An anti-galvanic replacement reaction of DNA templated silver nanoclusters monitored by the light-scattering technique†

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An anti-galvanic replacement reaction (AGRR) of copper(ii) ions reduced by ultra-small ssDNA-templated silver nanoclusters forming Ag–Cu alloy nanoparticles was observed. The reaction is against the classic galvanic theory and was monitored sensitively by the light-scattering technique.

Galvanic replacement reactions (GRR) are often used for fabricating metal nanostructures.1 The reactions occur spontaneously when atoms of one metal meet ions of another metal with a higher electrochemical potential in solution,2 i.e., metals can reduce less reactive metal ions. Conversely, metal ions are difficult to be reduced by less reactive metals owing to the negative driving force. In a recent report, silver ions were reduced by thiolate-protected gold nanoparticles,3 wherein the thiolate ligand plays an important role in the reaction because it provides partial negative charges attached to the surface of gold nanoparticles. In this contribution, we demonstrate that ultra-small DNA templated silver nanoclusters (DNA–Ag NCs) reduce copper(i) ions to form bimetallic nanoparticles without thiolate-protection, which is opposite to the classic galvanic theory. Such a novel chemical reaction process, namely anti-galvanic replacement reaction (AGRR), is applied as an ON/OFF sensor and sensitively monitored by using the light-scattering technique.

In a typical assay (Scheme 1), a single-stranded DNA (ssDNA) sequence is selected as a template for synthesizing silver nanoclusters (Ag NCs). The obtained ultra-small DNA–Ag NCs exhibit a strong fluorescence signal, which is a superior characteristic compared with nanoparticles. Upon introduction of copper(ii) ions, DNA–Ag NCs reduce Cu2+ to Cu0, producing non-fluorescent Ag/Cu alloy nanoparticles, while an anti-galvanic replacement reaction occurs. To monitor the occurrence of AGRR, the light-scattering technique is applied. The light-scattering signal of prepared DNA–Ag NCs is low showing an “OFF” state. Upon addition of copper(ii) ions, DNA–Ag NCs reduce Cu2+ ions to Cu0, forming bimetallic alloy nanoparticles, thereby activating the light-scattering signal significantly with an “ON” state. The light-scattering technique provides a feasible and powerful tool for monitoring the synthesis of bimetallic nanomaterials by the AGRR protocol.

Scheme 1 Schematic illustration of the anti-galvanic replacement reaction of DNA–Ag NCs monitored by the light-scattering (LS) technique.

Silver nanoclusters were prepared by using a ssDNA sequence (ODN1, 5’-CGCTAACGCTAACGCTAACGCTA-3’ or ODN2, 5’-GGCTAAGGCTAAGGCTAAGGCTA-3’) as a template in aqueous solution (see Table S1 and synthesis details in the ESI†). Upon excitation at 450–460 nm, the synthesized Ag NCs exhibit an emission band centered at 554 or 515 nm for ODN1 or ODN2 ssDNA sequence, respectively (Fig. S1 and Table S2 in the ESI†). In addition, the fluorescence lifetimes of DNA–Ag NCs were measured to be 2.35 and 2.31 ns for ODN1 and ODN2 ssDNA–Ag NCs, respectively (Fig. S2 and Table S3 in the ESI†), which are consistent with those of silver nanoclusters reported.5 X-ray photoelectron spectroscopy (XPS) analyses suggest that silver in ODN1 and ODN2 ssDNA–Ag NCs is neutral. The transmission electron microscopy (TEM) image offers the morphological property of the prepared DNA–Ag NCs (Fig. 1a). In short, ultra-small fluorescent DNA–Ag NCs were successfully obtained.

TEM images (Fig. 1a and b) of DNA–Ag NCs clearly showed that the particle size increases from several nanometers (ultra small size fluorescent nanoclusters) to above 10 nanometers (non-fluorescent nanoparticles) upon the addition of Cu2+ ions. The process was also monitored by light-scattering spectroscopy, an extremely sensitive

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and selective technique for monitoring molecular assembly. As displayed in Fig. 1c, the light-scattering signal of prepared ODN1 ssDNA–Ag NCs is quite weak over the whole scan range of 250–700 nm. However, a remarkable enhancement in the light-scattering signal can be observed when a trace amount of Cu2+ was introduced under the same conditions (Fig. 1c), and the intensities increase continuously with a gradual increment of Cu2+ concentration. A similar phenomenon also appears for ODN2 ssDNA–Ag NCs (Fig. S3, ESI†). These are mainly due to the increase of the diameters of scattering particles according to Rayleigh scattering theory. The conclusion is verified by the TEM image (Fig. 1b).

We speculate that DNA–Ag NCs reduce Cu2+ ions to Cu0, producing Ag/Cu alloy nanoparticles with a large size, thereby inducing the enhanced light-scattering signal. The uneven color of one nanoparticle in the TEM image (Fig. 1b) reveals that the nanoparticle is probably an alloy.

