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Useful multivariate kinetic analysis: Size determination based on cystein-induced aggregation of gold nanoparticles

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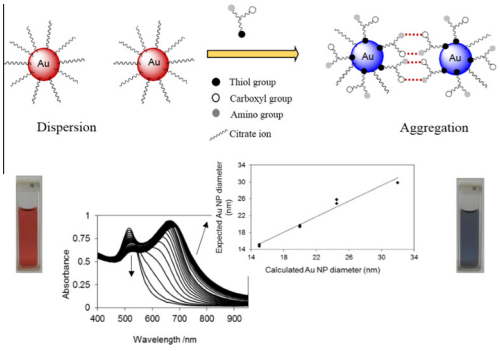
HIGHLIGHTS

- Size effect of Au NP on aggregation was used to Au NP size determination.
- A multivariate calibration model was constructed for Au NP size determination.
- The average sizes of unknown samples were determine using this method.
- We showed the direct size and concentration effects of Au NP on aggregation.
- The pH effect on aggregation is more significant for lower Au NP concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

This study describes spectrometric monitored kinetic processes to determine the size of citrate-capped Au nanoparticles (Au NPs) based on aggregation induced by L-cysteine (L-Cys) as a molecular linker. The Au NPs association process is thoroughly dependent on pH, concentration and size of nanoparticles. Size dependency of aggregation inspirits to determine the average diameters of Au NPs. For this aim the procedure is achieved in aqueous medium at pH 7 (phosphate buffer), and multivariate data including kinetic spectra of Au NPs are collected during aggregation process. Subsequently partial least squares (PLS) modeling is carried out analyzing the obtained data. The model is built on the basis of relation between the kinetics behavior of aggregation and different Au NPs sizes. Training the model was performed using latent variables (LVs) of the original data. The analytical performance of the model was characterized by relative standard error. The proposed method was applied to determination of size in unknown samples. The predicted sizes of unknown samples that obtained by the introduced method are interestingly in agreement with the sizes measured by Transmission Electron Microscopy (TEM) images and Dynamic Light Scattering (DLS) measurement.

Introduction

Au nanoparticles (Au NPs) with high stability among the other metal nanoparticles have great interest due to their using in many fields such as sensors, biosensors, medicine, catalysis and many emerging areas of nanotechnology [1–3]. Recent interest in nanoparticles stems from the fact that, nano-sized materials exhibit

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unique optical, electronic and magnetic properties which depend on their shape, size, and local environment. The foundation of nanotechnology research is based on the size, distribution and shape of nanoparticles because these parameters are the most important characteristics of the systems [4]. Usually, the standard methods for determination of the metallic nanoparticles size are transmission electron microscopy (TEM), for nanoparticles larger than 2 nm [5,6] and mass spectrometry for clusters smaller than 1.5 nm [7,8]. Both require sophisticated and highly expensive instrumentation. Therefore, alternative methods for the accurate determination of the NPs size are essential. When nanoparticles made of silver and gold dispersed in liquid media, these nanoparticles exhibit a strong UV–Vis extinction band that is not present in the spectrum of the bulk metal. This extinction band results when the incident photon frequency is resonant with the collective excitation of the conduction electrons, and is known as the surface plasmon resonance (SPR) [9,10]. The resonance frequency and intensity of this SPR are sensitive to the size, shape, dielectric properties and local environment of the nanoparticles [11–15]. As the size of Au NPs increases, the color of the solution varies from red to pink, and the SPR of the Au NPs undergoes a red shift with increasing size as predicted by Mie theory [16].

Controlled aggregation of Au NPs leads to a change in their optical properties (i.e. a red shift in surface plasmon band) which is a topic of considerable scientific interest in nanotechnology and materials science, as it can be exploited for various applications [17,18]. Different studies showed that the change in the localized surface plasmon band is related to the aggregated size of Au NPs [19–21]. Typically the Au NPs can be readily modified with thiol-containing biomolecules because the thiol group exhibits a strong interaction on the metal surface [22]. Generally, modified Au NPs aggregate when the terminal amino group of a biomolecule forms hydrogen bonding with the carboxyl group of another biomolecules on an adjacent nanoparticle [23,24]. Further studies have been carried out on the effect of nanoparticles size on biomolecules induced aggregation and to understand the kinetics of the aggregation process [25–31].

