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A rapid estimation of the average size of the core-shell nanoparticles by calcination and modelling

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A rapid and simple method for the evaluation of the average size of the hard core - shell nanoparticles in a sample is presented. It is based on the combination of two procedures (calcination and modelling) easy to perform. The application to a series of magnetite – amino acid nanoparticles (amino acid: aspartic, glutamic, proline, tryptophan, arginine) leads to satisfactory values for the average size of the nanoparticles if they are compared with those experimentally determined by Transmission Electron Microscopy.

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1. Introduction

Nanoparticles have a large area of interest due to the structure – property relations that have led to remarkable applications [1-6]. In the characterization of the nanoparticles, the size and the distribution of the nanoparticles are currently made using various techniques such as TEM, BET, XRD or the motion of the particle in response to some force, such as gravity, centrifugal force, Brownian motion or electrostatic force, etc. Almost all of these techniques need sophisticated equipments, the measurement being the fruit of a thorough case-study regarding the size, shape and dispersion. Nevertheless, the estimation of the nanoparticle average size, important for industrial or medical applications, needs simple and rapid procedures. The estimation of the average size of the nanoparticles from a sample is useful to substantiate

The aim of this brief communication is to present a less costly and easy hand determination of the average size of the nanoparticles with a hard core – shell structure combining two different procedures, and namely an experimental one (calcination) and another theoretical (molecular modelling).

The proposed method applied to some magnetite – amino acid nanoparticles (aspartic acid, glutamic acid, proline, tryptophan and arginine) leads to average size values close to those obtained experimentally with TEM procedure [6].

2. Experimental

Theory

Let M be the total mass of the sample $M = M_1 + M_2$, where M_1 represents the mass of the hard cores and M_2 the mass of the one-layer shells of all nanoparticles contained in the sample.

By calcination, the following ratio is experimentally determined:

$$q = \frac{M_2}{M_1} = \frac{M_2}{M - M_2} \tag{1}$$

where M_2 is the lost mass and $M_1 = M - M_2$ the mass remaining after calcination.

If the polydispersion of the nanoparticles in the sample is not considered, we can regard the sample as being composed from nanoparticles of the same average size. In this case, the "q" ratio between M_2/M_1 masses from the sample must be equal to the m_2/m_1 ratio of the masses from the "average size " nanoparticle (see Fig. 1), where m_1 is the hard core mass and m_2 the mass of all molecules from the one-layer shell.

$$q = \frac{M_2}{M_1} = \frac{m_2}{m_1} \tag{2}$$

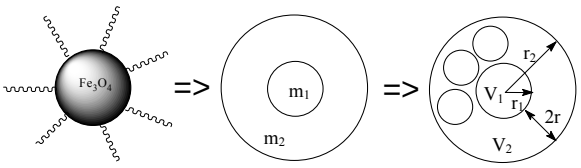

Fig. 1. The structure of a core - shell nanoparticle.

Ratio "*q*" can be written, as follows (Fig. 1)

$$q = \frac{m_2}{m_1} = \frac{\rho_2}{\rho_1}\frac{V_2}{V_1} \tag{3}$$

or

$$q' = q\frac{\rho_1}{\rho_2} = \frac{V_2}{V_1} = \frac{\frac{4\pi}{3}(r_2^{\,3} - r_1^{\,3})}{\frac{4\pi}{3}r_1^{\,3}} = (\frac{r_2}{r_1})^3 - 1 \quad (4)$$

where ρ_1 , ρ_2 are the core and shell densities respectively and V_1 and V_2 the core and shell volumes.
From expression (4), we find:

$$\frac{r_2}{r_1} = (q'+1)^{\frac{1}{3}} \quad (5)$$

As may be seen in Fig. 1, the nanoparticle diameter "*D"* can be expressed in terms of hard-core (r_1) and shell (r) radii

$$D = 2r_2 = 2(r_1 + 2r) = 4r\frac{(q'+1)^{\frac{1}{3}}}{(q'+1)^{\frac{1}{3}} - 1} \quad (6)$$

where "2*r*" is the diameter for a molecule in the shell and *q'* an experimentally determined quantity according to the expressions 4 and 1.

The density ρ_2 in expression (4), as well as the molecular radius "r" for the molecules in the shell can be estimated from the following expression:

$$\rho_2 = \mathrm{m} / V' \quad (7)$$

$$r = [\frac{3V'}{4\pi}]^{1/3} \quad (8)$$

where "m", *V'* are the mass and volume of a single molecule in the shell and "r" its radius in the approximation of the spherical shape.

