“Hot spots” growth on single nanowire controlled by electric charge†

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“Hot spots” – a kind of highly active site, which are usually composed of some unique units, such as defects, interfaces, catalyst particles or special structures – can determine the performance of nanomaterials. In this paper, we study a model system, i.e. “hot spots” on a single Ag nanowire in the galvanic replacement reaction (GRR), by dark-field microscopy. The research reveals that electric charge can be released by the formation reaction of AgCl, and consequently the electrochemical potential on Ag nanowire drops. The electric charge could induce the reduction of Ag+ to form the “hot spots” on the nanowire during the GRR. The appearance probability of “hot spots” is almost even along the Ag nanowire, while it is slightly lower near the two ends. The spatial distance between adjacent “hot spots” is also controlled by the charge, and obeys a model based on Boltzmann distribution. In addition, the distance distribution here has an advantage in electron transfer and energy saving. Therefore, it’s necessary to consider the functions of electric charge during the synthesis or application of nanomaterials.

1. Introduction

“Hot spots” (HSs), a kind of highly active site, are usually composed of some unique units, such as defects, interfaces, catalyst particles or special structures. For example, Pt,8 Au,9 Pd11 nanoparticles are usually deposited on 1D nanostructures, such as hollow nanospheres,22 nanoboxes,23 nanostructures, such as hollow nanospheres,22 nanoboxes,23 nanowires,24,25 were prepared successfully. Ag and Au are typical plasmonic materials, which are suitable for optical probing at the single nanoparticle level.26 According to the principle of GRR,21 the dissolving of Ag will cause a decrease of plasmonic scattering (eqn (1)), while the deposition of Au will cause an increase (eqn (2)).

$$\text{Ag} - \text{e}^- \rightarrow \text{Ag}^+ \quad \phi_{\text{Ag}/\text{Ag}^+} = 0.799 \text{ V}$$  \hspace{1cm} (1)

$$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} \downarrow + 4\text{Cl}^- \quad \phi_{\text{Au}/\text{AuCl}_4^-} = 1.000 \text{ V}$$  \hspace{1cm} (2)

In this paper, we find and study a model system, i.e. “hot spots” on a single Ag nanowire during a GRR, by using dark-field microscopy (DFM). The study reveals the multi-functions of electric charge on the formation of “hot spots” at the single nanoparticle level.

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2. Results and discussion

2.1. Detect the “hot spots” on single Ag nanowires during GRR by DFM

Experimentally, some Ag nanowires\textsuperscript{27} with 50.1 ± 8.5 nm diameter and 6.3 ± 3.6 µm length (ESI 2\textsuperscript{†}) were well dispersed and immobilized on a glass slide, which was fabricated to a micro-fluidic flow cell afterwards (Fig. 1A). Then, the flow cell was loaded on a DFM, and was flowed into a certain concentration of HAuCl\textsubscript{4} ([HAuCl\textsubscript{4}]) to make the GRR happen. Simultaneously, the GRR was measured by the light scattering from single Ag nanowires \textit{in situ} and in real time.

Fig. 1B shows the dark-field scattering snapshots of some single Ag nanowires before the GRR, \textit{i.e.} at time 0 kilo second (ks). At this moment, the single Ag nanowires are bright and smooth. This result is consistent with their TEM measurement (Fig. S1\textsuperscript{†}), which shows that the side wall of the Ag nanowire is smooth, and the width is uniform. Fig. 1C shows that a lot of bright spots, \textit{i.e.} “hot spots”, generate on Ag nanowires after the GRR for 2.4 ks. These hot spots indicate the growth of nanoparticles on Ag nanowires. But the growth rate is highly heterogeneous along a single Ag nanowire, since the “hot spots” near the two ends of the Ag nanowires are brighter (more examples in Fig. S2\textsuperscript{†}).

Fig. 1D and E show the scattering intensity of the nanowire as pointed by arrows in Fig. 1B and C. The intensity variation indicates the GRR and the growth of “hot spots” at different locations. Therefore, the growth of “hot spots” above presents an excellent model to study the essential problems of “hot spots” on 1D nanomaterials during charge coupled reaction.

2.2. Structure, composition and growth of the “hot spots”

The as-synthesized Ag nanowire is smooth and straight (Fig. S1\textsuperscript{†}), but becomes a nanotube after the GRR.\textsuperscript{24,25,28} Fig. 2A shows a SEM image of single Ag nanowires with “hot spots” after 2.4 ks GRR at 0.02 mM HAuCl\textsubscript{4}. The size of the “hot spots” is more than two hundred nanometers, which is big enough to scatter the light strongly. Fig. 2A and its inset also show that most of the “hot spots” are of cubic shape. Fig. 2B and C show that the cubic “hot spots” are not a single crystal particle but a cluster of many small nanoparticles.

