Solid State Phenomena Vols. 121-123 (2007) pp. 251-254
online at http://www.scientific.net

One-Step Preparation of Fibrous Aggregates of Gold Nanoparticles Using Aniline as Reducing Agent as well as Monomer

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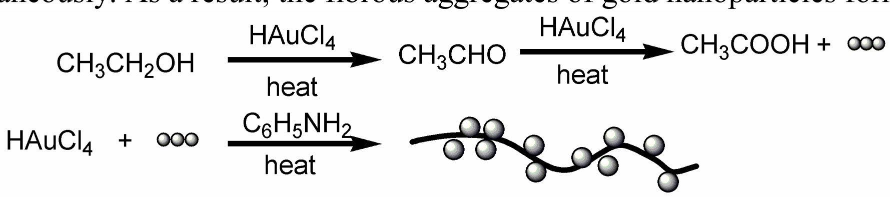
Keywords: gold nanoparticles, fibrous aggregates, aniline, ethanol

Abstract. Nanoscaled fibrous aggregates of gold nanoparticles have been synthesized by a simultaneous reduction-oxidation polymerization process using aniline as reducing agent as well as monomer in an ethanol medium. Time-dependent UV-Vis absorption spectroscopy was used to track the formation process of gold nanoparticles. The transmission electron microscopy (TEM) images and Fourier transform infrared (FT-IR) spectrum of the as-preapred products indicate these gold nanoparticles were binded by the oxidation polymerization resultant of aniline.

Introduction

With the development of materials science and nanotechnology, nanomaterials have been widely studied due to their fascinating size-dependent electrical, optical, biologic, physical and chemical properties different from those of common bulk materials [1-3]. Recently, fabrication of metal nanoparticles into low-dimensional nanostructures has been highly focused on their promising applications in constructing nanosized electronic and optical devices [4]. In a general way, these low-dimensional nanostructures can be fabricated by non-covalent or covalent interconnect strategies [5, 6]. Numerous researches have been exerted in using certain materials (especially DNA or peptide that have specific binding sites for molecular recognition and self-assembly) as templates to organize and interconnect nanoparticles on their surfaces [7,8]. Representatively, Nakao and coworkers organized gold nanoparticles with well-aligned and long-range order on DNA molecules due to the electrostatic interaction between the negatively charged phosphate backbone of DNA and surface-positive charged gold nanoparticles[9]. Furthermore, Kimura and Shirai demonstrated a fibrous network structure of gold nanoparticles constructed by a site-exchange reaction using thiol-terminated gelators [10]. To the best of our knowledge, most of these routes reported have to prepare the metal nanoparticles beforehand and the materials used as templates are usually expensive. Up to now, Report based on a facile method of fabricating low-dimensional metallic nanostructures is still scarce. We herein develop a novel approach to low-dimensional nanoarchitectures of gold nanoparticles by a reduction-oxidation polymerization route using aniline both as reducing agent and polymeric monomer in an ethanol medium. By this method shown in Scheme 1, $AuCl_4^-$ was reduced to Au^0 by the assistant of aniline accompanying with the oxidation polymerization in the ethanol medium simultaneously. As a result, the fibrous aggregates of gold nanoparticles formed.



Scheme1. Possible formation mechanism of fibrous aggregates of Au nanoparticles

Experimental Section

Materials

In our experiments, all chemicals were analytical pure agents and purchased from Shanghai Chemical Reagent Co. Ltd. (China). Aniline was redistilled under a reduced pressure with the presence of zinc metal powder; anhydrous ethanol and chloroauric acid ($HAuCl_4 \cdot 4H_2O$) were used as received.

Synthesis

A typical procedure to prepare the fibrous aggregates of gold nanoparticles is as follows: a 50ml anhydrous ethanol solution containing 0.8 × 10-3mol/L HAuCl4 in ethanol solution was degasified by N2 bubbling and heated to reflux at boiling point in a flask for 40 min. then, a twofold molar amount of freshly distilled aniline was added in it and stirred vigorously for about 2 hours. The color of the reaction mixture changed gradually from pale yellow to wine-red indicating the formation of gold nanoparticles [11]. The resulted solution was stored at 4 ℃overnight and enriched by a rotatory evaporator under dynamic vacuum at 40 ℃. The obtained precipitate was used for further characterization after washing with anhydrous ethanol for several times thoroughly.

Characterization

Transmission electron microscopy (TEM) images were obtained on a JEM-2000EX microscope using an accelerating voltage of 120.0 KV. FT-IR spectrum was surveyed on a Nicolet Magna FT-IR-750 spectrometer and the dried samples were pressed into a tablet with KBr before characterization. Time-dependent UV-Vis spectra of the reaction process were measured on a SHIMADU UV-3501 recording spectrophotometer.

Results and discussion

The morphology of the resultant was examined by TEM. As shown in Fig.1 (a), nanoscaled fibrous structures with length more than one micrometer and mininum width of about 50nm were found and the electronic patterns (ED) of these fibrous structures proved the presence of gold nanoparticles . The TEM image under dark field shown in Fig. 1 (b) indicated clearly these gold nanoparticles with the size of about 10 nm were contained in the fibrous structures by the oxidized resultants of aniline.

