Chloride-induced shape transformation of silver nanoparticles in a water environment

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ABSTRACT

The effects of chloride on dissolution and toxicity of silver nanoparticles (AgNPs) have been well studied. However, their intermediate shapes during the transition have not been illustrated to-date. Herein, the chloride-induced shape transformation process of AgNPs under long-term, low-concentration conditions is explored. A unique triangular Ag—AgCl heterostructure is observed. The structure then evolves into a symmetric hexapod and finally into a smaller AgNP. This transformation process could be affected by other environmental conditions, such as 0.4 mg/mL humic acid, 5% surfactants and 1 mg/mL bovine serum albumin protein. Our results offer new knowledge regarding the shape transformation process of AgNPs in the presence of chloride, which can be valuable in relevant studies concerning the effect of water chemistry on the behavior of AgNPs.

1. Introduction

Due to their inherent antimicrobial properties, silver nanoparticles (AgNPs) are widely used in a variety of products, including textiles, bandages, deodorants, baby products, toothpaste, air filters and household appliances (El-Temsah and Joner, 2012; Kumari et al., 2009). The increasing number of products containing AgNPs will lead to a larger release of AgNPs into the environment during the manufacture, use, cleaning and disposal of the products (Chen et al., 2013). This release could cause a mass interaction between AgNPs and many environmental factors (inorganic anions, metal cations, and even natural organic matters), leading to alterations in the composition, structure, and surface properties of the AgNPs (Chambers et al., 2013; Levard et al., 2013a, 2013b; Liu et al., 2013; Ma et al., 2013; Wirth et al., 2012). Accordingly, these alterations could in-turn affect the toxicity and transportation of AgNPs in natural water. Therefore, the environmental transformations of AgNPs should be investigated to determine their changes in morphology and size. However, many of the former toxicity studies that have been conducted regarding AgNPs are not

environmentally relevant (Burchardt et al., 2012; Poynton et al., 2012; Schultz et al., 2012; van Aerle et al., 2013; Yu et al., 2013). The shape transformations of the nanoparticles under various environments conditions have been scarcely evaluated. In particular, knowledge of the intermediate products during the transforming process, which significantly affects the stability of AgNPs and consequently their bioavailability and toxicity, is limited.

Structurally, well-defined silver nanoparticles include nanospheres, nanocubes, nanoplates, nanoprisms, nanorods, nanowires and nanobelts, etc. (Jana et al., 2001; Jin et al., 2003, 2001; Liu et al., 2009; Sun et al., 2003; Zhang et al., 2009), yet most of these shapes are not thermodynamically stable in the presence of certain etching agents and tend to develop into new morphologies with lower surface free energies (An et al., 2008). This instability offers a great opportunity to utilize nanocrystals as environmental tracers by studying their transformation process under environmental exposure. Here, we chose Ag triangular nanoplates (Ag-TNPs) with relatively sharp corners as a typical example to demonstrate the susceptibility of AgNPs to environmental transformations based on the well-established localized surface plasmon resonance (LSPR) of Ag-TNPs (Jin et al., 2001; Kelly et al., 2003).

Ag triangular nanoplates, which exhibit striking color changes during structural transformations, along with the intrinsic strong

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in-plane dipole resonance, have been explored as indicators to visually depict shape conversion, which can be utilized in long-term research with low-concentration exposure to various environments. The interactions between Ag-TNPs and anions, which extensively exist in natural environments, have been widely investigated (An et al., 2008; Cathcart et al., 2009; Hou et al., 2014; Hsu et al., 2010; Jiang and Yu, 2008; Yang et al., 2013). For example, researchers have found that Cl^- can etch the corners and side faces of the Ag-TNPs, resulting in the transformation of Ag-TNPs to disk-like shapes (An et al., 2008). Further studies have shown that in addition to Cl^-, anions such as Br^-, I^-, $H_2PO_4^-$, and SCN^- can also interact with Ag-TNPs and shift the SPR band of the Ag-TNPs. Therefore, Jiang and Yu demonstrated a simple sensing method to detect inorganic anions by SPR shifts of Ag-TNPs (Jiang and Yu, 2008). Huang's group studied the time-dependent surface plasmon resonance spectroscopy of silver TNPs in the presence of halide (Hsu et al., 2010). However, from an environmental point of view, the long-term, low-concentration and multi-factor co-exposure are far different from the chemical contexts, and therefore, further environmentally-relevant studies are required. This work explores the shape transformation of Ag-TNPs in a water environment using LSPR and transmission electron microscopy (TEM), with an emphasis on the intermediate stages during the environmental transformation process. In addition, a systematic evaluation of the shape transformations and environmental fates of Ag-TNPs mediated by environmental factors are illustrated in this study, which are valuable for expanding our knowledge of the effect of water chemistry on the behavior of AgNPs.