Furthermore, Fig. S3\textsuperscript{†} shows that the DFM image and SEM images on the same sample after 2.4 ks GRR have a good correlation with each other. The STEM and EDX analysis in Fig. S4A–B\textsuperscript{†} clearly show that the “hot spots” generated at low concentrations of HAuCl\textsubscript{4} are composed of pure Ag. Fig. S4B\textsuperscript{†} also show that no gold and only trace chloride elements are detected in the cluster.

The formation of pure Ag clusters on Ag nanowire is a very interesting result, which has not been observed by other researchers. The formation of pure Ag clusters is not possibly due to the direct migration of Ag atoms from the nanowire, since the reaction temperature is at the room temperature. The Ag atoms are trapped in the crystal lattice at such low temperature. Hence, the formation of pure Ag clusters should be due to the reduction of Ag\textsuperscript{+} from solution.

The reduction of Ag\textsuperscript{+} at least needs three necessary conditions including enough Ag\textsuperscript{+} in solution, the exhaustion of HAuCl\textsubscript{4} and a lower electrochemical potential than 0.799 V (eqn (3)). The first condition, \textit{i.e.} enough Ag\textsuperscript{+} in solution, will provide enough silver element for the reduction reaction. For the second condition, the redox potential of HAuCl\textsubscript{4} is about 1.0 V (eqn (2)), which is much higher than silver (eqn (3)). If the HAuCl\textsubscript{4} doesn’t exhaust completely, HAuCl\textsubscript{4} will be reduced first, and the reduction of Ag\textsuperscript{+} will not happen. For the third condition, a lower electrochemical potential than 0.799 V could induce the reduction of Ag\textsuperscript{+} (eqn (3)).

When the GRR (eqn (1) and (2)) happens for a while at low concentration of HAuCl\textsubscript{4}, these three conditions will be satisfied at the same time. Due to the dissolution of Ag, more and more Ag\textsuperscript{+} will be formed in solution. Due to the consumption and slow flow rate (only 10 µL min\textsuperscript{−1}), HAuCl\textsubscript{4} could be exhausted in the downstream locations of the flow cell. Due to the formation of AgCl from Ag and Cl\textsuperscript{−} (eqn (4)), the potential could drop lower than 0.799 V.

![Fig. 1 Growth of “hot spots” on single Ag nanowires during the GRR in 0.02 mM HAuCl\textsubscript{4}. (A) Schematic of DFM and a micro-fluidic reactor to image the growth of “hot spots” in the GRR. (B)–(C) Dark-field images of many single Ag nanowires in the GRR at time 0 ks (B) and 2.4 ks (C). (D)–(E) Scattering intensity along the length of nanowires as pointed by arrows in (B) and (C).](image-url)
In order to verify if the potential could drop lower than 0.799 V, we did a measurement of open circuit potential (OCP) at 0.02 mM [HAuCl₄]. Fig. S6† shows that the OCP can drop to ~0.7 V, which is lower than the reduction potential of Ag⁺ in eqn (3). Ag⁺ could be reduced to a metal Ag cluster at such a low potential. In fact, the potential is a mixed potential of reactions in eqn (1)–(4).29 The formation mechanism of Ag nanoclusters on a single Ag nanowire is shown in Fig. 2D.

\[
\begin{align*}
\text{Ag}^+ + \text{e}^- & \rightarrow \text{Ag} \quad \phi_{\text{Ag/Ag}^+} = 0.799 \text{ V} \quad (3) \\
\text{Ag} + \text{Cl}^- - \text{e}^- & \rightarrow \text{AgCl} \quad \phi_{\text{Ag/AgCl}} = 0.222 \text{ V} \quad (4)
\end{align*}
\]

So far we speculate that the residue ligand, i.e. PVP, may be the reason for the nanoparticle assembly with a cubic shape. Although the nanowires were thoroughly washed during the experiment, trace residue ligand, i.e. PVP, still can exist in the flow cell. Possibly, similar to the example of the cubic crystal,30 as the Ag nanoparticle formed PVP may bound on (100) plane preventing (100) plane attach with each other, while left the (111) plane of the particle unbounded. Therefore, the (111) plane of nanoparticles will be attracted together along (111) plane, leaving (100) plane of the nanoparticle exposed. Then, the assembly of cluster with cubic structure formed.

At high [HAuCl₄], e.g. 0.50 mM, the OCP is usually between 0.799 V and 1.5 V (Fig. S6†), which only can cause the deposition of Au by the reduction of AuCl₄⁻ in eqn (2). EDX analysis shows that the cluster is composed with both Ag and Au at high concentration (Fig. S4†).

