Study of spectroscopic properties of nanosized particles of core-shell morphology

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Abstract. Method of studying spectroscopic properties of nanosized particles and estimation of resonance wavelength range for determination of specific and unique “spectral” signatures in purpose of sensing, identification of nanobioparticles, viruses is proposed. Elaboration of relevant models of viruses, estimation of spectral response on interaction of electromagnetic (EM) field and viral nanoparticle is the goal of proposed methodology. Core-shell physical model is used as the first approximation of shape-structure of virion. Theoretical solution of EM wave scattering on single spherical virus-like particle (VLP) is applied for determination of EM fields in the areas of core, shell and surrounding medium of (VLP), as well as scattering and absorption characteristics. Numerical results obtained by computer simulation for estimation of EM “spectra” of bacteriophage T7 demonstrate the strong dependence of spectroscopic characteristics on core-shell related electric and geometric parameters of VLP in resonance wavelengths range. Expected spectral response is observable on far-field characterizations. Obtained analytical EM field expressions, modelling technique in complement with experimental spectroscopic methods should be the way of providing the virus spectral signatures, important in bioparticles characterization.

1. Introduction

Nanoparticles (NPs) are known as zero-dimensional materials-substances of about 100 nm and less sizes. Nanoparticles reveal the properties somewhat intermediate between small molecular clusters of 0.2-1 nm dimensions and bulk. Binary, core-shell structured nanoparticles are finding widespread applications. Optical properties of nanoparticles - gold nanospheres, silica-gold nanoshells, gold nanorods of various nanoparticle sizes or dimensions are highly dependent on the nanoparticle size, shape, and core-shell composition. Gold nanoshells are found to have optical cross-sections comparable to and even higher than the nanospheres and optical resonances fall favorably in the near-infrared region, nanospheres offer resonance wavelengths in the visible region [1].

Target of presented work is nanoparticles of biological origin. Nanobioparticles should reveal the properties common of inorganic analogues and specific of biomaterials. Among nanobioparticles the viruses, the smallest infectious agents are of particular interest of diversified works. The sizes of the most viruses range from 20 to 300 nm, are about 1/100 the size of bacteria. Viruses are also perfectly defined organic nanoparticles which are commonly used as scaffolds or nano-vectors in materials engineering and nanotechnology.

In context of detection and identification priorities, study of viruses, nanosized particles in common physical point of view is proposed. Physical, especially spectroscopic properties of virus-like particles...
(VLPs) by examination of optical, electrical and geometrical characteristics are considered. The advanced analysis of physical properties of nanoparticles would be done with electromagnetic (EM) wave and associated microscopy techniques or spectroscopic approaches, including infrared (IR), visible (Vis), ultraviolet (UV), Raman, Sum Frequency Generation (SFG) spectroscopies, and methods of particle analysis, with conventional approaches. Spectroscopic study of nanobioparticles, estimation of oscillation/vibrational modes, possible resonance wavelength range in purpose of determination of the unique spectra of viruses is the main goal of ongoing research activities. Raman spectra of some viral capsids (STNV, CCMV, M13) were calculated using the atomistic approach based on the idea that each viral capsid would have a set of unique frequencies and mode patterns due to the shape and composition of its capsid [2, 3]. Visible or near-infrared laser via impulsive stimulated Raman scattering (ISRS) techniques applied for excitation of mechanical modes of viral capsids resulted in mechanical resonances, possibility of damage the capsid shell rendering it inactive or even destroyed were considered [4, 5]. Number of works based on the elastic network models (ENMs), the empirical bond polarizability model, the rotation translation block method (RTB) declared the presence of vibrational frequency modes related to viral capsids and possibility to appreciate the activation (resonance or other type) of that by means of proper spectroscopic and laser techniques [2-6]. One of the ways for estimation of resonance frequencies range is the method determining the eigenvalues and corresponding eigenvectors obtained by algebraic system of functional equations which could be written based on the solution of electrodynamic task considering EM wave-VL particle scattering [7-10]. Algebraic system has more complicated form when VL particle is of core-shell structure with different electric parameters. Resonant wavelength range is predicted theoretically in the vicinity of values corresponding the maximums of intensity of particular scattered partial waves [7-8]. Estimation of resonant wavelength range based on determination of far-field characteristics such as scattering or absorption cross sections, the intensity of energy, wholly representing the response on wave-particle interaction is considered as the reasonable and decisive solution preferable for studying the spectroscopic properties and determination of possible spectral signatures of bioparticles, viruses.

2. Method of decision

Method of studying spectroscopic characteristics based on elaborated physical models of viruses represents the new possibility for estimation of spectroscopic properties and resonance wavelength range of viral nanoparticles, virions.

