

## A facile photochemical route for the synthesis of triangular Ag nanoplates and colorimetric sensing of H<sub>2</sub>O<sub>2</sub>



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### ABSTRACT

We describe a facile photochemical route for the synthesis of triangular Ag nanoplates using NADH model compound, N-benzyl-1,4-dihydronicotinamide (BNAH) and the shape-dependent colorimetric sensing of H<sub>2</sub>O<sub>2</sub>. Synthesis of Ag nanoplates involves the irradiation of an aqueous mixture of Ag(I) and BNAH in the presence of trisodium citrate with sunlight for 30 min. The photoexcited BNAH reduces Ag(I) to Ag(0) and quasi-spherical nanoparticles were obtained at the initial stage of the reaction. The spherical nanoparticles undergo shape transformation by light and yield nanoparticles of different shapes. The spherical nanoparticles first undergo light-induced transformation to hexagonal nanoplates (~50 nm) and then to triangular nanoplates (40 nm) in 30 min of irradiation. The triangular nanoplates exhibit two main bands corresponding to the quadrupole and dipole in-plane plasmon resonance at 407 and 620 nm, respectively, along with a shoulder band ~335 nm corresponding to out-of-plane quadrupole resonance. The Ag nanostructure of different shapes has been used for the colorimetric sensing of H<sub>2</sub>O<sub>2</sub>. The thermodynamically favorable oxidative etching of triangular Ag nanoplates by H<sub>2</sub>O<sub>2</sub> turns the initial green color of Ag nanostructures to gray. In the presence of H<sub>2</sub>O<sub>2</sub>, the surface plasmon band at 407 nm completely vanishes and the absorbance of the band at 620 nm significantly decreases. The oxidative etching transforms the triangular nanoplates into nanodisc with an average size of 15 nm in 1 min. The shape transformation-induced visible color change was used for the quantification of H<sub>2</sub>O<sub>2</sub>. Interestingly, the oxidative etching reaction depends on the shape of the nanoparticles. The shape of the Ag nanoparticles actually controls the redox reaction. The triangular Ag nanoplates are highly sensitive toward H<sub>2</sub>O<sub>2</sub> and it could detect H<sub>2</sub>O<sub>2</sub> at sub-micro molar level without any interference from coexisting other analytes. The high reactivity of the triangular nanoplates can be ascribed to the existence of coordinatively unsaturated reactive atoms at the corners of the triangular nanostructure.

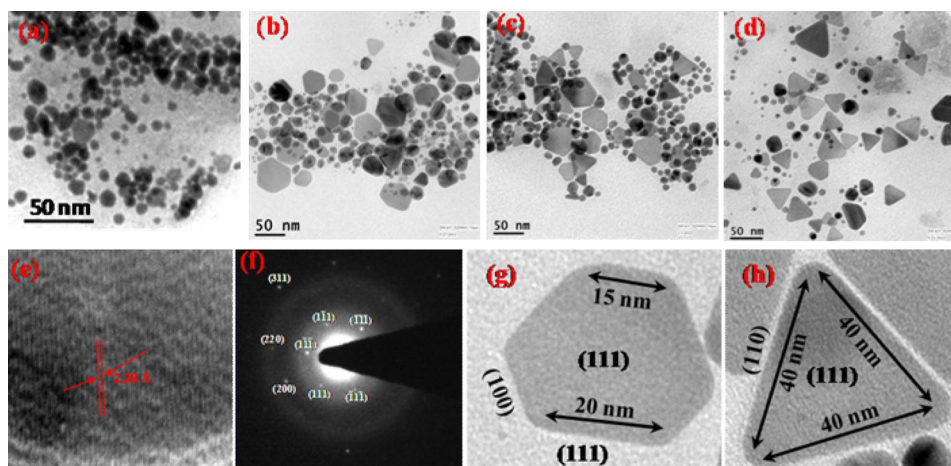
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### 1. Introduction

The synthesis of Ag nanoparticles received significant attention owing to the fascinating optical properties. The interesting properties have been exploited for sensing, drug delivery, imaging, etc. [1]. Among the noble metals, Ag nanoparticles exhibit the highest efficiency of plasmon excitation [2]. They interact more efficiently with visible light than any organic/inorganic chromophore [3]. Ag nanoparticle can capture more light than its physical size limit, as the absorption or scattering cross section exceeds the geometric cross section of the particle [3]. The optical property of Ag nanoparticles strongly depends on the size, shape, dielectric constant of the surrounding medium, and interparticle distance. Among the various shapes, triangular Ag nanoprisms/nanoplates are very promising for various applications [4]. The surface plasmon band of Ag nanoplates can be easily tuned

by controlling the aspect ratio [5]. In the past, a variety of synthetic methods have been developed for the synthesis of library of Ag nanostructures with different shapes and size in aqueous and non-aqueous media [4–11]. The chemical and photochemical routes with shape regulating reagents have been employed in the past for the synthesis of triangular nanoprisms/nanoplates [5,11]. The chemical routes involve the use of multiple reagents such as citrate, H<sub>2</sub>O<sub>2</sub>, polyvinylpyrrolidone, etc. In the photochemical synthesis, the Ag nanoplates were obtained by tuning the wavelength of the light source [10]. The photochemical conversion of spherical Ag nanoparticles to nanoprism/nanoplate was achieved using various stabilizing agents [9]. One of the primary requirements in the photochemical conversion of spherical Ag nanoparticles to nanoplate is the overlap of the incident light with surface plasmon of the nanoparticles [5]. In most of the cases, the Ag nanoparticles undergo shape transformation first to triangular nanoplates and then to hexagonal nanoplates. To the best of our knowledge, only one report describes the photo-induced shape transformation of hexagonal to triangular nanoplates [12].

