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Solvothermal synthesis and formation mechanism of chain-like triangular silver nanoplate assemblies: Application to metal-enhanced fluorescence (MEF)

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ABSTRACT

Novel silver chain-like triangular nanoplate assemblies (CTNAs) were synthesized via a solvothermal approach. The shape of CTNAs was determined by some dominant parameters, including the concentration of poly (vinyl pyrrolidone), reactive time and temperature. Each CTNA is a single crystal with continuous lattice fringes in the inner, and could be considered as the combination of one-dimensional nanobelt and two-dimensional nanoplates. The formation of the CTNAs could be ascribed to the secondary growth of the nanocrystals. The edges of the nanoplates in the assembly were parallel to each other in order to maintain the lower surface energy. Interestingly, this novel nanostructure is a significant improvement for application in metal-enhanced fluorescence. Typical 88- and 13-fold enhancement in the emission intensity of dye Rhodamine B could be respectively achieved on the surface of silver colloids and silver coated-glass. The CTNAs have wide potential applications in the improvement of the sensitivity for medical or biological assays.

1. Introduction

Preparation of metal nanostructures has been an active research area for many decades because of their extremely interesting properties, especially the optical property, which are strongly depended on their shapes and sizes [1–5]. Thus, these properties of metallic nanoparticles could be usually tuned by controlling their sizes and shapes, leading to extensive applications in optical filters, photon energy transport, surface-enhanced Raman scattering (SERS), metal-enhanced fluorescence (MEF), biological diagnostics, LED materials, and lasers [6–13].

Among various metallic nanostructured materials, silver has received much attention owing to its excellent electrical conductivity, thermal conductivity, and good chemical stability under ambient conditions. Much efforts were devoted to synthesize silver nanostructures with various shapes, such as nanodecahedrons [14], nanocubes [15], nanodisks [16], nanoprisms [17,18], nanoplates [19,20], nanorods [21,22] and nanowires [23–25]. In 2001, Mirkin and co-workers [17] reported a photo-induced approach to transform small silver nanospheres into nanoprisms with the help of citrate and bis(p-sulfonatophenyl) phenylphosphine dehydrate dipotassium. From then on, works on synthesis of silver nanoprisms and triangular nanoplates via various approaches were reported continually [26–29]. Xia and co-workers showed the transformation of silver nanospheres into nanobelts and triangular nanoplates through a thermal process [30]. Well-defined silver dendritic nanostructures with fractal features were organized by a simple solvent-thermal method, using poly (vinyl pyrrolidone) as an adsorption agent and architecture template [31]. Recently, Xie and co-workers [14] prepared silver nanodecahedrons using N,N-dimethylformamide in the presence of poly (vinyl pyrrolidone). Xia and co-workers [32] synthesized silver right bipyramids 75–150 nm in edge length. More recently, Han and co-workers [33] synthesized silver nanosheets, chain-like sheets, and microwires via decomposition of $AgNO_3$ in ethanol with ammonia.

The development of various synthesis approaches largely promoting the shape-dependent properties of the nanomaterials was obtained. By now, novel nanostructures are still required in the fabrication and design of the nanodevices due to their new properties.

On the other hand, metallic particles exhibit unique and intense colors due to collective oscillations of electrons, which are known as plasmon absorption of metal particles. These resonating plasmons create local electromagnetic fields close to the particles surface. The local field can modify the free-space condition of nearby fluorophores [34]. The fluorescence intensity of the fluorophores could be increased due to the presence of nearby

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metallic nanoparticles. This phenomenon is known as metal-enhanced fluorescence, which has been utilized in high-sensitive bioassays and regarded as an attractive tool in miniaturized sensing devices development. Recently, Lakowicz's group made excellent contributions for the development of metal-enhanced fluorescence [35–38], and successfully applied it in the fields of biochemistry and bioassay.

In this work, we synthesized the chain-like triangular silver nanoplate assemblies using N,N-dimethylformamide in the presence of poly (vinyl pyrrolidone). It is expected that these chain-like assemblies could behave fascinating properties of chemistry, physics, optics, catalysis and electronics. Besides, the effects of silver colloids and silver colloids coated-glass slides on fluorescene property of Rhodamine B were also investigated.

2. Experimental

2.1. Preparation of the chain-like triangular nanoplate assemblies

All raw materials were of the highest quality commercially available: N,N-dimethylformamide (DMF), silver nitrate ($AgNO_3$), poly (vinyl pyrrolidone) (PVP, K30) and Rhodamine B (RhB) were purchased from Shanghai Chemicals Co., Ltd., PR China and used without further purification. In a typical synthesis, 0.6 mmol PVP was firstly dissolved in 75 mL DMF at room temperature to generate 8.0 mmol/L PVP, and then 0.3 mmol $AgNO_3$ was rapidly added into the solution. The mixed solution was poured into a Teflon autoclave of 200 mL capacity at once to seal and heat at 150 °C for 5 h in silicon oil, and then cooled down to room temperature naturally. The resulting product was separated by centrifugation for several times, and then the precipitates were re-dispersed in ethanol solution to obtain suspension for further characterization.

