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L-Phenylalanine functionalized silver nanoparticles: Photocatalytic and nonlinear optical applications

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ABSTRACT

An extensive study on the behavior of L-Phenylalanine capped silver nanoparticles (Phe-Ag NPs) in the aqueous phase and in a sol–gel thin film showed different UV/Vis, Transmission Electron Microscope (TEM), Dynamic Light Scattering and Zeta potential profiles. Scanning Electron Microscope (SEM) images of the samples in the sol gel film showed Ag embedded in the SiO_2 matrix. Surface Enhanced Raman Spectra (SERS) confirmed that both in the aqueous media and in the sol gel film, the attachment of Phe to the Ag NP surface was through the benzene ring, with the sol–gel film showing a better enhancement. Photocatalytic degradation of crystal violet was measured spectrophotometrically using Phe-Ag NPs as a nanocatalyst under visible light illumination. Intensity-dependent nonlinear optical absorption of Phe-Ag measured using the open aperture Z-scan technique revealed that the material is an efficient optical limiter with potential applications.

1. Introduction

Particles of silver and gold an order of magnitude smaller than the wavelengths of visible light strongly absorb light due to surface plasmon resonance (SPR) – the collective oscillation of conduction electrons induced by incident light [1]. Of the two metals, Ag exhibits a higher efficiency of Plasmon excitation. Further, Ag NPs are 2 orders of magnitude better than gold at enhancing the Raman signals of the adsorbed molecules. The optical and electronic properties of these nanomaterials depend on their size and shape [2,3].

Phe (alpha-amino-beta-phenyl-propionic acid) is one of the twenty naturally occurring amino acids that can be found in proteins. It contains an amino group, a phenyl ring and a carboxylic acid. Tanaka et al. reported the adsorption of Phe on Tungsten oxide NPs and used it as a colorimetric probe for sensitive label free detection of amino acid compounds [4]. Ota et al. reported the SERS of Phe adsorbed on Ag NPs [5]. We investigated the characteristics and potential applications of Phe-Ag NPs in the aqueous medium. The morphology and mode of attachment of Phe to Ag NP is found via Transmission TEM and SERS respectively. The structure and stability of the crystal is identified through X-ray Diffraction (XRD) and Zeta Analyzer.

Nanocomposites are known to exhibit novel optical properties as the plasmon resonance is affected by the surrounding matrix [6]. The Phe-Ag NPs prepared by the sol–gel method showed an increased enhancement of Raman peaks by a factor of 4 as compared to the normal Raman Spectrum (nRS) due to the increased interaction between Ag and Phe. Furthur, the size of the NPs is reduced as revealed by the SEM analysis when compared to bare Ag NPs. Bharathi et al. have reported stable colloidal suspensions of gold NP sols [7]. The silica precursor used for our study is Tetra Ethyl Ortho Silicate (TEOS). The metal salt is incorporated with the silica precursor and then reduced with Sodium borohydride ($NaBH_4$) to produce Phe capped Ag NPs.

Crystal violet, a hazardous carcinogenic compound is known to cause long time adverse effects in aquatic environments [8]. Recent studies indicate that Ag NPs are a promising photocatalyst in the degradation of organic pollutants under visible/solar irradiation [9]. We have studied the effect of Phe-Ag NPs in the photocatalytic degradation of crystal violet in an aqueous suspension under light irradiation over different time intervals. Our results reveal that Phe-Ag enhances the photocatalytic activity of the dye when compared to the bare Ag NPs.

Interest in the SPR of metal NPs in the visible spectral region is sustained by its contribution in photonic applications, bio-optical sensors, photo-thermal tumour ablations and optical power limiters [10]. It is well known that noble metal particles like Ag, Au and Cu have interesting nonlinear optical (NLO) properties. Currently

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there is considerable interest in the synthesis of organic materials combined with metal NPs for NLO applications. Phe has an importance in NLO applications in particular, because it has a chiral symmetry and the molecules crystallize in non-centro-symmetric space groups [11]. We measured the intensity-dependent NLO absorption of an aqueous solution of Phe capped Ag using the open aperture Z-scan technique, which revealed that the sample is an efficient optical limiter.

2. Experimental

2.1. Materials

Silver Nitrate, $AgNO_3$, of 99.8% purity (NICE) was used as a precursor, Phe ($C_9H_{11}NO_2$ 99.0%-HIMEDIA) as the capping agent and $NaBH_4$, of 95% (MERCK) as the reducing agent. All chemicals were of analytical grade and used as purchased without further purification. Millipore water was used throughout the experiments.

2.2. Synthesis

2.2.1. Preparation of silver colloid

Silver sol was prepared according to Creighton's method [12]. In brief 20 ml of silver nitrate solution (1 mM) was added dropwise to 60 ml of $NaBH_4$ solution (1 mM) with vigorous stirring. Before mixing, both solutions were chilled to ice temperature. After the complete addition of $AgNO_3$, a yellow solution (silver sol) was obtained which was stable for more than 6 months.

