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Controlled synthesis of silver nanostructures stabilized by fluorescent polyarylene ether nitrile

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ABSTRACT

In this work, the intrinsically fluorescent polyarylene ether nitrile (PEN) was explored to realize the controlled synthesis of fluorescent silver nanostructures with different morphology for the first time. Specifically, it was found that silver nitrate ($AgNO_3$) can be effectively reduced to silver nanoparticles using PEN as both reducing and surface capping agents in N, *N*-dimethylformamide (DMF). More interestingly, the morphology of obtained fluorescent silver nanostructures can be tuned from nanospheres to nanorods by simple variation of reaction time at 130 °C using a relative PEN:$AgNO_3$ molar concentration ratio of 1:8. Meanwhile, the obtained Ag nanostructures exhibited both localized surface plasmon resonance (LSPR) band and fluorescent emission around 420 nm, which would find potential applications in biochemical sensing and optical devices fields.

1. Introduction

Silver nanostructures have attracted increasing research interests both in academic and industrial fields, mainly due to their outstanding physicochemical and biological properties [1]. For instance, silver nanostructures with different morphology can be employed as the building blocks of advanced nano-antennas to manipulate the light-mater interaction in the nanoscale thanks to their inherent near-field optical properties (*i.e.* localized surface plasmon resonance) [2]. Thus, they have been widely involved in various surface enhanced spectroscopy techniques including surface enhanced Raman spectroscopy (SERS) [3], metal enhanced fluorescence (MEF) [4], etc. Besides, silver nanostructures were widely used as the good catalyst in various chemical reactions [5] as well as effective anti-bacterial agent in biochemical and microbiological fields [6]. Generally, the morphology control of silver nanostructures is one of the most important factors to determine their efficiency in the above mentioned applications.

The polyol based synthesis, initially developed by Xia's group [7], is the prevalent protocol to realize the morphology control of silver nanostructures. It has been reported that different silver nanostructures ranging from nanospheres, nanorods, nanocubes to nanowires can be synthesized by varying the experimental parameters. Especially, the water soluble polyvinyl pyrrolidone (PVP) is generally used as the surface capping agent to modulate the nucleation and subsequent nanocrystals growth process in these polyol-based protocols, since several studies indicated that the strong chemical interaction between N, O atoms of PVP and silver would promote the selective nanoparticle growth along certain crystal planes, which would contribute to the formation of various anisotropic silver nanostructures [8]. On the other hand, polyarylene ether nitrile (PEN) is a kind of high performance linear thermoplastic mainly developed in our laboratory in recent years [9–11], and we assumed that the fluorescent PEN could be employed as effective surface capping agents to modulate the morphology of silver nanostructures due to the presence of large amount of carboxyl, ether and nitrile group in the polymer backbone structures.

In this work, the fluorescent PEN containing phenolphthalin moiety was explored as both the reducing and surface capping agent to synthesize silver nanostructures in DMF solvent using $AgNO_3$ as silver ions precursor. Several important experimental parameters, such as relative concentration ratio of PEN and $AgNO_3$, reaction temperature as well as reaction time, were optimized to control the morphology evolution of silver nanostructures from nanospheres to nanorods. Furthermore, we found that the obtained silver nanostructures possess both obvious localized surface plasmon resonance band and fluorescent emission around 420 nm,

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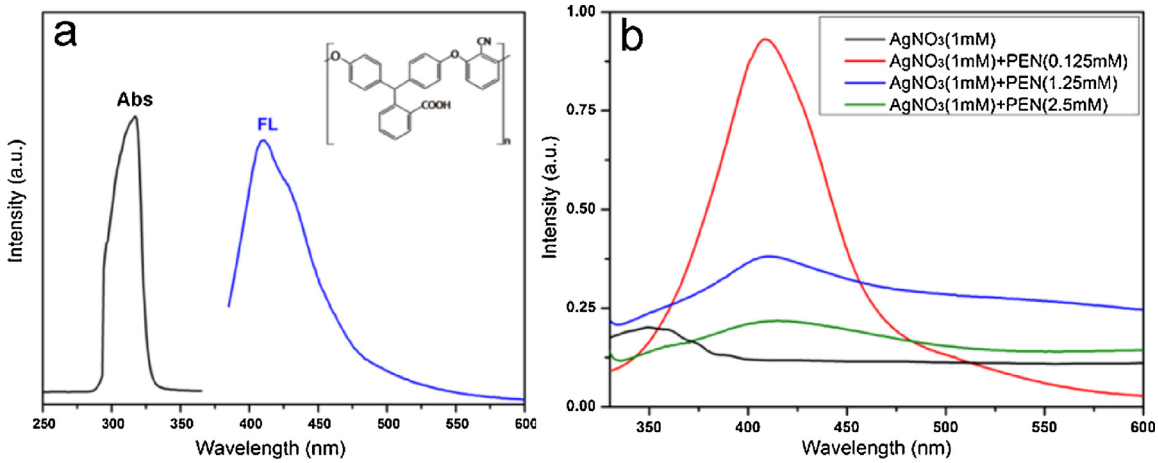

Fig. 1. The electronic absorption (Abs) and fluorescent emission (FL) spectra of PEN involved in Ag nanoparticles synthesis, the backbone chemical structure of PEN was shown in inset (a), UV–vis absorption spectra of Ag nanostructures synthesized at different relative content of $AgNO_3$:PEN (b).