2.3. Distribution of “hot spots” on single nanowires

Fig. 3A shows a schematic of the “hot spots” on a single Ag nanowire. Fig. 3B–E show that the distribution of “hot spots” is almost homogeneous in the mid part of the nanowire at different [HAuCl₄]s. Therefore, the appearance probability is even in the mid part of Ag nanowire. But the distribution near the two ends becomes slightly lower and lower with the increase of [HAuCl₄] (red arrow in Fig. 3B–E). We suppose that some electric charges could accumulate on the two ends of nanowire due to the tip effect according to electrostatic theory. Since the population of “hot spots” is lower near the two ends,
the “hot spots” near the two ends will not affect our conclusion.

We also measured the distance between adjacent “hot spots”, i.e. $d$ in Fig. 3A. Fig. 3F–I show the statistics of $d$. If assume the appearance is a random Poisson process, the distance between adjacent “hot spots” should be a single exponential distribution, \[ p(d) = \frac{1}{\lambda} \exp \left( -\frac{d}{\lambda} \right) \] (5) where $p(d)$ is the probability density for the distance between adjacent “hot spots”, $\lambda$ is the distribution density (a constant for a typical Poisson process), and $d$ is the distance between adjacent “hot spots”. However, the distributions in Fig. 3F–I are not a single exponential distribution, but always has a peak, which indicates that the appearance of “hot spots” are not a simple Poisson process. The peak distribution indicates that the existed “hot spots” have some effects on the ones to be appeared. In the following part, we will deeply discuss the distribution of “hot spots” during the GRR.

2.4. Interaction between “hot spots” through surface charge

During the GRR, Ag acts as a reduction agent, which injects electrons into the Ag nanowire through the reactions in eqn (4). Since Ag nanowire is conductive, the electric charges will exist on the surface of the nanowire according to electrostatic theory. However, the surface charges were shielded by the same number of opposite charges in solution.32 An electric double layer will be formed on the interface between the electrode and solution. The surface charges can only interact with other charged objects within the electric double layer. The thickness of the electric double layer can be calculated by \[ D = \frac{0.304}{\varepsilon C^{*1/2}} \] (6) where $D$ is the thickness of the electric double layer (nm), $z$ is the number of charges on the ion, and $C^*$ is the concentration of electrolyte (M). Eqn (6) indicates that the electric double layer will be thicker when the concentration of electrolyte is lower. If there is no reaction on Ag nanowire in 0.02 mM HAuCl$_4$, the thickness of the electric double layer $D$ is only $\sim 68$ nm.

But, the electric double layer will be much thicker in the diffusion layer when the GRR happens on Ag nanowire. Fig. 4A and B show that a diffusion layer with low concentration of electrolyte should be formed when the GRR happens. The diffusion layer will be thicker, when the reaction rate is faster.32 Fig. 1C shows that the rapid growth of clusters needs the supply of electrons from many other locations on Ag nanowire. Considering the fast reaction rate and relatively low flow rate of reactant solution, low concentration of HAuCl$_4$ could be totally exhausted with the GRR occurring. At the same time, the ion Cl$^-$ is consumed rapidly to form AgCl, and Ag$^+$ is converted to Ag or AgCl. A limited diffusion could be reached due to the fast reaction. The thickness of the diffusion layer ($H_d$) could be up to several tens micrometers.32 Then a kind of “tunnel” several tens of micrometers thick around the nanowire will be formed as shown in Fig. 4B and C. The electric double layer will be much thicker (up to the micrometer scale) in the diffusion layer, which is like a “tunnel” with low [HAuCl$_4$] around a single nanowire. The surface charges on a single Ag nanowire could interact with each other or with other charged objects through the “tunnel”. This “tunnel” will be extremely important for the charge controlled reactions in eqn (1)–(4).

Since the hot spots have a higher surface curvature than the body of the nanowire, the surface charges are much easier to converge to the hot spots according to Gauss’s law in electrostatic theory. Then, the clusters have a higher ability to attract more cation Ag$^+$ through the “tunnel” for reduction reaction of Ag$^+$. Hence pure Ag clusters with a clear shape are selectively formed on the nanowire at low [HAuCl$_4$] (Fig. 2).