2. Materials and methods

2.1. Materials

Silver nitrate ($AgNO_3$), L-ascorbic acid (AA), sodium citrate (Na_3CA), sodium borohydride ($NaBH_4$), poly(vinyl pyrrolidone) (PVP, MW $\approx$ 29,000), and potassium chloride (KCl) were purchased from Sinopharm Chemical Reagent Co. Lid. (Shanghai, China). Humic acid (HA), sodium dodecyl sulfate (SDS), tween 20, triton X-100, bovine serum albumin (BSA) and 11-mercaptoundecanoic acid (11-MUA) were purchased from Sigma–Aldrich. All of the chemicals were used as received without further purification. Ultrapure Millipore water (18.2 MΩ cm) was used as the solvent throughout.

2.2. Preparation of Ag triangular nanoplates

The Ag nanoplates were prepared using a previously reported seed-mediated procedure (Zeng et al., 2010, 2011). Two steps were involved. In the first step, Ag seeds were prepared as follows: 0.3 mL of aqueous $NaBH_4$ (5 mM) was injected into an 11-mL aqueous solution containing $AgNO_3$ (0.11 mM) and Na_3CA (2.05 mM) under magnetic stirring. Stirring was stopped after 10 min. This seed solution was then aged at room temperature for 5 h prior to use. In the second step, 100 mL of ultrapure water was mixed with aqueous $AgNO_3$ (2.5 mL, 5 mM), aqueous PVP (7.5 mL, 0.7 mM), aqueous Na_3CA (7.5 mL, 30 mM), and the as-prepared seed solution (0.2 mL), followed by slow dropping into aqueous AA (62.5 mL, 1 mM) under magnetic stirring. The color of the solution gradually changed into cyan. The product was directly used for the environmental shape transformation tests without further purification or treatment.

2.3. Instrumentation

TEM images were taken using a Hitachi H-7650 transmission electron microscope at an acceleration voltage of 100 kV. The UV–Vis–NIR extinction spectra were obtained using a Shimadzu UV-VIS-NIR spectrophotometer (UV-3600). The concentration of Ag-TNPs was determined via inductively coupled plasma atomic emission spectroscopy (ICP-AES, Atomscan Advantage, Thermo Jarrell Ash Corporation, USA). The X-ray photoelectron spectra (XPS) analysis was performed using an ESCALAB 250 (Thermo-VG Scientific). The specimens for XPS were prepared by covering the Ag–AgCl hybrid nanoplates on silicon wafers. The X-ray diffraction (XRD) analysis was performed using a MiniFlex 600 (Rigaku). The specimens for XRD were prepared by covering the Ag–AgCl hybrid nanoplates on glass sheets.

2.4. Shape transformation studies of the Ag triangular nanoplates under various environmental conditions

Using a standard procedure for the chloride-induced Ag-TNP shape transformation experiment, 10 or 20 portions of 0.1 mL KCl solution was added to 25 mL of the aqueous suspension of triangular Ag nanoplates (500 ng L^{-1} determined by ICP-AES, pH 6.8) during each titration under magnetic stirring. The reaction was quenched at a specific time point via centrifugation at 12,000 rpm for 5 min. The product was then precipitated twice with 10 mL water via centrifugation and decantation. The final product was re-dispersed in water for further structural analyses and UV–Vis–NIR measurements. For the reactions involving other environmental factors, the Ag nanoplates were incubated with the different environmental factors (HA, surfactants, protein, and thiol) in a vial for 24 h before the addition of KCl. A similar procedure was used. The typical resolution of the time course spectra that were recorded every 2 min was approximately 1 nm under constant Cl-ions concentration. All experiments were repeated at least three times.

3. Results and discussion

3.1. Properties of the Ag triangular nanoplates (Ag-TNPs)

The synthesized Ag-TNPs were characterized based on TEM and the UV–Vis–NIR extinction spectrum. As shown in the TEM image, the Ag-TNPs exhibit an average thickness of approximately 5 nm and with edge lengths varying in the range of 70–80 nm (Fig. 1 and Fig. S1). The Ag-TNPs display three distinct peaks at 332 nm, 555 nm and 804 nm (Fig. 1). According to previous studies, the small, sharp peak at 332 nm is attributed to the out-of-plane quadrupole SPR band of the Ag-TNPs. The peaks centered at 555 nm and 804 nm are attributed to the in-plane quadrupole and
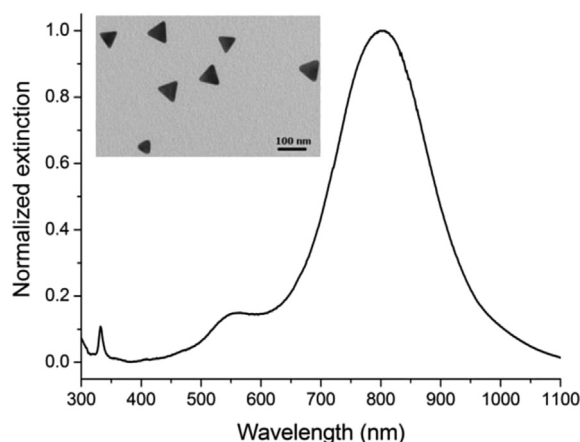

Fig. 1. UV–Vis–NIR extinction spectrum and TEM image of Ag-TNPs (inset).