Invited Paper

Microwave Preparation of Ag Nanoparticles for Chemiluminescence Enhancement

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Chemiluminescence applications frequently require signal enhancement. We report a major improvement of the chemiluminescence of luminol in alkaline peroxide solutions by silver nanoparticles prepared by chemical reduction of $AgNO_3$ by NaH_2PO_2 in ethylene glycol solution, with polyvinylpirrolidone as capping agent and using a simple microwave approach and set up. The luminescence emission is also shown to be much faster. The nanoparticles were characterized spectroscopically and by dynamic light scattering showing an average particle size of 36 nm.

Keywords: Luminescence; Luminol; Silver nanoparticles; Microwaves.

INTRODUCTION

The applications of chemiluminescence are mainly analytical in nature, ranging from forensics to environmental uses. The weakness of the emitted light signals often require enhancement, which can be achieved by the addition of metal nanoparticles (NPs) as described below. Ag NPs display a variety of interesting properties including high thermal conductivity, antimicrobial effects, and catalytic properties in oxidation reactions.[1,2] Typical methods to obtain Ag NPs are based on the reduction of Ag(I) ions with common reducing agents such as sodium borohydride, hydrazine, polyols, photoreductions, and biological processes. Some of these methods can yield a variety of nanostructure shapes, a wide spread of particle sizes, and may require long reaction times and several steps. In this regard, synthesis using microwave irradiation is a good alternative to obtain Ag NPs in a short time. Microwave heating is more promising than thermal heating[3,4] since microwaves increase formation rates and homogenize Ag NPs sizes.[5] The thermal and non-thermal microwave effects on nanoparticle synthesis produce a significant heating rate acceleration and a more uniform temperature distribution, respectively.[4,6] Variable frequency microwave irradiation (VFM) can heat up the material quickly and uniformly, producing a more homogeneous nucleation and shorter synthesis time compared to those for conventional heating.[4] This is favorable for the formation of uniform metal colloids.

Due to the high rate of particle formation, capping agents are required to cover the Ag NPs to avoid particle agglomeration and to restrict their growth. The metal:polymer ratio may affect the particle morphologies and sizes.[4,6] Typical polymers employed as stabilizers of Ag NPs include polyvinylpirrolidone (PVP),[4] carboxymethylcellulose (CMC),[6] and polyvinyl alcohol (PVA).[7] For example, spherical Ag NPs with diameters of 10 ± 5 nm have been prepared by microwave irradiation of $AgNO_3$ solutions in ethanolic media using PVP as capping agent.[8] Other works include the synthesis of Ag NPs (< 50 nm) employing a mixture of PVP, glucose and sodium hydroxide in water at 60 °C by thermal heating.[9] Additionally, Ag decahedrons with 80-nm edge sizes have been obtained by PVP-assisted N,N-dimethylformamide (DMF) reduction at 140 °C.[10]

In the present work we prepared Ag NPs capped with PVP by mimicking a method for the production of Cu NPs using NaH_2PO_2 as reducing agent in ethylene glycol as re-

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action medium under microwave irradiation. The Ag NPs thus synthesized were used to enhance the luminescence emitted from the reaction between luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) and hydrogen peroxide. The water-soluble luminol zwitterion is converted into a dianion by the removal of its protons in an alkaline medium. This dianion is easily oxidized (for example by H_2O_2) to produce an intermediate, unstable excited species that decomposes by losing a nitrogen molecule to produce the 3-aminophthalate dianion in the triplet state. It has been long known that when this excited state relaxes to its ground state, a blue photon is emitted.[11] Trace amounts of Fe, Cu, Ag, Co or $[Fe(CN)_3]^{3+}$ species catalyze this reaction by increasing the rate of H_2O_2 decomposition.[12] In particular, Ag NPs are known to catalyze this decomposition into strongly oxidizing species (hydroxyl radicals and superoxide anions) that react with luminol emitting a large amount of photons.[12]

EXPERIMENTAL

An LG-MS-0847C microwave oven (2450 MHz) adapted with a perforation of 1.5 cm in diameter on the top was used in this work. A mechanical stirrer was introduced from the top through this perforation into a glass beaker that served as reaction vessel (see Fig. 1). Reagents: ethyleneglycol (Baker, 100%), polyvinylpirrolidone (PVP 10, Sigma-Aldrich), $AgNO_3$ (Baker, 97%), NaH_2PO_2 (Q. Meter reagent), luminol (Sigma-Aldrich, 97%), and NaOH (PQF, 97%) were used as received. A Malvern Zetasizer, model Nano Zs was used for the particle size measurements. A UV-Vis Varian Model Cary 50 Conc spectrophotometer was used to obtain the necessary spectra.