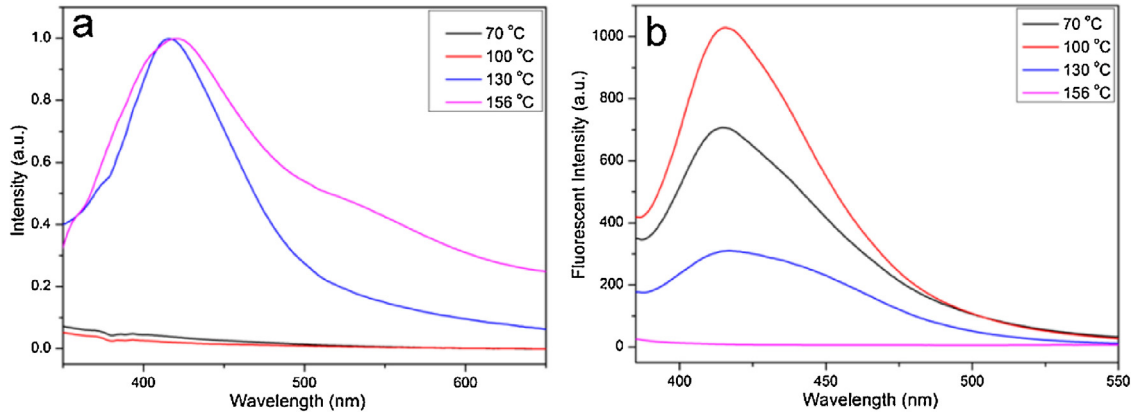

Fig. 2. UV–vis absorption (a) and fluorescent emission spectra (b) of Ag NPs synthesized at different temperature.

which could be used as promising nano-emitters for biochemical sensing and optical devices applications.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$, 99.99%) and N, *N*-dimethylformamide (DMF, analytic grade) were purchased from Sigma-Aldrich, fluorescent polyarylene ether nitrile (FPEN, weight-average molecular weight $\bar{M}w = 21640$ g/mol, number-average molecular weight $\bar{M}n = 14426$ g/mol, polydispersity index PDI = $\bar{M}w/\bar{M}n = 1.5$) was synthesized in our laboratory. DMF solvent was dried via vacuum distillation prior to its use.

2.2. Silver nanostructures synthesis

All the silver nanostructures were synthesized in DMF solvent by reducing $AgNO_3$ with FPEN. The $AgNO_3$ concentration was fixed at 1 mM, while various FPEN concentrations of 0.125 mM, 1.25 mM and 2.5 mM were used. Meanwhile, the different reaction temperature (70 °C, 100 °C, 130 °C and 156 °C) as well as reaction time (1 h, 2 h and 4 h) were explored in the experiment. In a typical synthesis, 0.05 g FPEN was dissolved into 20 mL previously dried DMF solvent in a flask equipped with a magnetic stirrer, thermometer and reflux condenser. Next, 100 μL $AgNO_3$ solution in DMF (1 mM) was rapidly injected into the previous reaction mixture protected by nitrogen, afterward the reaction temperature was maintained at 130 °C for certain reaction time, then 2 mL aliquot of reaction mixture was acquired and subjected to ultracentrifugation (10 min, 14000 rpm) and washing with fresh DMF solvent to remove the excess polymer capping agent. Finally, the purified silver nanostructures were dispersed in fresh DMF for further characterization.

2.3. Characterization

The UV–vis absorption and fluorescent emission spectra of as-synthesized silver nanostructures were recorded using a Persee TU1901 UV–vis spectrophotometer and a Hitachi F-4600 fluorescent spectrophotometer, respectively. The surface morphology of obtained silver nanostructures was characterized using transmission electron microscope (TEM, Hitachi, H600) operating at 120 kV. The X-ray diffraction (XRD) spectra of obtained silver nanostructures were characterized with a Shimadzu XRD-7000 X-ray diffractometer operated at 40 kV and 30 mA with CuKα radiation wavelength of 1.5406 Å.

3. Results and discussion

Although PEN has been intensively used as the high performance matrix for fabrication of various functional polymer composites [12,13], its application as surface capping agents for silver nanoparticles synthesis is virtually unreported. As indicated in Fig. 1a, the PEN emits strongly at 420 nm when excited at 365 nm, and the carboxyl and nitrile groups in the backbone structures could serve as the possible reactive sites for synthesis and stabilization of silver