2.2. Characterizations

The morphologies of the products were characterized by scanning electron microscopy (SEM, TSM-5610LV), transmission electron microscopy (TEM, JEM-2010) and high-resolution transmission electron microscopy (HRTEM, JEM-2100F). The crystal structure of the products was examined using a D/max-RB rotating (Rigaku) powder diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54178 Å). UV–vis absorption and fluorescence spectra were respectively taken on a UV-Vis spectrometer (UV-1601, Shimadzu) and Fluorescence spectrometer (RF-5301PC, Shimadzu) with a 150 W Xenon lamp as the excitation light source at room temperature.

2.3. Measurement of metal-enhanced fluorescence

Original concentration of RhB solution was maintained at 1.0 mM. To eliminate the influence of the solvent on the fluorescence intensity, silver colloids previously dispersed in ethanol were re-centrifuged and re-dispersed in water. Two different and simple experimental formats were designed to investigate metal-enhanced fluorescence. For the first experimental format, silver colloids were directly mixed with RhB solution. For the second one, silver colloids coated-glass were obtained by immersing the slides in the silver colloids solution at room temperature, and then were placed in the quartz cell containing RhB solution. The angle between the metal surface and the incident light was set at 45°. In the presence of silver colloids and silver colloids coated-glass slides, the emission intensity of RhB solution was measured, respectively.

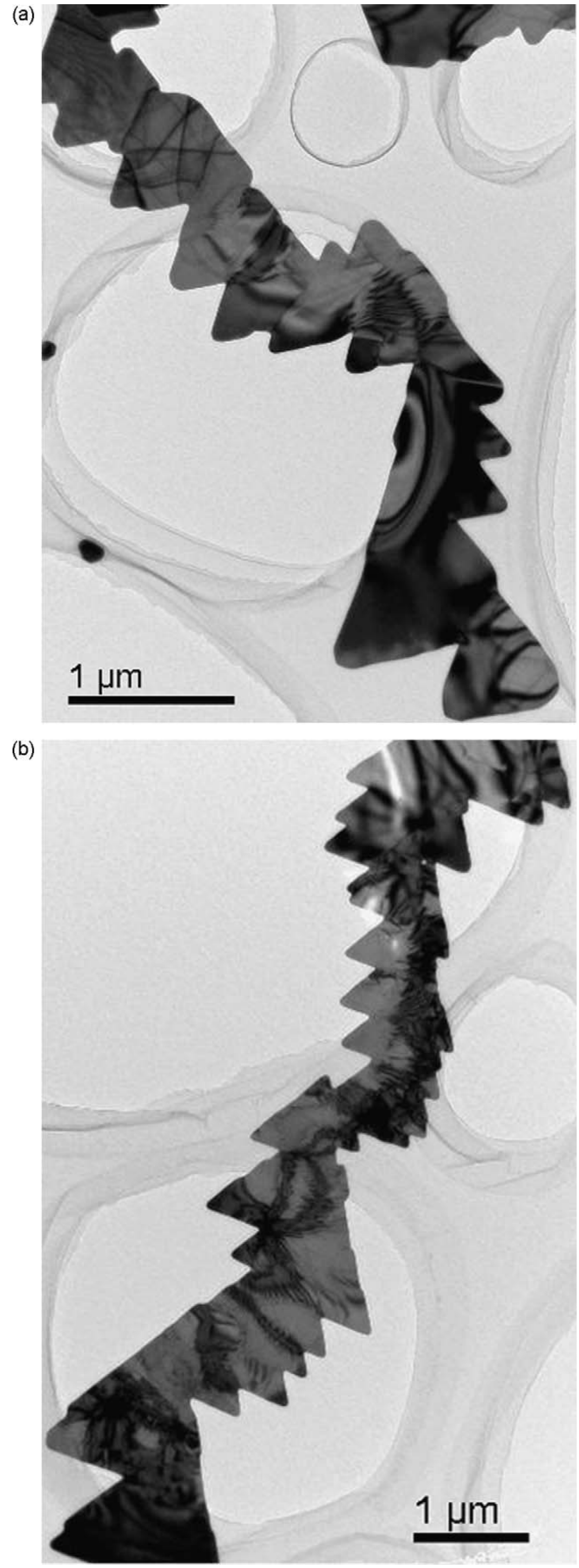

Fig. 1. TEM images (a and b) of the chain-like triangular nanoplate assemblies.