2.2.2. Preparation of Phe-Ag colloid

Phe capped Ag colloid was prepared by two methods – in one method, different millimolar concentration ratios of Phe and $AgNO_3$ (1:1, 10:1 and 20:1) were tried. Of these only the 1:1 ratio produced a stable solution. Specifically, 8 ml of Phe (1 mM) was added drop by drop to 20 ml of $AgNO_3$ (1 mM) and stirred vigorously. After 3 h a pale pink colour was observed and it was stable for 48 h. In the second method, a mixture of Phe (1 mM) and $AgNO_3$ (1 mM) in the ratio 2:5 was added drop by drop to 60 ml of $NaBH_4$ (1 mM) under vigorous stirring. Noticeable colour changes from yellow to greenish grey were observed (Fig. 1). The solution was stable for more than a month. The pH was further optimized for NP stability and it was found that an alkaline (8.6) medium was the most stable.

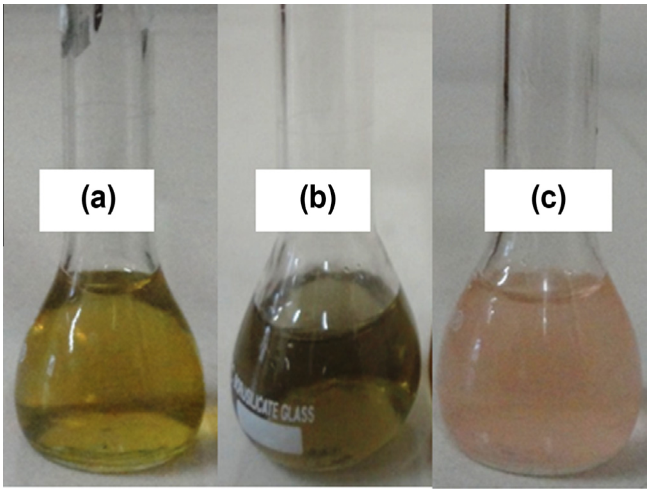

Fig. 1. Photograph of the (a) Ag sol, (b) Phe-Ag colloid 'with' and (c) 'without' the reducing agent.

2.2.3. Film preparation

Glass microscope slides (thickness 1 mm), were cut into 8 × 20 mm sections, washed in detergent, rinsed in Millipore water, soaked in ethanol and kept in an oven at 60° to dry until use. The preparation of the substrate is as follows: working at room temperature, TEOS (1.1 M), ethanol and 0.1 M $AgNO_3$ solution were mixed in a volume ratio of 1:2:2. The solutions were vigorously stirred for 1 h. Hydrolysis and condensation reactions take place while the mixture ages. Shortly after the mixing of the solutions, a suspension of colloidal particles (sol) is produced due to the initial hydrolysis and polycondensation reactions between TEOS and water. The solution had an oily appearance and remained transparent. Under the present experimental conditions, the time-window between liquid sol and solid gel was about 48 h and thereafter the formation of a solid gel takes place.

The Ag-doped sol–gel films were prepared by a dip coating process consisting of three steps: dipping, withdrawal and drying. After 36 h ageing time, the pre-cleaned glass plate was dip coated with the TEOS + ethanol + $AgNO_3$ nitrate solution at a rate of 30 mm per minute. The sol–gel solution spread onto the glass plate, adhered to the glass surface, and solidified slowly through evaporation of the solvent. The glass plate coated with sol–gel film was left to dry in air at ambient temperature for 30 min to remove the excess water and solvent within the sol–gel matrix. The plates were then soaked in 0.02 M $NaBH_4$ solution when the Ag ions trapped within the xerogel films were reduced to Ag NPs. After a few seconds, the glass plate was rinsed thoroughly with water to remove the excess $NaBH_4$ and left to dry at room temperature for one hour. The glass slide now takes on a pale yellow colour. The process is repeated with the incorporation of 0.1 M Phe to TEOS, ethanol and $AgNO_3$ in the ratio 1:1:2:2 to obtain Phe-Ag NPs trapped in the xerogel film.

The hydrolysis and condensation reactions for TEOS [13], which is one of the most important precursors in sol–gel processing, can be carried out by the mechanism of nucleophilic substitution as shown in the following reaction:

$$Si(OC_2H_5)_4 + H_2O \rightarrow HO - Si(OC_2H_5)_3 + C_2H_5OH \tag{1}$$

Silicic acid is obtained according to the next reaction

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \tag{2}$$

Condensation finally takes place according to either of two equations.

$$\begin{aligned}&(C_2H_5O)_3 - Si - OC_2H_5 + C_2H_5O - Si\\&\quad \rightarrow (C_2H_5O)_3 - Si - O - Si - (OC_2H_5)_3 + C_2H_5OH\end{aligned} \tag{3}$$

$$\begin{aligned}(C_2H_5O)_3 - Si - OH + HO - Si \rightarrow (C_2H_5O)_3 - Si - O - Si\\ - (OC_2H_5)_3 + H_2O\end{aligned} \tag{4}$$

2.3. Characterization

A Double beamed spectrophotometer (Helious alpha) was used for absorption spectra measurements with millipore water taken as the blank solution in every case. To obtain the TEM images the colloid was drop casted on a carbon coated Cu grid and the solvent evaporated. The sample was examined on a FEI-Tecnai $30G^2S$-Twin Transmission Electron Microscope at 300 kV. SEM images were analyzed by JEOL JSM-6701F Field Emission Scanning Electron Microscope.

The Zeta potential and Hydrodynamic size of the synthesized uncapped and Phe capped Ag NPs were determined by a Zetasizer (Malvern instruments) with 173° backscattered detection angle equipped with a He–Ne laser of wavelength 632.8 nm and beam