Preparation of the stock solutions

0.042 g of luminol was dissolved in 4.0 mL of 1.3 M NaOH. The resulting solution was diluted to 100 mL in a volumetric flask. In the same way, 0.020 g of $K_3[Fe(CN)_6]$ were dissolved in 5 mL of water; then, 4 mL of 3 wt % H_2O_2 were added and the resulting mixture was also diluted to 100 mL.

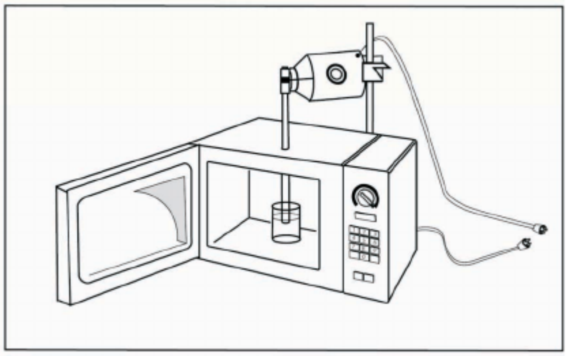

Fig. 1. Experimental set up.

Synthesis of Ag NPs

25 mL of a 0.01 M $AgNO_3$ solution in ethyleneglycol were placed in a 150-mL beaker and 0.200 g of PVP was added slowly under magnetic stirring. The resulting mixture was stirred vigorously for 30 min. Then, 25 mL of a 0.02 M NaH_2PO_2 solution in ethyleneglycol (prepared separately) were added to the reaction mixture resulting from the previous step and stirred for 15 min.

The beaker was placed inside the microwave oven and aligned with the mechanical stirrer coming down from the top, connected to a Heidolph Type RZR 1 variable speed motor. Vigorous stirring (at 320 rpm) was kept during the reaction time, avoiding solution losses by splattering. The sample was irradiated for 120-240 s at the lowest power of the microwave oven (ca. 100 W). This procedure yielded Ag NPs that provided a yellow coloration to the reaction mixture. When the temperature of the reaction mixture substantially increased - as produced by a longer irradiation time or by using a higher power -, the nature of the colloidal suspension was affected (as signaled by a different coloration) and the experiment was aborted.

Light measurement

Light emitted by the chemiluminescent reaction was monitored with a Vernier Light Sensor LS-DIN connected to a Vernier Lab Pro interface, using the Logger Pro 3.0 software. This light measuring system was aligned by placing the sensor in touch with the wall of a 20-cm tall Pyrex test tube that served as the chemiluminescence reaction chamber. To ensure reproducibility of the position of the sensor, the system was mounted on a cardboard structure and aligned with the bottom of the tube. Previous to the reaction onset, the sensor was calibrated against the backgound of the darkened room. Both the sensor and the interface were set at their highest sensitivity.

Chemiluminescence enhancement

1.5 mL of the luminol solution was drawn into a 2-mL pipet, and 1.5 mL of the hydrogen peroxide solution into another 2-mL pipet. The contents of both pipets were added simultaneously into the bottom of the test tube and the light intensity was registered as a function of time. This procedure was then repeated by adding 1.0 mL of the Ag NPs

suspension to the empty tube prior to the other reaction components.

Particle size measurement

The hydrodynamic diameter of the Ag NPs was measured at 25 ºC. The samples were diluted at 10 ppm. The measurements were made in triplicate.

