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ARTICLE TYPE

Ligand-assisted etching: the stability of silver nanoparticles and the generation of luminescent silver nanodots

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The etching mechanism of silver nanoparticles was investigated. Though a strong binding agent to silver and an oxidising agent synergistically etch the nanoparticles, the balanced etching power has to be optimized to generate 10 **luminescent silver nanodots. This indicates that active centres facilitate the formation of nanodots.**

Stable noble metal clusters have been prepared with atomic precision.[1] The preliminary characterization of such clusters has illustrated their excellent photophysical properties, which are 15 useful for chemical and biological sensing.[2, 3] It is believed that both the size of the cluster and the binding between the cluster and its surroundings determine the photophysical properties of noble metal clusters.[4] The general approach towards the synthesis of such clusters is based on bottom-up strategies. Typically, noble 20 metal ions are reduced in the presence of protection groups, resulting in a mixture of nanoparticles, non-luminescent clusters, and luminescent clusters referred to as nanodots or nanoclusters.[5-7] Another approach towards nanodot synthesis is top-down etching of noble metal nanoparticles.[8] Nanoparticles degrade 25 gradually in an aqueous solution due to oxidation by dissolved oxygen.[9] However, no luminescent species have been observed as the nanoparticles dissolve naturally in the absence of protection groups. Ligands such as polyamine or thiolated molecules, accelerate the transformation from nanoparticles to noble metal 30 clusters. This method is widely used for the preparation of gold nanodots,[10, 11] but rarely for silver nanodots as the strong binding between the ligands and silver ions may dissolve the nanoparticles further to silver ions.[12] Moreover, silver nanodots stabilized with thiolated molecules are much less stable compared 35 to their gold cluster counterparts.[13]

The degree of etching is a key factor in controlling the cluster size. Many factors, such as the etching agents, oxidizing agents and stabilizing groups, will determine the efficiency of the etching process. However, the generation of luminescent silver 40 nanodots might require more sophisticated ligand design. The photophysical properties of silver nanodots are strongly environmentally dependent.[14] Peptide, poly(acrylic acid)-derivative or thiolated molecule-protected silver nanodots usually show less than 10% luminescent quantum yield.[2, 12, 15] ssDNA, 45 however, builds an environment good for the generation of bright silver nanodots. We therefore for the first time investigated the etching of silver nanoparticles based on the ssDNA scaffold to clarify the factors that lead to efficient silver nanodot formation

and new methodologies to generate silver nanodots.

50 Even though ssDNA, for example 5'-CCCCCCCCCCCC-3' (C12), is able to protect silver nanodots well, the luminescence
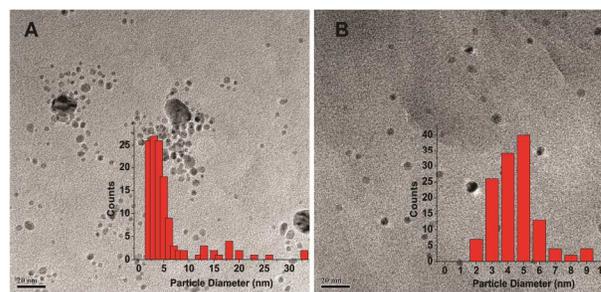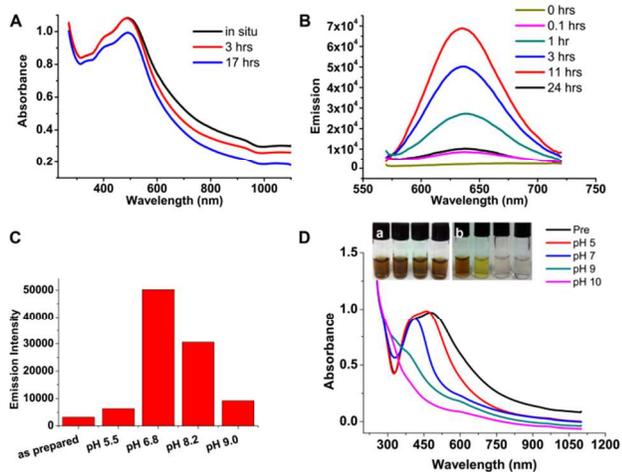