To further confirm the product of the reaction between neutral DNA–Ag NCs and Cu2+ ions, MALDI-TOF mass spectrometry was used. In the mass spectrum of ODN1 ssDNA–Ag NCs, the most abundant species detected are [ODN1 + Ag2] and [ODN1 + Ag3] (7194 m/z, 7302 m/z, Fig. 2a). The results are consistent with the simulated conclusion that Ag3 could be fabricated by cytosine.

For the product of the reaction of ODN2 ssDNA–Ag NCs with 1 mM Cu2+ ions, the bimetallic nanoparticles peak of [ODN1 + Ag2Cu3] (7320 m/z, Fig. 2b) is observed, indicating the replacement reaction between neutral silver of DNA–Ag NCs and Cu2+ ions. Similar results for ODN2 ssDNA–Ag NCs in the absence and presence of Cu2+ ions were also observed (Fig. S7, ESI†). According to the electrochemical potential, silver is less reactive than copper. It is a spontaneous process that copper metal can reduce silver ions, while the reverse reaction is difficult in light of the classic galvanic theory. However, in our assays, ultra small DNA templated Ag NCs reduce Cu3+ to Cu0, forming bimetallic nanoparticles without thiolate-protection in the aqueous phase at room temperature, which is against the classic galvanic theory.

XPS of ssDNA–Ag NCs in the absence and presence of copper(II) ions were measured (Fig. 3) to further verify the reduction process. XPS of the prepared DNA–Ag NCs show the binding energies of 368.2 eV and 374.2 eV (assigned to Ag3d5/2 and Ag3d3/2, respectively), revealing that the silver in ODN1 ssDNA–Ag NCs is neutral (Fig. 3a). The binding energy of 932.6 eV (assigned to Cu2p3/2, Fig. 3b) indicates that the incorporated copper exists in neutral

![Fig. 1](a) The TEM image of synthesized ODN1 ssDNA–Ag NCs, scale bar: 20 nm. The inset is a high-resolution TEM (HRTEM) image, scale bar: 5 nm. (b) The TEM image of obtained ODN1 ssDNA–Ag NCs in the presence of Cu2+ ions (1 mM), scale bar: 50 nm. The inset is an HRTEM image, scale bar: 10 nm. (c) Light-scattering spectra of ODN1 ssDNA templated silver nanoclusters in the absence and presence of various concentrations of copper ions at room temperature. Conditions: 1 (black), buffer solution; 2 (red), ODN1 ssDNA–Ag NCs; 3–6: as for 2 + Cu2+ ions (mM): 0.125 (green), 0.375 (blue), 0.75 (cyan), 1.5 (magenta). The inset figure displays the plot of the increment of the light-scattering intensity of ODN1 ssDNA–Ag NCs versus the concentration of Cu2+ ions. (d) The absorption spectra of the synthesized ODN1 ssDNA–Ag NCs in the absence (1) and presence (2) of 4 μM Cu2+ ions, meanwhile the emission spectra of the obtained ODN1 ssDNA–Ag NCs in the absence (3) and presence (4) of 640 μM Cu2+ ions. The addition of Cu2+ ions induces the significant enhancement of absorption spectra and remarkable decrease of fluorescence spectra.

![Fig. 2](MALDI-TOF mass spectra of synthesized ODN1 ssDNA–Ag NCs in the absence (a) and presence (b) of 1 mM Cu2+ ions.)
charge state. Meanwhile, similar results from the XPS of ODN2 ssDNA–Ag NCs with several other metal ions was investigated (Fig. S9, ESI†). We found that Cu2+, Pb2+ and Hg2+ ions can be reduced after the addition of more reactive metal ions without thiolate protection in the aqueous phase at room temperature. The Cu2+ ions were reduced by DNA templated silver nanoclusters at room temperature as an anti-galvanic replacement reaction.

To evaluate the reliability of monitoring the occurrence of AGRR by the light-scattering technique, reactions of DNA-Ag NCs with several other metal ions was investigated (Fig. S9, ESI†). We found that Cu2+, Pb2+ and Hg2+ ions can be reduced by both ODN1 and ODN2 ssDNA–Ag NCs, which is consistent with the reported work.3a Thus, the light-scattering technique can be used for monitoring the occurrence of AGRR.

In summary, we found a novel anti-galvanic replacement reaction (AGRR) of DNA templated noble-metal nanoclusters after the addition of more reactive metal ions without thiolate protection in the aqueous phase at room temperature. The AGRR provides a facile and mild method to synthesize alloys in the nanoscale, which nicely complements the current synthetic methods for bimetallic nanomaterials. Moreover, the light-scattering technique is used for the first time for sensitively monitoring the reaction, offering a new and reliable tool for the tunability of the synthesis of bimetallic nanomaterials.