RESULTS AND DISCUSSION

The UV-vis spectra of the Ag NPs obtained as a function of irradiation time is shown in Fig. 2. The observed peak wavelengths match well with those expected for Ag NPs (410-430 nm). In the case of samples irradiated at t > 5 min, no well-defined peaks were observed likely due to thermal instability of the nanoparticle system that may result in a broader size dispersion.[13]

From measurements of dynamic light scattering, different particle diameter moments were calculated using equations (1) and (2).

$$D_n = \frac{\Sigma n_i D_i}{\Sigma n_i} \tag{1}$$

$$D_W = \frac{\Sigma n_i D_i^4}{\Sigma n_i D_i^3} \tag{2}$$

$$D_Z = \frac{\Sigma n_i D_i^5}{\Sigma n_i D_i^4} \tag{3}$$

Here, D_n is the average diameter number, D_w is the weighted average diameter, D_z is the Z average diameter, and n_i is the number of Ag NPs with a diameter = D_i. The polydispersity index (PDI) was determined using equation (3):

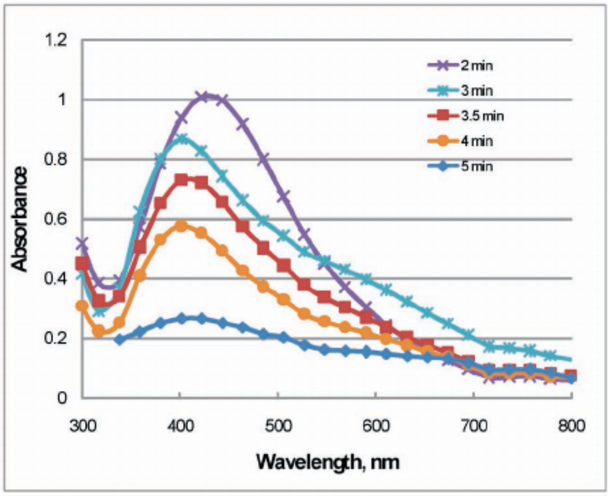

Fig. 2. UV-vis spectra of the Ag NPs system as a function of microwave irradiation time.

Table 1. Particle size distribution corresponding to Fig. 3

Size d, nm	Mean Number %	Std Dev Number %
8.721	4.5	1.4
10.1	16	3.7
11.7	24.5	3.3
13.54	22.6	1.5
15.69	15.4	1.9
18.17	8.7	2.3
21.04	4.4	2.0
24.36	2.1	1.3
28.21	1.0	0.8
32.67	0.4	0.4
37.84	0.2	0.2
43.82	0.1	0.1

Dz = 36.14 nm
Polydispersity index = 1.37480941

$$\mathrm{PDI} = \frac{D_W}{D_n} \tag{4}$$

The particle size distribution for samples irradiated for 3 min (measured in triplicate) is shown in Fig. 3 and in Table 1, where D_z = 22.18 nm and PDI = 1.37. This translates into a relatively small particle size dispersion. The Z average diameter is very important because it is comparable to the average particle diameter obtained through electronic microscopy.

The spectral response of the Ag NPs system stored in the dark was relatively stable with time, tending apparently towards a higher polydispersity as a result of Ostwald's rippening. See Fig. 4.

Since Cu NPs are known to catalyze the luminol chemiluminescence, we tested the Ag NPs for the same purpose. Fig. 5 shows a typical experiment using the Ag NPs produced as specified above (irradiation time = 2.5

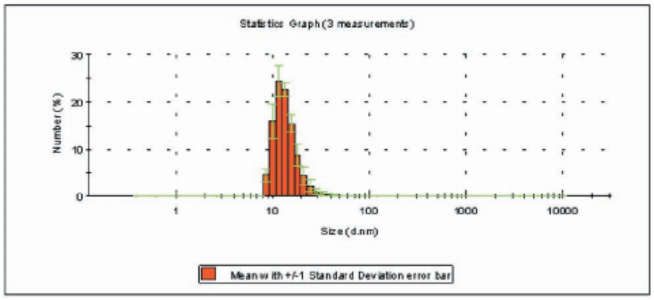

Fig. 3. Particle size distribution of a typical colloidal sample obtained after 3 min of microwave irradiation.