Photoinduced Outgrowth of Gold Nanotadpoles in Aqueous Bilayer Dispersions

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An aqueous-phase synthesis of gold nanotadpoles by using bilayer membranes as growth regulating factor is newly developed. The gold nanotadpoles are formed by photoreduction of $Au(OH)_4^-$ in aqueous bilayer dispersion. The outgrowth of tails occurred from spherical nanoparticles, which are regulated depending on the photoirradiation time.

Gold nanocrystals have attracted much interest because of their diverse use in catalysis, photonics, electronics, biological labeling and imaging.[1] Their physicochemical properties are tunable depending on the size, shape, and interactions between them.[2] The morphology of nanoparticles especially plays a decisive role in determining their surface-related characteristics, and accordingly the development of synthetic strategies for anisotropic gold nanocrystals has been emerging as a challenging issue. Classical nonspherical nanostructures include rods,[3] wires,[4] and plates,[5] whereas nanocrystals with higher order complexities such as branched nanocrystals,[6] star-shaped nanocrystals,[7] porous nanocrystals,[8] and tadpoles[9] are emerging as new families of exotic nanostructures. They show unique optical properties which are distinct from isotropic nanoparticles.

We describe herein a simple photochemical route to gold nanotadpoles in the presence of ammonium bilayer membranes. The tadpole-shaped gold nanocrystals are interesting objects because of their unusual chimeric structure consisting of a nanoparticle head and a nanowire tail. Since gold has a highly symmetric face-centered cubic (fcc) structure, nanotadpoles are thermodynamically unfavorable or unstable nanostructures, i.e., have high surface energy. Consequently, their formation is governed by reaction kinetics rather than thermodynamics, and the kinetics of both nucleation and growth need to be properly controlled. Tian et al. recently reported synthesis of nanotadpoles by reducing gold ions with sodium citrate in the presence of capping agents such as sodium dodecylsulfonate.[9a] Others have devised a combined seeding and rapid cooling approach,[9b] or the use of poly(vinylpyrrolidone) as mild reducing agent and stabilizer.[9c] However, these protocols all employ reducing agents which require seed crystals and delicate control of the concentration and temperature. In addition, causal correlation between synthetic conditions and morphology of nanocrystals is not well understood. Thus, the development of simple room temperature synthetic methods for nanotadpoles is still in its infancy. Our strategy is to use $Au(OH)_4^-$ complex as an activated precursor for photoreduction.[10] It allows us to omit the use of reducing agent and seed crystals. Bilayer membranes display higher self-organizing properties than surfactant micelles and often provide better interfaces for inorganic nanosynthesis.[11] Ammonium amphiphile **1** (Chart 1) was employed since it was expected to electrostatically interact with negatively charged precursor ions and growing nanocrystals.

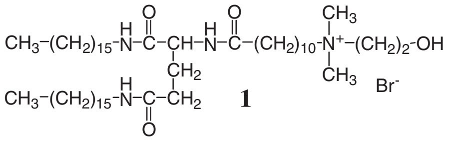

Chart 1.

Aqueous solution of colorless $Au(OH)_4^-$ ions (pH, 10) was prepared by adding aqueous sodium hydroxide (1 M) dropwise to a pale yellow solution of $AuCl_4^-$ in pure water (21.6 mM).[10] Amphiphile **1** (L-form; concentration, 10 mM; 1 mL) was dispersed in pure water by ultrasonication (Branson Sonifier Model 185). Compound **1** possesses three amide units which form multiple hydrogen-bond networks in aqueous bilayers, giving developed nanofibrous structures (Figure S1).[12] 1 mL of the $Au(OH)_4^-$ aqueous solution was added to the aqueous bilayer dispersion at room temperature (final concentration, $[\mathbf{1}] = 5$ mM, $[Au(OH)_4] = 10.8$ mM). The dispersion was then photoirradiated with a high-pressure mercury lamp (Ushio UI-501C, $\lambda > 300$ nm, $I_{300-400} = 7.2$ mW cm^{-2}) for 40 min at 20 °C under gentle stirring. The color of the dispersion gradually changed to purple during photoirradiation. The products were collected by ultracentrifugation and washed with chloroform, methanol, and water. Finally, the nanoparticles were redispersed in water by ultrasonication.

Figure 1A shows a typical transmission electronmicroscopy (TEM) image of the obtained gold nanocrystals. Nanotadpoles with a head width of ca. 25 nm and a tail length of ca. 85 nm are abundantly seen. Formation of nanotadpoles was also confirmed by scanning electron microscopy (SEM, Figure S2).[12] A vis–NIR absorption spectrum of aqueous nanotadpoles is shown in Figure 1B. A plasmon peak was observed at 538 nm, which is blue shifted compared to previously reported nanotadpoles.[9] It implies that the electron oscillation corresponding to

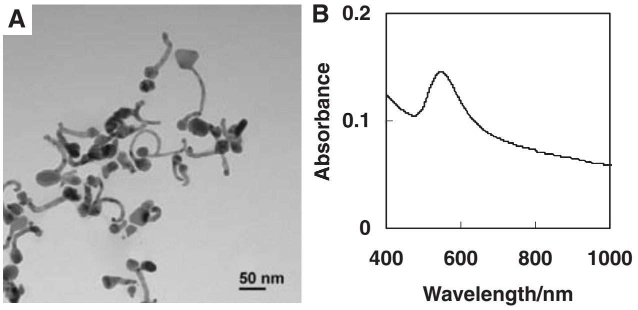

Figure 1. TEM image (A) and UV–vis–NIR spectrum (B) of gold nanotadpoles obtained by photoreduction of $Au(OH)_4^-$ in aqueous bilayer **1**. $[\mathbf{1}] = 5$ mM, $[Au(OH)_4^-] = 10.8$ mM.

