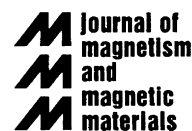




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A quantum dot model for the surface charge density in ferrite-based ionic magnetic fluids

P.C. Morais^{a,*}, Fanyao Qu^b

^a Instituto de Física, Núcleo de Física Aplicada, Universidade de Brasília, C.P. 004455 Campus Universitário, 70919-970, Brasília-DF, Brazil

^b Faculdade de Física, Universidade Federal de Uberlândia, 38400-902, Uberlândia-MG, Brazil

Abstract

Calculation of the surface charge density in semiconductor metal-oxide quantum dots (QDs) dispersed in aqueous colloids, in a wide range of pH values (1–13), is presented. Surface charge density in the range $\pm 0.4 \text{ C/m}^2$ was obtained for spherical nanoparticles in the typical diameter range. The shape of the calculated surface charge density curve as well as the range of the values obtained, in excellent agreement with the data reported in the literature, are obtained as long as a proton transfer mechanism through the semiconductor–electrolyte interface takes place. The data reported here explain the stability found in ionic magnetic fluids at the usual lower/higher pH values.

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Keywords: Charge transfer; Low-dimensional systems; Magnetic fluids; Quantum dots

Colloidal stability in ferrite-based ionic magnetic fluids is a complex issue, though stability has been achieved (over decades) using a set of empirical laboratory procedures. The electric surface charge density and the corresponding built-in mechanism play a key role in the understanding of the colloidal stability of nanosized ferrite species in water-based media. Prediction of the pH dependence of the surface charge density probably represents the finest test to any model picture addressed to the description of the colloidal stability. In this study the spherical ferrite-based nanoparticle will be treated as semiconductor quantum dots (QDs), whose surface behaves as a Brønsted–Lowry system when immersed in electrolytic medium, to draw conclusions about the surface charge density.

The negative charge developed in a metal oxide-based nanoparticle (M_xO_y) in aqueous media is assumed to be due to partially bonded oxygen atoms ($\text{M}-\text{O}^-$) at the nanoparticle surface [1,2]. The neutral hydroxyl group bonded to the nanoparticle surface ($\text{M}-\text{OH}$) also plays

a key role in the chemical equilibrium involving the positively and negatively charged nanoparticle [3]. It is assumed here that negative charge is built up at the aqueous dispersed nanoparticle due to proton (H^+) transfer out from the nanoparticle surface toward the solvent. Thus, starting at the zero point of charge and increasing the pH value in the aqueous medium, the chemisorbed proton (H^+) is assumed to move out from the nanoparticle surface ($\text{M}-\text{OH}$), leaving behind electron in the partially bonded oxygen atom ($\text{M}-\text{O}^-$) [1,2]. The electron left behind would be accommodated in the nanoparticle conduction band while the surface oxygen atom is stabilized by a strongly bounded water layer (WL) surrounding the nanoparticle surface [4]. Such proton transfer mechanism sets in a negative charge, which is mainly localized at the nanoparticle surface. In contrast, starting at the zero point of charge and lowering the pH in the aqueous medium the available protons (H^+) are assumed to transfer from the acid solvent back to the nanoparticle surface, thus setting up a positive charge at the nanoparticle surface ($\text{M}-\text{OH}_2^+$) [1,2]. Therefore, the charge–discharge process of an M_xO_y semiconductor QD in aqueous solution is assumed to involve proton (H^+) transfer through the

*Corresponding author. Tel.: +55-61-273-6655; fax: +55-61-272-3151.

E-mail address: pcmor@unb.br (P.C. Morais).

strongly bounded WL at the M_xO_y/H_2O interface. Magnetic resonance measurements indicate that the WL is typically one nanometer thick and strongly bounded at the nanoparticle surface [5]. Experimental data obtained from M_xO_y semiconductors in aqueous media indicate that band offset values go typically up to 1 eV [6], being very sensitive to the pH value [7].