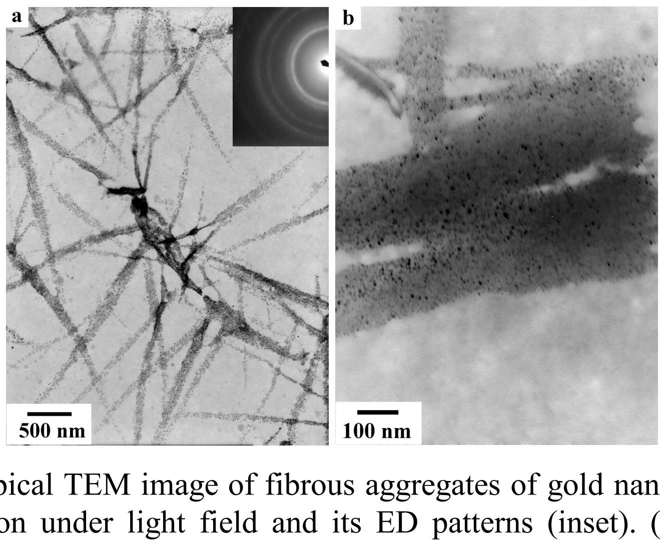


Fig.1 (a) typical TEM image of fibrous aggregates of gold nanoparticles at lower magnification under light field and its ED patterns (inset). (b) TEM image of fibrous aggregates of gold nanoparticles under dark field at higher magnification.

Time-dependent UV-Vis spectrum of the reaction process are shown in Fig. 2. As evident from Fig. 2, during the time rise of $HAuCl_4$-ethanol refluxing, the characteristic peak of $AuCl_4^-$ got weaker, which means some gold seeds generated due to oxidation-reduction between $HAuCl_4$ and ethanol [12] during heating and these gold seeds may act as catalysis during the addition of aniline(scheme 1). At the end of the reaction, the characteric peak of $AuCl_4^-$ vanished and a distinct absorption peak at 543 nm indicated the formation of gold nanoparticles . It should note that the maximum of the absorption peak position is positively shifted 23 nm with bathochromic effect compared with that (c.a. 520nm) of previously described corresponding sized Au nanoparticles [13, 14]. It can be suggested that coupling with the resultant of aniline oxidation induces the further bathochromic effect.

As characterized by FT-IR spectrum (Fig. 3), the fibrous aggregates of gold nanoparticles discussed above have sharp absorption at 1490 and 1570 cm^{-1} that are the features of bezenoid and quinoid ring deformation respectively [15]. This spectrum is similar to the report [16] of Au-polyaniline nanocomposites synthesized in aqueous solution, which indicates the occurrence of the oxidation polymerization of aniline. By the reference to Fig. 1 (b), it can be deduced that the polymeric resultants of aniline act as a carrier to bind the simultaneously formed gold nanoparticles during the reduction-oxidized polymerization process. Further investigations will be going on to the detailed formation machanism and the properties of these as-prepared fibrous aggregates of gold nanoparticles.

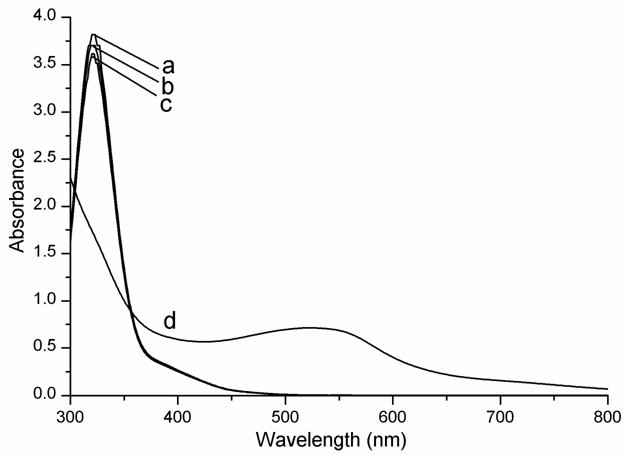


Fig. 2 Time-dependent UV-Vis absorption spectra of the reaction process (a) at room temperature; (b) 20 min at boiling point; (c) 40 min at boiling point and (d) 2 h after the

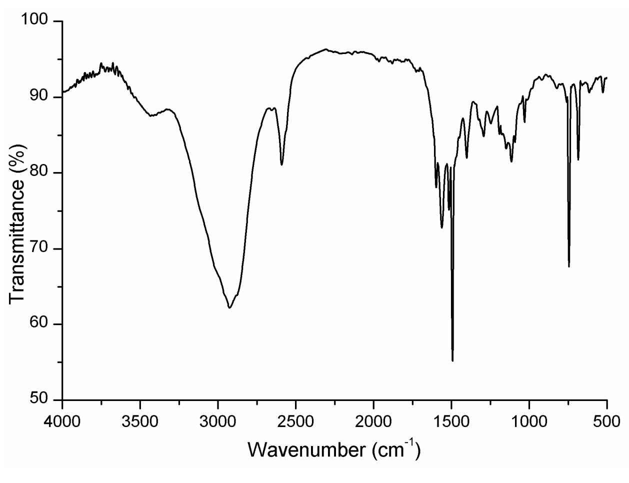


Fig. 3 FT-IR spectrum of as-prepared fibrous aggregates of gold nanoparticles

Conclusion

In summary, we have demonstrated a facile approach to construct nanoscaled fibrous aggregates of gold nanoparticles by simultaneous reduction of $HAuCl_4$ and oxidized polymerization of aniline in the ethanol solution without any additional assistants. The characterization of the as-prepared fibrous aggregates by TEM and FT-IR spectroscopy revealed that these gold nanoparticles were binded by the fibrous oxidation polymerization resultant of aniline. These fibrous structures containing gold nanoparticles will be a novel advanced material valuable for the fabrication of optical and electronic nanodevices.

Acknowledgment This research was supported by project (No. 60371027, 60171005 and 90406023) of National Natural Science Foundation of China.

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