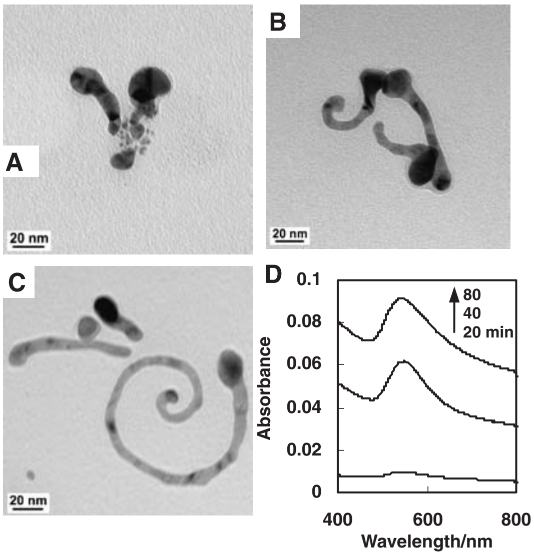

Figure 2. TEM images (A)–(C) and absorption spectra (D) of gold nanotadpoles obtaind at different photoirradiation periods; (A) $t = 20$, (B) 40, and (C) 80 min. [**1**] = 5 mM.

the plasmon absorption of these nanotadpoles is mostly attributed to the head nanoparticle moiety.

To gain insight into the growth process of nanotadpoles, those at the intermediate stages of photoreduction were characterized by TEM and vis-absorption spectra. Figures 2A–2C show morphological changes with time. Spherical nanoparticles and embryonic nanotadpoles were observed at $t = 20$ min. As the reaction proceeds, the length of tails increased with irradiation time (Figures 2B and 2C), while the initial size of head moiety was maintained. Thus, the formation of nanotadpoles consists of two distinctive stages; nucleation of the head moiety followed by the tail elongation. The growth in tail moiety probably occurred via the fusion of small gold nanoclusters at the energetically most unstable nucleation site, which resulted in the multicrystalline structure as a whole. The polycrystalline nature of nanotails is also supported by curled structures observed in Figures 2B and 2C. These observations can account for the unchanged plasmon absorption peak with the growth in tail length (Figure 2D).

The mixing ratio of amphiphile **1** and $Au(OH)_4{}^-$ is important in determining the morphology of gold nanocrystals. TEM images of gold nanoparticles obtained at varied concentration of amphiphile **1** are shown in Figure S3.[12] The formation of nanotadpoles was not induced when the concentration of **1** is below 5 mM ($[Au(OH)_4{}^-] = 10.8$ mM). Therefore, structural evolution of nanotadpoles requires the presence of bilayer assemblies on which a fair amount of $Au(OH)_4{}^-$ ions preorganized.

A plausible mechanism for evolution of gold nanotadpoles is shown in Figure 3. Spherical gold nanocrystals are formed by photoreduction of $Au(OH)_4{}^-$ in the initial reaction stage. They are electrostatically bound to fibrous bilayer assemblies which assisted the succeeding directional growth of nanotails. The presence of nanofibrous bilayer is important, since photoreduction of $Au(OH)_4{}^-$ ions in aqueous micelles of cetyltrimethylammonium bromide (CTAB) only gave disordered nanocrystals (Figure S5).[12]

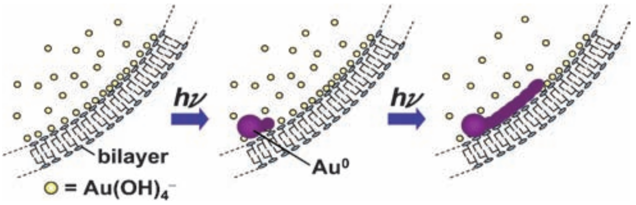

Figure 3. A schematic illustration of the growth of gold nanotadpoles assisted by fibrous bilayer assembly.

In conclusion, gold nanotadpoles are formed in aqueous bilayer dispersions by photoreduction of $Au(OH)_4{}^-$ ions. This methodology is simple, does not require any seed crystals and proceeds at room temperature. The outgrowth of tails from nanotadpoles is basically tunable by photoirradiation period. We envisage the photoreduction of activated precursor adsorbed at the surface of ordered molecular self-assemblies would be widely applied to the synthesis of varied anisotropic inorganic nanoarchitectures which are not available from conventional methodologies conducted under thermal equilibirum.

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