2.5. Model for “hot spots” distribution on single nanowires

For a typical Poisson process, $\lambda$ is a constant value. But, $\lambda$ becomes a distance dependent function in our research as shown in Fig. 3F–I. For an existent “hot spot”, i.e. cluster, it has a higher density of surface charge than the body of the nanowire. The charge density on the body of the nanowire will be even lower near the existent “hot spot”, due to the repulsion between homocharges. The appearance probability of new “hot spots” will be lower near an existent one. The adjacent “hot spots” will be kept in a certain distance. Then, $\lambda$ becomes a distance dependent function, which obeys the Boltzmann distribution, \[ \lambda(d) = n_0 \exp \left( -\frac{MQ^2}{Td} \right); \quad M = \frac{e^2}{4\pi\kappa k_B T} \] (7)
where \( n_0 \) is the average distribution density without the effect of electric field, \( e \) is the charge of one electron, \( Q \) is the average number of electrons on one “hot spot”, \( k \) is the Boltzmann Constant, \( \varepsilon_0 \) is the vacuum permeability, and \( T \) is the temperature. Submitting eqn (7) to eqn (5), the distance distribution between adjacent “hot spots” will be

\[
p(d) = \frac{1}{n_0} \exp\left(\frac{MQ^2}{Td} - \frac{d}{n_0} \exp\left(\frac{MQ^2}{Td}\right)\right)
\]

Eqn (8) can fit the distribution peaks for different [HAuCl₄]s in Fig. 3F–I very well. Somehow, the model is proved to be reasonable. The fitting also gives the value of some interesting parameters, such as \( Q \) and \( n_0 \). Fig. 5A and B show that the average number of electrons \( \langle Q \rangle \) on one “hot spot” and the average distribution density \( \langle n_0 \rangle \) decrease with [HAuCl₄]. These two trends are consistent, since higher \( Q \) implies stronger reduction activity, and consequently higher ability to generate more “hot spots” \( \langle n_0 \rangle \).

In addition, we find that the distribution of eqn (8) has a high advantage in charge transfer and energy saving. The energy loss \( \langle E_{\text{loss}} \rangle \) of Joule heat is different for different distributions of distance in a charge coupled reaction (ESI 7†).

Fig. 5C shows that the distribution of eqn (8) has a very low energy loss as the uniform distribution. Therefore, it’s better to prepare a more uniform distribution of “hot spots” for the charge coupled reactions in the fields, such as photo-(photo-electro)-chemistry, and electrochemistry.

4. Experimental

4.1. Dark-field imaging of single Ag nanowires

Dark-field measurements were performed using an Olympus IX71 microscope. The single Ag nanowires were illuminated by a Cold White Collimated LED (MCWHL2-C1) lamp source for an Olympus BX & IX focused through an Olympus U-DCW NA1.2-1.4 oil immersion dark-field condenser. The scattering signal was collected by a 60× NA1.2 water-immersion objective, and detected by an ANDOR iXon DU-897D-C50-8BV EMCCD camera operating at a 200 ms frame rate. An additional 1.6× magnification on the microscope was also used. In order to correct the unavoidable stage drifting in nanometer accuracy, some gold nanoparticles with a size of tens of nanometers were used as markers to accurately localize the location on single nanowires.

4.2. Dark-field imaging of the GRR on single Ag nanowires

A flow cell, 100 μm (height) × 2 cm (length) × 5 mm (width), formed by double-sided tapes sandwiched between a glass slide (Henghao, China) and a borosilicate coverslip (Citoglas, China), was used to hold aqueous reactant solutions for dark-field measurements. Reactant solutions were supplied in continuous flow at 10 μL min⁻¹ using a syringe pump. All dark-field imaging experiments were carried out at room temperature with 0.02, 0.05, 0.10, and 0.50 mM HAuCl₄ (Nanjing Precious Metal Factory, China). This flow cell based reaction reactor provided a steady-state reaction condition, under which all GRR kinetics of single Ag nanowires was measured.

To immobilize Ag nanowires on the glass slide, 2 μL (depending on the concentration of Ag nanowires) Ag nanowires were first dispersed in 20 μL ethanol by sonication. 5 μL of this solution was drop-casted onto a clean glass slide once, and dried in air at room temperature. The glass slide was then assembled into a flow cell for dark-field imaging experiments.

3. Conclusions

In summary, we adopt clusters formed in the GRR on single Ag nanowires as a model reaction system to study the growth and working mechanism of “hot spots” on 1D nanomaterials. The compositions of “hot spots” are controlled by the interaction between the surface charges and ions in solution. The appearance probability of “hot spots” is almost even along the Ag nanowire, while it is slightly lower near the two ends. We suppose that slightly lower appearance probability is attributed to the electric charges accumulating on the two ends of the nanowire due to the tip effect according to the electrostatic theory. The distribution of “hot spots” is controlled by the interaction between the surface charges on the existent “hot spot” and the one to be generated. Surface charge is common in the fields of nanoscience, such as nano-synthesis, and electrochemistry, and catalysis. Therefore, this research not only helps us understand the “hot spots”, but also reveals the multifunctionality of electric charge in nanomaterials.
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