Virion, the extracellular infective form of a virus, is considered as a nanoparticle, consisting of inner core of nucleic-acids (RNA or DNA) and outer protective protein coat called capsid. The structure of a large number of viral capsids are icosahedral or near-spherical with icosahedral symmetry. A regular icosahedron is nature's optimum method of producing a closed shell from identical sub-units. Capsid separates the genome from surrounding area and may be considered as outside surface boundary layer or thick interface with specific geometrical, mechanical and electrical properties. Phenomena occurred on inner and outer surfaces of capsid or within the surface layer seems to be dominant in determining the mechanical, electrical and spectroscopic properties of ultrafine bioparticles as it takes place in metal or semi-conductive materials.

Thus, two main mediums of different structures and properties constitute the virion: capsid of protein capsomeres and nucleic acids into the capsid. Type, number and arrangement of capsomers and length of nucleic acid are essential in defining the size of capsid designed mostly in near-symmetrical geometry, having the unique self-assemble mechanism.

A simple calculation shows, that the ratio of inner (core) and outer spherical volumes of icosahedral capsid of bacteriophage T7 (of diameters inner \(d_1 = 42.6\) nm and outer \(d_2 = 56.6\) nm) is approximately \(0.426\) [11], so quite a large portion (0.57) of volume in virion is occupied by the capsid proteins. Capsid’s size is large enough than the “discrete” nature of protein subunits, therefore the influence of that on capsid whole geometry could probably be less significant. This fact allows virion to be
modelled as a spherical core-shell particle of smooth inner or outer surfaces. Core-shell VLP model of spherical geometry could be used as the first approximation of shape-structure of icosahedral unenveloped virion [9-10]. The structure and geometry of capsids as well as processes happening inside a layer probably dominate in determination of physical, spectroscopic properties of nano-sized particles, virions.

Theoretical approach of studying spectroscopic properties of VLPs is based on classical Maxwell's EM theory, separation of variables method for solving Helmholtz's (wave) equation. Solution of Helmholtz’s equation leads to the Bessel’s and/or Legendre’s equations [12]. EM fields in different areas of VLP are written as the sums of multipole-waves with unknown multipole coefficients. Application of boundary conditions to EM field components on core-shell surfaces and labour-consuming mathematical transformations leads to rigorous theoretical solution of EM scattering problem on single VL particle. Analysis of EM field expressions show that arguments of functions determining the multipole coefficients and scattered fields depend only on relative values of particles diameters over wavelength. Therefore, it makes possible to expand the research area, and the findings of well-established Mie theory [13] considering the light scattering on a homogeneous sphere be applied to nanoparticles of core-shell morphology and particles of biological origin as well.

Spectral response on EM wave-VLP interaction is determined by estimation of far-field \( r \gg 2d/\lambda \) [14]) characteristics representing the angular distribution of scattered (absorbed) energy. Scattering properties are characterized via expressions such as: the total scattering cross section

\[
\sigma_r = 2\pi \frac{1}{\lambda} \sum_{s=1}^{\infty} \left| A_s^r \right|^2 \frac{s(s+1)^2}{(2s+1)}
\]

(1)

the forward and backward cross sections with respect to propagation direction of excitation wave:

\[
\theta = 0, \quad \sigma_r = \frac{1}{\lambda} \sum_{s=1}^{\infty} \frac{1}{2} s(s+1)(A_s^r + A_s^m)^2
\]

(2)

\[
\theta = \pi, \quad \sigma_r = \frac{1}{\lambda} \sum_{s=1}^{\infty} \frac{1}{2} s(s+1)(A_s^r - A_s^m)^2
\]

(3)

Multipole coefficients \( A_s^r \) and \( A_s^m \) are calculated by expressions: for \( E \)-type waves (\( H_e^r = 0 \))

\[
A_s^r = \frac{i^{i-1}(2s+1)}{s(s+1)} \left[ G_s^r(k b, k b, L_s(k a, k a) - L_s'(k b, k b) G_s^r(k a, k a) \right] 
\]

(4)

for \( H \)-type waves (\( E_s^m = 0 \))

\[
A_s^m = \frac{i^{i-1} 2s+1}{s(s+1)} \left[ G_s^m(k b, k b, L_s^m(k a, k a) - L_s^m(k b, k b) G_s^m(k a, k a) \right] 
\]

(5)

In expressions (4) - (5), functions \( G_s^r(k a, k a), G_s^r(k b, k b), L_s(k a, k a), L_s'(k b, k b) \), \( \Lambda_s^r(k b, k b), \Gamma_s^r(k b, b_k), \) \( G_s^m(k a, k a), G_s^m(k b, k b), L_s^m(k a, k a), L_s^m(k b, k b), \Lambda_s^m(k b, k b), \Gamma_s^m(k b, k b), \) are defined by Riccati-Bessel Spherical and Associated Legendre functions and derivatives of that [8-10].