Besides the proper volume of the molecule (van der Waals volume), the volume *V'* in equation (7) must obviously include some empty space between molecules situated in the layer (see Fig. 1). For this reason, the quantity ρ_2 = m/*V'* (g/cm^3) has been calculated using the Solvent Accessible Surface - Bounded Molecular Volume for the solvent radius equal to 1.4 Å (water). This means the molecular volume *V'* is obtained considering a spherical probe (solvent) as it is rolled over the molecular model representing the molecule in the nanoparticle shell [7]. Volume *V'* estimated in this way, simulates better the real arrangement of the molecules disposed in the shell around the hard – core. As may be seen in the following, the chosen radius of 1.4 Å for the spherical probe leads to satisfactory results for the magnetite – amino acid nanoparticles herein considered. The method used to calculate the molecular volume bounded by the solvent accessible surface is that reported in the literature [8]. Reliable values for *V'* can be obtained with dedicated QSAR programs (e.g. Hyperchem).

3. Results and discussion

Formula (6) has been applied to a series of amino acid – magnetite nanoparticles whose average diameter determined by us using TEM method has been previously reported [6].

The calcinations results for the nanoparticle samples (M is total mass and M_2 the lost mass) are summarized in Table 1.

Table 1. Calcination results for magnetite/amino acid nanoparticles.

Amino acid	M(g)	M_2(g)
aspartic	0.0257	0.0042
glutamic	0.0294	0.0035
proline	0.0206	0.0020
triptophan	0.0170	0.0014
arginine	0.0125	0.0012

The calculated diameter of the average nanoparticle "*D*" using formula (6) and the experimental diameter "D_{exp}" reported [6] are given in Table 2.

The density ρ_2(g/cm^3) (equation 7) was estimated from the molecular mass and the molecular volume bounded by the solvent accessible surface V' evaluated for the molecular geometries obtained with Molecular Mechanics (MM+), semi-empirical quantum- molecular calculations semi semiempirical (RHF, PM3) and ab initio (RHF, STO3, MP=2).[9] and for the spherical probe radius equal to 1.4 Å. For the magnetite contained in the nanoparticles core, the density is equal to ρ_1 =5.16 (g/cm^3) [10].

Table 2. The calculated average size for magnetite/amino acid nanoparticles.

Amino acid	Method	ρ_2(g/cm^3)	D(nm)	D_{exp}(nm) (TEM)
aspartic	MM: PM3: STO3:	0.550 0.540 0.532	7.8 7.0 7.0	8.76
glutamic	MM: PM3: STO3:	0.535 0.526 0.515	8.5 8.4 8.3	6.87
proline	MM: PM3: STO3:	0.482 0.477 0.470	9.2 9.1 9.0	7.72
tryptophan	MM: PM3: STO3:	0.547 0.539 0.529	11.2 11.1 11.0	11.78
arginine	MM: PM3: STO3:	0.504 0.491 0.481	9.5 9.3 9.2	5.26

Because the density values ρ_2 calculated for different molecular geometries take almost the same value irrespective of the procedure used (MM, PM3 or ab initio STO3), due to its simplicity, the Molecular Mechanics (MM+) is recommended.

As may be seen in Table 2, the calculated average diameter for the studies nanoparticles assumes values which can favorably be compared with those experimentally determined (column 4).

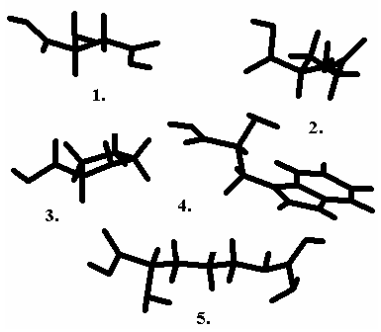

Fig. 2. Amino acid molecules: 1. Aspartic 2.Glutamic 3. Proline 4. Tryptophan 5. Arginine

The discrepancy for arginine - magnetite between the calculated values equal to ≈ 9 nm and that experimentally found of 5.26 nm can be explained by the departure from the spherical shape assumed for arginine molecules situated in the nanoparticle shell. As may be seen in Figure 2, the molecular geometry for arginine can be considered as having almost a linear rather than a spherical shape. Further studies and improvements of the presented method are in progress.

5. Conclusions

The application of the presented method for the evaluation of the average size of a series of amino acid – magnetite nanoparticles leads to satisfactory values if they are compared with those obtained by Transmission Electron Microscopy. The method based on simple calcination experiments and molecular modeling can in principle be applied to hard core – shell nanoparticles. Further studies and improvements of the method are in progress.

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