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Optimization of silver nanodendrites for surface enhanced Raman spectroscopy (SERS) in an acidic environment

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ABSTRACT

Silver nanodendrites (Ag NDs) are synthesized by chemical reduction with silver nitrate ($AgNO_3$) as a precursor, ethanol as reducing agent and polyvinyl pyrrolidone (PVP) as a stabilizer. The as-synthesized Ag NDs are then characterized by UV–vis Spectroscopy ((UV–vis)) and sample 15% Ag shows the most absorbency. Transmission Electron Microscopy (TEM) confirms the morphological of dendritic structure. The pH of 15% Ag NDs sample were then modified to acidic condition and the Surface Enhanced Raman Scattering (SERS) investigation is done using 4-Aminobenzebethiol (4-ABT) as a molecular probe. 15% Ag NDs with pH 3 shows the best performance in SERS application and the optical properties.

1. Introduction

Surface enhanced Raman spectroscopy (SERS) is a useful technique for amplifying signals of weak Raman [1,2]. Recently, SERS technique has become one of the most sensitive spectroscopic tools in many areas including biological, clinical, chemical and environmental fields [3,4]. This is due to SERS can provide rich structural information in a non-destructive manner. Metallic nanoparticles have been proved to be good candidates for use in SERS exhibiting the dual roles of substrates and signal enhancers [5,6]. Among them, silver nanoparticles usually exhibits the highest SERS activity due to their broad plasmon resonance in the visible and near Infrared regions and high stability [7,8]. However, compared to nanoparticles, silver nanodendrites (AgNDs) posses many multi-level branching nanostructures. This allows a large specific surface area and the corresponding complex nanostructure may be favorable to absorption of probe molecules [9,10]. This factor favor AgNDs as a high-active SERS substrates. There are a few techniques used to synthesis Ag NDs, such as irradiation reduction [11], ultraviolet radiation photoreduction technique [12] and electroless metal deposition technique [13].

In this paper, Ag NDs were synthesized via a green technique which involve two stages [14]. The first stage was synthesizing of Ag NDs colloid. $AgNO_3$ was chemically reduced by ethanol, with PVP act as stabilizer. Different concentration of $AgNO_3$ were used to observed the effect on the morphology and size distribution of the resulting AgNDs by using TEM and (UV–vis). The second stage starts after the confirmation of presence of AgNDs. The pH of the aqueous AgNDs will be altered in acidic condition and deposited on 4-ABT as a SERS probe molecule to determine the optimum sample. pH plays a very

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Table 1
Weight fraction of $AgNO_3$ and PVP added to perform a 40 mL solutions mixture.

Concentration of Ag in the mixture solution (%)	Weight of $AgNO_3$ powder in 15 ml of distilled water (g)	Weight of PVP powder in 10ml of distilled water (g)	Volume of ethyl ethanol (ml)
0.3	0.1207	0.00407	5
1.0	0.4058	0.1366	5
10	4.0075	1.3378	5
15	6.0040	2.0015	5
20	8.0090	2.6681	5

important role in the property of the AgNDs prepared, including their SERS activity [15]. A change in the ionic strength in the medium leads to the formation of clusters of particles or layers of surface particles.

2. Experimental method

2.1. Sample preparation

2.1.1. Preparation of Ag NDs colloid

$AgNO_3$ and PVP (58, 000 average molecular weight) was dissolved separately in 15 mL and 20 mL of distilled water respectively. The solution was mixed with 5 mL of ethanol in 100 mL round bottom flask and magnetically stirred for homogeneous reaction. The mixture was then heated to 70 °C for 2 h. Five samples were prepared using different amount of $AgNO_3$ (0.3%, 1%, 10%, 15%, and 20%) with the weight ratio of $AgNO_3$:PVP fixed at 3:1 The calculated amount of $AgNO_3$ and PVP were tabled in Table 1.

2.1.2. Preparation of Ag NDs solution in different pH condition

Sample with 15% of Ag was diluted with distilled water and divided into four different containers. Diluted nitric acid and ammonia was added to the samples to obtain the desired pH value while the solution was stirred continuously. The pH of the samples was measured by using pH meter from Eutech Instruments. Samples with pH 2.33, 3.17, 5.10 and 7.34 are successfully prepared.

2.1.3. Preparation of Ag NDs thin film

Glass slides as a substrate was firstly cleaned using distilled water and acetone. Samples with modified pH was dropped on the glass substrate surface separately and leave dried in the vacuum oven. Once the samples dried, 0.01 M 4-ABT solution was dropped as molecular probe and dried again in the vacuum oven.

2.2. Characterization

These samples are then being characterized for UV–vis spectra using UV–vis Spectroscopy from Cary. Transmission Electron Microscope from Libra 120 was used to determine the size an morphology. Raman spectra were obtained from the microraman spectrometer from Horiba.

3. Results and discussion

3.1. Transmission electron microscope (TEM) analysis

Fig. 1(a) shows the TEM image for 0.3 wt% of well dispersed AgNPs with the average size of 26 nm with spherical shape. Meanwhile, Fig. 1(b) shows the TEM image for 1.0 wt% of Ag with particles start to aggregate and form larger particles with an average size of 32 nm. Fig. 1(c) shows the TEM image for 10 wt% of Ag with a dendritic structure. Since no AgNPs are spotted in this image indicate that the critical weight for AgNPs to completely transform into silver nanodendrites (AgNDs) structure. The dendritic growth at the tip of the stems and branches as the tip region consists of shorter branch. The branches will be form near the top region continuously when the stem grows longer [16]. As the concentration of Ag increases to 15%, the dendritic structures get thicker and denser as shown in Fig. 1(d). The sharp edges are getting rounder due to more AgNPs accumulated on the structures.

Sample with 20% of Ag shows the thickest branch of the dendritic structures as shown in Fig. 1(e). As the concentration of Ag increases, the nanoparticles tend to accumulate at the branches. There are new formations of dendritic structure on the branches. Many branches have stacked together, due to the aggregation of particles. In can be concluded that by reaching 20% of Ag, the formation of Ag NDs has reached the saturation level.