Fig. 1 TEM images of C12-stabilized silver nanoparticles. (A) Freshly prepared. (B) After dEtA-oxygen etching. The inset indicates their size 55 distribution. Scale bar, 20 nm

of silver nanodots vanished completely at a Ag^+/DNA base of 2.8:1. Instead, the absorption spectrum and TEM images of the solution indicated that silver nanoparticles were formed (**Fig 1A** and **Fig. 2A**). The degradation of such silver nanoparticles was 60 slow, with only 7% decrease in absorbance in three months, whereas no luminescence of this solution was observed. However, when ligands, such as diethylenetriamine (dEtA, 30 mM), were added, the degradation was accelerated, with the observation of strong silver nanodot emissions from the etched 65 silver nanoparticles (**Fig. 2B**). The emission intensity increased gradually but finally decreased close to background levels in 24 hrs due to redundant etching. The emission intensity of the above solution was pH-dependent (**Fig. 2C**), lowest in acidic solutions (pH 5.5), but higher in neutral solutions. This is in line with the 70 chelating power of polyamines since the protonated amino groups in acidic solutions lose the capability to coordinate silver ions. However, higher pH destabilized the emission, likely due to the strong affinity of silver for amino groups that erode the nanodots. Since organic molecules may evolve into fluorescent species,[16] 75 the generation of the above emissive species was not due to the derivatives of polyamines (**ESI**). Interestingly, the absorption of the nanoparticles decreased especially at the 600 nm to 900 nm region at the very beginning (**Fig. 2A**). This indicates that the large and non-spherical silver nanoparticles were first dissolved,[17] 80 which opposes the impression that larger silver nanoparticles are more stable than smaller nanoparticles. However, TEM supports the UV-Vis spectrum. The freshly prepared, silver nanoparticles

showed wide distributions in size, with a majority between 2 nm and 5 nm in diameter, but also with a large number of nanoparticles above 10 nm in diameter that showed crystalline structure (**Fig. 1A** and HRTEM in **Fig. 2S**). After the etching process, the large nanoparticles (>10 nm) disappeared, and the major size distribution centred at 3 – 5 nm (**Fig. 1B**). Such a phenomenon was observed in various ssDNA-stabilized silver nanoparticles (**Fig. 2S** and Ref. 21). Be noted that likely due to the weak stability of silver clusters, nanoparticles less than 2 nm in diameter are hard to be observed. It has been reported that smaller silver nanoparticles (<5 nm in diameter) are able to stabilize chemical bonding of oxygen species, whereas large nanoparticles experience more severe conditions of oxidation on their surface.[18] The observed stable stage of silver nanoparticles during etching process might be critical to the generation of emissive silver nanodots, by which smaller nanoparticles are prevented from being oxidized further to even smaller nanoparticles and finally dissolving fully. The accumulation of silver nanoparticles with a narrow size
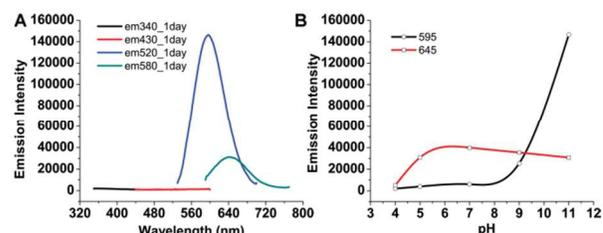

Fig. 2 Polyamine etching of C12-stabilized silver nanoparticles. (A) Absorption spectra of silver nanoparticles in the presence of dEtA (30 mM). (B) Emission spectra of the solution shown in (A); excited at 560 nm. (C) The emission intensity shown in (B) at varied pH (3 hrs incubation). (D) Absorption spectra of silver nanoparticles in the presence of dEtA (30 mM) and hydrogen peroxide (5 mM). Inset: images before (a) and after (b) the addition of the above agents solutions at pH 5, 7, 9 and 10 (from left to right).

distribution leads to a higher chemical yield of silver nanodots. Our hypothesis was supported by the fact that emissive specie cannot be generated in a stronger etching condition (**Fig. 2C**, pH 9 and **Fig 2D**).

