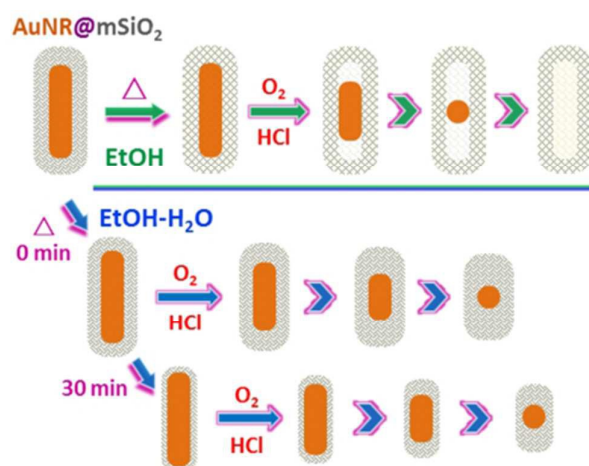
## Structural Controls of AuNR@mSiO<sub>2</sub>: Tuning of the SPR, and Manipulations of the Silica Shell Thickness and Structure

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Ends-selective etching the AuNR of AuNR@mSiO<sub>2</sub> can be managed to produce cavities-possessed, rattle-type, hollow, and shape-adaptive silica-coated nanocomposites, respectively.