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Preparation of silver nanoparticles in inorganic clay suspensions

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Abstract

We have successfully developed a simple method for preparing silver nanoparticles via photoreduction of $AgNO_3$ in layered laponite suspensions without any addition of reduction agent or heat treatment. The properties of silver nanoparticles were studied as a function of the UV irradiation time. A bimodal size distribution and relatively large silver nanoparticles were obtained when irradiated under UV for 3 h. Further irradiation disintegrated the silver nanoparticles into smaller size with a single mode distribution until a relatively stable size and size distribution were achieved. The results from optical absorption spectra of silver nanoparticles agree well with the detailed microstructure studies performed by transmission electron microscopy (TEM). The synthesized laponite suspensions containing silver nanoparticles are stable up to several months and have potential applications as antimicrobial ointments.

Keywords: A. Nano composites; A. Nano particles; D. Rheology; D. Transmission electron microscopy (TEM)

1. Introduction

Recently, metal nanoparticles have aroused worldwide research interests due to their unique physical and chemical properties which lead to many potential applications. For example, they can be used as catalysts for various reactions [1] due to their high surface-to-volume ratio. The unique size- and shape-dependent surface plasmon resonance enhanced light scattering and absorption properties of metal nanoparticles have made them applicable to a wide range of applications including optoelectronics [2], biological labeling [3] and surface-enhanced Raman scattering [4,5]. They can also serve as a model system to experimentally probe the effect of quantum confinement on electronic properties [6].

There exist many preparation methods for the synthesis of metal nanoparticles, such as the photoreduction or chemical reduction in aqueous medium with various polymer surfactants [7,8], chemical reduction in soft matrixes e.g. reverse micelles [9] or in solid matrixes e.g. mesoporous silicate [10], and chemical vapor deposition [11]. However, complicated reaction systems or tedious preparation procedures are necessary in many of these methods. Here we report a simple photoreduction method to synthesize silver nanoparticles. As compared with most of the reduction methods, reductants, such as sodium borohydride etc., are usually required [7]. In our method, such reductants are not necessary. Instead, we used an inorganic clay laponite as the protective colloid preventing nanoparticles from aggregation and it was found that laponite also assists in the photoreduction process of silver. In deionized water without laponite, photoreduction is negligible.

Laponite is a synthetic layered silicate. When dispersed in water, it is in the form of disk-shaped crystals which is about 30 nm in diameter and 1 nm in thickness. It can be viewed as an inorganic polymer with its unit cell repeated in two-dimension. The unit cell of laponite with a height of 1 nm consists of six octahedral magnesium ions sandwiched between two layers of four tetrahedral silicon atoms balanced by twenty oxygen atoms and four hydroxyl groups. Under dry condition, laponite crystals are stacked with cations (such as sodium ions) between neighboring layers to balance the negative charge of each clay layer.

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In water, although each laponite crystal is insoluble, the layer stack swells significantly owning to the hydration of inter-lamellae cations. Due to the electrostatic attraction between the positive charge on the crystal edge and the negative charge on the disk surface, laponite crystals will form a highly thixotropic gel under certain conditions. It has the unique and novel rheological properties, such as, high viscosity at low shear rate which provides very effective anti-settling properties, low viscosity at high shear rates, an unequalled degree of shear thinning, and progressive and controllable thixotropic restructuring after shear. It is expected that charged sites on clay particles can provide cooperative binding with metal ions. This property together with the anti-settling properties makes laponite crystals the effective protective colloids for metal nanoparticles. It is therefore interesting to study the role of layered silicate in the preparation of metallic particles.

2. Experiments

Laponite RD (Rockwood Additives, UK) was used as received in the present study. Its cationic exchange capacity was 0.5 m · mol/g. In a typical experiment, 6 g of laponite clay was dispersed in 100 ml deionized water and vigorously stirred for 1 h. A 100 ml aqueous solution of $AgNO_3$ (15 m · mol/L) was added into the laponite aqueous sus-

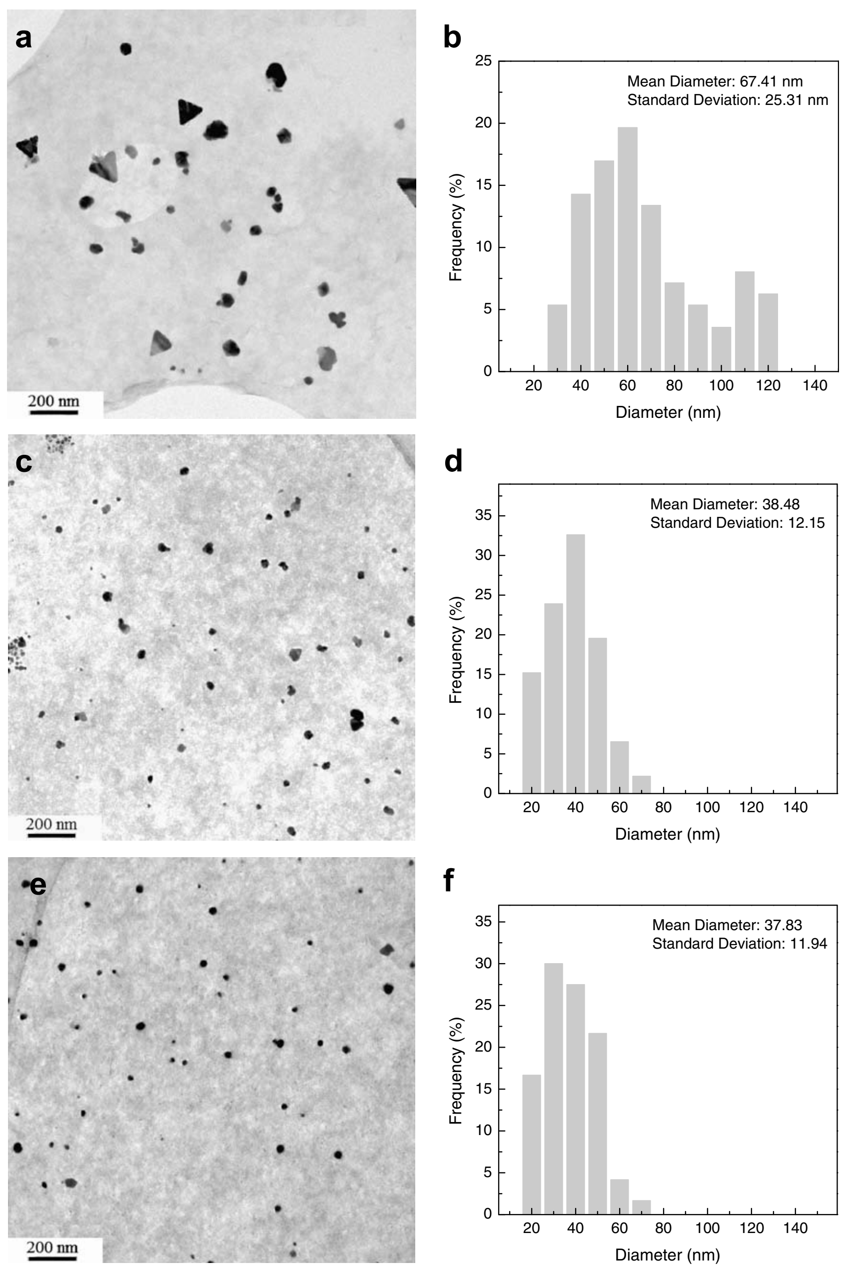

Fig. 1. Bright field TEM images and the corresponding particle size distributions of silver nanoparticles irradiated under UV for 3 h (a and b), 18 h (c and d), and 93 h (e and f).