Even though the emissive species were obtained, there were still considerable amount of silver nanoparticles in the solution. As shown in **Fig. 2A**, longer incubation of the above solution (17 hrs) resulted in only 8% drop in absorbance. Since silver clusters can be stabilized with either positively charged metal ions or a metal surface,[19, 20] it is not clear whether the luminescence originates from silver clusters on the surface of nanoparticles. After spinning the solution of etched silver nanoparticles, the precipitates (silver nanoparticles) showed no luminescence but the supernatant showed even higher emission intensity due to less particle scattering (**ESI, Fig. 1S**). Therefore, the active centres that formed silver nanodots must have been independent from the

large silver nanoparticles

One way to improve the yield of silver nanodots is to increase the formation rate of active centres. Hydrogen peroxide was therefore added to strengthen the oxidising power. The addition of hydrogen peroxide in this case, however, did not induce the


Fig. 3 C12 etching of C12-stabilized silver nanoparticles. (A) The emission spectra of silver nanodots generated by the addition of C12 (50 μM) to C12-stabilized silver nanoparticles at pH 11. "*xxx*" in Em*xxx*_1day stands for excitation wavelength. (B) The emission intensity at 645 nm (red) and 595 nm (black) of the solutions shown in (A) at varied pH.

formation of any luminescent species in the C12-stabilized silver nanoparticles, and the absorption of silver nanoparticles faded much faster when combining the hydrogen peroxide and dEtA as etching agents. The majority of the absorption almost disappeared after the addition of dEtA (30 mM) and hydrogen peroxide (5 mM) at pH 10 (**Fig. 2D**). The above etching tendency was contrary to the oxidising power of hydrogen peroxide, which has a lower redox potential (0. 878 V) in basic solution compared to that in acidic solution. This suggests that the formation of silver complexes between silver and polyamines is critical to the etching process. The synergetic effect of oxidation and chelation led to the fast oxidation of silver nanoparticles by hydrogen peroxide, but it was not accompanied by the formation of more luminescent silver nanodots. Instead, the emission intensity of the red started to decrease an hour after the addition of hydrogen peroxide (**ESI, Fig. 3S**) due to its sensitivity to oxidising agents.[21] In addition to the red, yellow and blue silver nanodot emitters were also observed.[21]

The strong affinity of cytosine-rich DNA to silver ions might enable the etching of silver nanoparticles.[22] Our results showed that the addition of extra C12 molecules to the C12-stabilized silver nanoparticles led to the formation of silver nanodots. Such a process was also pH-dependent. Emission of silver nanodots was barely observed at low pH. As the solution became more basic, the emission intensity of the red silver nanodots (λ_{em} = 645 nm) increased and then levelled off (**Fig. 3**). Interestingly, there was a new orange silver nanodot emitter (λ_{em} = 595 nm) observed with a large Stokes' shift of 75 nm. Its intensity was five times higher than the red emitter at pH 11. The absorption peak of the resulting nanodot emitter was screened by the strong plasmonic absorptions due to the presence of large amount of silver nanoparticles (**Fig. 2A**). Even though it was hard to observe an absorption peak from where the peak of the excitation spectrum of the nanodots locates, we have obtained emissions from the nanodots that show lower absorption but similar emission intensities compared to a known silver nanodot emitter (CGCGC12-encapsulated silver nanodot, **Fig. 4S**). Therefore, we believe that the silver nanodots generated by etching are as good as the regular silver nanodots. It was a great approach since the intensity reached close to half the intensity of silver nanodots

synthesized by the bottom-up method with the same amount of ssDNA and silver nitrate, given that the red and the orange have similar photophysical properties. Moreover, the C12-based etching did not induce the quenching of the freshly generated 5 silver nanodots.