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**Fig. 1.** TEM images of Ag nanostructure obtained at (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min of the reaction. The HRTEM and SEAD pattern for the triangular Ag nanoplates are shown in (e) and (f). Selected hexagonal and triangular plates are shown in (g) and (h).

$\text{H}_2\text{O}_2$  is an oxygen metabolite and has dual role in the living system. It has been considered as a “*necessary evil*” due to the fact that it involves in the redox signaling for the normal function and it is an unwanted “*killing agent*” [13]. The abnormal generation of  $\text{H}_2\text{O}_2$  induces oxidative stress and is associated with aging and cancer. Moreover,  $\text{H}_2\text{O}_2$  is traditionally used as a food additive to control the growth of microorganism and bleaching. According to the “Code of Federal Regulations”  $\text{H}_2\text{O}_2$  was usually accepted as safe material for the use as a bleaching agent in agreement with good manufacturing practice [14]. In Japan,  $\text{H}_2\text{O}_2$  was used as a food additive for sterilizing and bleaching purposes until Feb 1980 [15]. Later, the Standards and Specifications were partially modified [15] as the drinking water administered with at 0.1–0.4% of  $\text{H}_2\text{O}_2$  was found to induce cancer in the duodenum of mouse [16]. The sensing of  $\text{H}_2\text{O}_2$  has also received enormous interest in the development of biosensors [17–19]; the working function of oxidase-based biosensors involves the sensing of enzymatically generated  $\text{H}_2\text{O}_2$  [17–19]. Several enzymatic [20] and non-enzymatic [21] analytical methods have been used for the detection and quantification of  $\text{H}_2\text{O}_2$  [20–23]. Willner’s group successfully exploited the fascinating optical properties of metal and metal oxide nanoparticles in the development of oxidase enzyme-based biosensing protocols [18,19]. Recently, Xia’s group demonstrated the tailoring of the optical property of Au–Ag alloy nanoboxes and the measurement of  $\text{H}_2\text{O}_2$  [24]. Fan’s group demonstrated that the in situ generated  $\text{H}_2\text{O}_2$  by Au nanoparticle catalyzed glucose oxidation induces the seed mediated growth of Au nanoparticles [25]. Although various methods have been proposed, the development of a simple cost-effective analytical protocol for the selective, reliable sensing of  $\text{H}_2\text{O}_2$  is still a challenging task. Our group is interested in the development of optical and electrochemical sensing methodologies for various analytes using nanoscale functional materials [26,27]. In continuation of our earlier works [26] in the development of photochemical route using visible light, herein, we describe a new photo-assisted route for the synthesis of triangular Ag nanoplates in aqueous medium using NADH model compound BNAH in presence of trisodium citrate as a stabilizer and the shape-dependent optical sensing of  $\text{H}_2\text{O}_2$  at sub-micromolar level based on the shape transformation-induced visible color change.

## 2. Experimental

### 2.1. Materials

$\text{AgNO}_3$ ,  $\text{H}_2\text{O}_2$ , and trisodium citrate were purchased from Merck and BNAH was purchased from Tokyo Chemical Industry Co., Ltd. All

other chemicals used in this investigation were of analytical grade and used without further purification.

### 2.2. Instrumentation

Electronic absorption spectra were taken using CARY 5000 UV–visible–NIR spectrophotometer. TEM images were acquired using JEOL JEM-2010 microscopes with an operating voltage of 200 kV. XRD patterns of the samples were collected using Panalytical X’pert PRO XRD unit with nickel-filtered Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). Electrochemical experiments were performed with CHI643B electrochemical analyzer (CHI) using a two-compartment, three-electrode electrochemical cell. A glassy carbon (GC) working electrode, Ag/AgCl (3 M KCl) reference electrode, and Pt wire auxiliary electrodes were used in the electrochemical studies.

### 2.3. Synthesis of Ag nanostructures

In a typical single step synthetic procedure, aqueous solution of 90  $\mu\text{L}$  of  $\text{AgNO}_3$  (20 mM), 2.86 mL of BNAH (0.32 mM), and 50  $\mu\text{L}$  of trisodium citrate (40 mM) were mixed and irradiated using a 125-W sunlamp with wavelengths  $>350 \text{ nm}$  for 30 min. Polyhedral shape Ag nanoparticles were synthesized according to our previous report [26].

### 2.4. Optical sensing of $\text{H}_2\text{O}_2$

For the optical sensing of  $\text{H}_2\text{O}_2$ , the as-synthesized colloidal Ag nanoparticles were quantitatively diluted as the absorbance was significantly high. The typical procedure for the optical sensing involves the addition of aliquots of  $\text{H}_2\text{O}_2$  solution to different vials containing 3 mL Ag nanoparticles. The spectral measurements were performed 1 min after the addition of  $\text{H}_2\text{O}_2$ .

## 3. Result and discussion

### 3.1. Characterization and growth mechanism

Fig. 1 displays the TEM images of Ag nanostructures acquired at different time interval during the reaction. The size and shape of the nanostructures depend on the irradiation time. At the initial stage (5 min), spherical and quasi-spherical Ag nanostructures with an average size of 10 nm were obtained whereas distorted hexagonal nanoplates with an average size of 50 nm were obtained at 10 min of irradiation. The edge lengths of hexagonal nanoplates are not

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