In this paper Au NPs with different sizes were prepared to investigate their aggregation kinetic depending on their average size. Citrate-capped Au NPs prepared by Frens method have been induced to aggregate upon addition of the L-cysteine (L-Cys), which can bind to Au NPs via a thiol group. We took the advantage of size-dependent nanoparticle aggregation to construct a calibration model for determination of Au NPs size, as the first application of aggregation kinetic for determining Au NPs size. In previous works [25–31], there was not any calibration model to determine the size of nanoparticles based on biomolecule-induced aggregation. As mentioned before in order to determine size of nanoparticles e.g. gold nanoparticles, several methods [5–8] are employed; besides of their time consuming and high costs aspects, these methods need considerable concentration of particles and also sample preparation should be considered. But in present work we will show ultra-low concentration of Au NPs will be used to build calibration model based on biomolecule-induced aggregation which makes this approach as a practical process for Au NPs size. Herein a kinetic data matrix was obtained per each Au NPs sample allowing exploit the advantage of multivariate data analysis. In multivariate data, the objects (independent variables) are described by many variables (dependent variables). Multivariate calibration is different from univariate calibration because it uses more than one dependent variable. This leads to new chances, e.g. using full spectra rather than the signal at a single wavelength. Using the entire spectral information may generally, cause to better results [32]. Chemometrics presents methods that allow the analysis of multivariate data where, the enormous amount of data is compressed to meaningful information [32]. A common type of quantitative chemometrics methods is partial least squares (PLS) modeling that relating two data matrices, X (dedependent variables) and Y (inpendent variables), by a linear multivariate model [33]. So in this experiment, the PLS modeling was used for the multivariate calibration of the UV–Vis data in order to relate the Au NPs sizes to aggregation kinetic process.

Experimental

Reagents and solutions

Hydrogen tetrachloroaurate ($HAuCl_4$, 99%), Sodium citrate (99%) and L-cysteine (97%), were purchased from Sigma–Aldrich. Disodium hydrogen phosphate and potassium dihydrogen phosphate, which used to prepare phosphate buffer (pH 5, 7) were purchased from Merck. Water was purified with a Milli-Q water system.

Instrumentation and software

The absorption spectrum of each solution was recorded with a UV–Vis s-2100 spectrophotometer (Scinco). Transmission electron microscopy (TEM) was carried out on a Hitachi H-9000NAR transmission electron microscope, operating at 200 kV. Dynamic light scattering (DLS) was performed on a standard laser light scattering spectrometer (BI-200SM) equipped with aBI-9000 AT to determine the hydrodynamic diameter for one set of nanoparticles in solution.

Each original kinetic data was arranged into a matrix format Y ($I \times J$), where I is the number of rows (measured spectra over times) and the J is the number of columns (measured wavelengths). The data were analyzed using MATLAB software, version 6.5 (The MathWorks), with 'PLS Toolbox', version 2.0.

Measurements

Absorption Spectra were collected over the range of 400–950 nm. Briefly, Au NP solution and buffer solution were quantitatively mixed and was allowed to react for 10 min, afterward, a quantitative amount of L-Cys was added, and the reaction was monitored via UV–Vis. Final concentration of L-Cys used for the study was 34.3 μM, and final concentrations of phosphate was 7.6 and 3.8 mM at pH 7 and 5, respectively. Different concentrations of two buffers were used, because when pH tends to the acidic range, lower ionic strength is needed to induce aggregation of Au NPs.

Synthesis of colloidal Au NPs

The citrate-capped Au NPs was prepared following the well-documented Frens method [34] to obtain monodispersed colloidal

Table 1
Details for the size-selective synthesis of Au NPs by Turkevich method.

Set	Amount of $HAuCl_4$ solution (12.5 mM, ml)	Amount of trisodium citrate solution (1%, ml)	Color	Average diameter (nm)	
				Observed[a]	Reported[b]
A	2	2	Red	15	16
B	2	1.75	Red	–	20
C	2	1.5	Red	24.5	25
D	2	1.25	Pinkish red	–	32
E	2	1	Pink	–	41
F	2	0.8	Pink	–	55

[a] Observed average diameter in present work by TEM image.
[b] Expected average diameter according to Ref. [30].