The number of active centres on silver nanoparticles might be a considerable factor in determining the efficiency of silver nanodot generation. When we examined the etching of poly(acrylic acid)-stabilized silver nanoparticles, except that 10 hydrogen peroxide, none of the above treatments, *i.e.*, dEtA etching, dEtA and hydrogen peroxide etching or C12 etching, led to the formation of silver nanodots (**ESI, Fig. 5S**). This suggested that the poly(acrylic acid)-stabilized silver nanoparticles consisted of significantly fewer active centres compared to the 15 C12-stabilized nanoparticles.
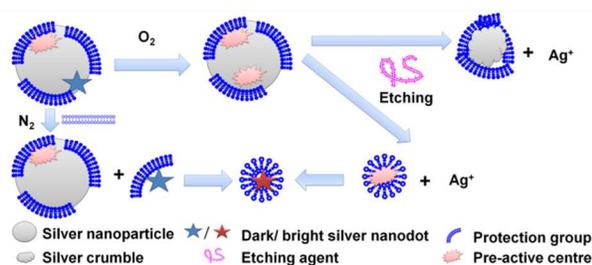
Scheme 1 Schematic showing the etching process and the generation of luminescent silver nanodots.

Interestingly, the freshly prepared silver nanoparticles 20 exhibited different properties from those aged. As C12 was added into the C12-stabilized silver nanoparticles under nitrogen protection, red emission was observed instantly and did not change in 24 hrs under nitrogen atmosphere (**ESI**, **Fig. 6SA**). However, once the silver nanoparticles were left in an aerated 25 solution, the addition of C12 triggered no emission at the beginning, but the emissions including both the blue and the red, emerged gradually (**ESI**, **Fig. 6SB**). It indicated that some dark silver nanodots had existed during the nanoparticle preparation but were oxidised once exposed to oxygen molecules (**Scheme** 30 **1**). The longer ageing time for the nanoparticles generated more active centres. Higher emission intensity was obtained in the 23 hrs-aged silver nanoparticles solution than the 16 hrs-aged samples (**ESI**, **Fig. 6SC**).

The silver nanodots were mainly generated from the active 35 centres (**Scheme 1**). The addition of different sequences of ssDNA that induce 615 nm, 560 nm and 700 nm silver nanodot emissions respectively to the C12-stabilized nanoparticles resulted in the generation of silver nanodots with the same emission spectra, but the emission intensity was strongly 40 sequence-dependent (**ESI, Fig. 7S**). Since the emission wavelength of a silver nanodot is so sensitive to its microenvironments, the same emission spectra indicated that the added ssDNA molecules did not contact directly with the active centres. Interestingly, such intensities correlated with the stability 45 of the corresponding ssDNA-encapsulated silver nanodots,[23] indicating that the stronger binding power of the ssDNA sequence etched the silver nanoparticles more efficiently to generate silver nanodots.

In summary, some dark silver nanodots have been generated 50 upon the synthesis of silver nanoparticles, but are oxidized once exposed to oxygen. The addition of chelating agents, such as polyamines or ssDNA molecules, accelerated the degradation of large silver nanoparticles to a stable stage of silver nanoparticles, which might be critical to the generation of emissive silver 55 nanodots. The etching process was strongly pH dependent, and the binding between silver and the etching groups was crucial for efficient etching. The active centres were especially important for the formation of silver nanodots. We have shown that etching of silver nanoparticles can be an alternative to generate new silver 60 nanodot emitters.

Notes and references

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