Wave number of free space and of (\( q \)) medium are correspondingly equal to \( k = \omega \sqrt{\varepsilon_0 \mu_0}, \) \( k_q = k\sqrt{\varepsilon_q \mu_q}, \) magnetic permeability \( \mu_q \approx 1, \) \( \varepsilon_q \) is a dielectric permittivity, \( q = 1 \) (core), 2 (shell), 3 (surrounded area of VLP), \( \varepsilon_m = 8.85 \cdot 10^{-12} \) F/m, \( \mu_q = 1.26 \cdot 10^{-6} \) H/m, the frequency of excitation wave is denoted by \( \omega, a = d_0/2 \) and \( b = d_2/2 \).
Dielectric properties of protein and nucleic-acids are still the subjects of experimental and simulation studies needed high-effective measuring and computing techniques. Dielectric constants are estimated from the molecular dynamics (MD) and normal mode (NM) simulations based on various theories, approximations or experimental measurements. Values of different proteins vary from as low as 1 or 2 to as high as 40 and more [15, 16]. In some studies dielectric constant measurements presumable values are about 6.3 (DNA containing virus) and 3.5 (capsid) for T7 viruses [17]. Proposed theoretical solution, analytical expressions of EM fields make possible to estimate the fields in the areas of core, shell and surrounding areas of VLPs based on machine learning and modeling techniques have been used for generating a simulated spectrum of nanoparticle of given size and available literature optical constants.

3. Results

Computer simulation based on theoretical findings and expressions (1) - (5) is used for studying the spectroscopic properties of VL particles by estimation of EM field characteristics vs excitation wavelength. Efficiency of model of studying the spectroscopic characteristics is demonstrated for estimation of “spectra” of bacteriophage T7 (figure 1, figure 2). Geometric data of icosahedral virions are gained from data bases [11], dielectric permittivities are experimentally measured [17].

Figure 1. “Spectra” of T7 virus. Scattering cross section (σ/d2) vs excitation wave length (λ). Parameters of core-shell model: diameters of core - d1 = 42.6 nm, shell - d2 = 56.6 nm, dielectric permittivity of core - ε1 =6.3, shell - ε2 =3.5, surrounding medium - ε3 =1.

Numerical results are obtained by computer simulation, based on MatLab software (R2011a). Theoretical outcomes and reliability of program units have been tested and compared with results known for spheres [7, 8, 13].

Analysis of result of VLP spectra in different wavelength ranges has revealed the strong dependence of far-field characteristics, scattering cross sections on core-shell related geometric (d1 and d2) and electric (ε1 and ε2) parameters in resonance wave length ranges (UV for VLP-T7). Expected spectral response is observable on far-field characterizations. Increasing of excitation wavelength leads to diminishing of number of maximums, redistribution and reducing of intensity of scattered wave.
Resonance wavelengths are associated with the values corresponding to the maximums of scattering cross sections and resonance wavelength range could be defined by the formula \( \lambda < \pi d_{1,2} \sqrt{\frac{\epsilon}{\epsilon_n}} \).

Thus, the proposed model may be used for investigation of spectroscopic properties of nanobioparticles and appreciation of possible resonant wavelength ranges correlating with scattering/absorbing efficiency of VLP. Experimental data obtained by applying exquisite techniques and outcomes of theoretical or simulation models should complement each other and verify factors such as possible anisotropy of core-shell areas of virion, surface roughness and inhomogeneity unforeseen in simplified approaches.

4. Conclusions
Model of studying of spectroscopic properties and estimation of resonance wavelength range of nanosized particles of core-shell morphology in purpose of sensing and identification of nanobioparticles is considered. Physical core-shell model of virus-like particle (VLP) is associated with morphology of un-enveloped virion, constructed of protein capsid and nucleic-acids (DNA or RNA). Rigorous theoretical solution of EM wave scattering on single spherical core-shell particle is applied for determination of EM fields in the areas of core, shell and surrounding medium of VLP, as well as scattering or absorption characteristics. Numerical results obtained by computer simulation for estimation of EM “spectra” of bacteriophage T7 demonstrate the strong dependence of spectroscopic characteristics on core-shell related geometric and electric parameters in resonance wave length ranges; expected spectral response is observable on far-field characterizations; resonance wavelengths are associated with the values corresponding to the maximums of scattering cross sections. The shape/structure, inner and outer diameters of capsid, nucleic-acid and protein capsid related dielectric permittivities are considered as the main parameters determining the set of resonance wavelength, as well as the spectral signatures of VLPs, virions. Findings based on well-established theoretical and modelling tools are applicable for studying the spectral properties of nanosized organic, inorganic or hybrid particles of different origin and spherical or core-shell morphology.

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