Fig. 1 shows the schematic energy band diagram, proposed for an isolated spherical M_xO_y semiconductor QD immersed in alkaline aqueous solution (negatively charged QD). The nanoparticle diameter is given by $2L_W$, the spacer layer (SL) thickness is $(L_S - L_W)$, the donor depletion layer (DDL) thickness is $(L_D - L_S)$, and the donor layer (DL) thickness is $(L_E - L_S)$. The confined bound states inside the QD are described by $E_{n,\ell}$, where n and ℓ are principle and orbital quantum numbers, respectively. E_D is the donor ionization energy and V_0 is the band offset. In alkaline aqueous colloids the DDL surrounding the nanoparticle corresponds to the region where the positively charged counterions are distributed [8]. The band offset value (V_0) represents the difference between the chemical potential at the band edge of the nanoparticle (M_xO_y) and the chemical potential of the pure solvent (H_2O). The M_xO_y nanoparticle dispersed in water solution is now treated as a spherically symmetric M_xO_y/H_2O QD. The QD electronic structure is then obtained numerically by solving self-consistently the Schrödinger and Poisson's equations in the frame of the finite-difference method (FDM) with a non-uniform mesh size [9].

Energy levels in spherical semiconductor QDs are obtained by solving $(1/2m)d^2\psi_{n,\ell}/dr^2 - U_{\text{EFF}}\psi_{n,\ell} = E_{n,\ell}\psi_{n,\ell}$ and $\varepsilon\nabla^2 V_H = 4\pi[n_D - n(r)]$, with $n, \ell =$

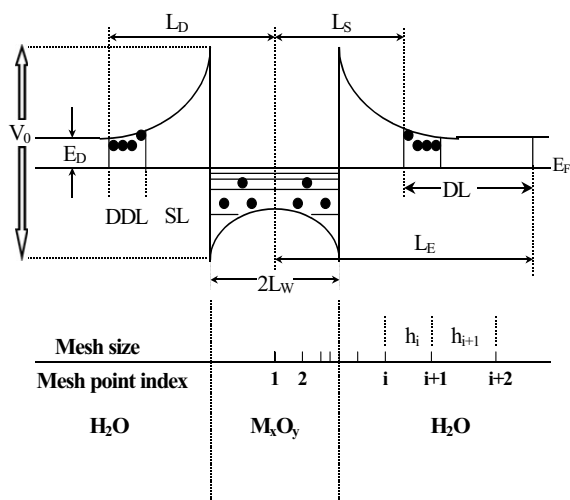


Fig. 1. Schematic energy-band diagram for the M_xO_y/H_2O QD. The discretization of the potential based on a nonuniform mesh is represented as well.

$0, 1, \dots, U_{\text{EFF}} = V_0 + V_H + \ell(\ell + 1)/2mr^2$, m the carrier effective mass, and ε the dielectric constant. The wave functions ($\psi_{n,\ell}$) and bound energies ($E_{n,\ell}$) are then computed considering an initial guess for the Hartree potential (V_H). Then, a new Hartree potential, $V_H^{(\text{NEW})}$, is calculated by numerically solving the Poisson's equation and comparing to the previous one, ($V_H^{(\text{OLD})}$). The calculation is carried out until some specified tolerance is achieved. Numerical calculation was performed for the charged M_xO_y/H_2O spherical QD considering: The strongly bonded WL thickness (1 nm), the ionization energy (50 meV), the effective mass in the barrier (1.40), the effective mass inside the QD (0.24), the barrier dielectric constant (80), the QD dielectric constant (3.7), and the temperature (300 K).

To systematically study the effect of the zero-dimensionality as well as the QD charge process, the zero-dimensional carrier gas (0DCG) density has been calculated. We found that the 0DCG starts with a finite value at the center of the QD and from there increases as one moves towards the M_xO_y/H_2O interface, reaching its maximum value near the interface. Therefore, carriers in the QD tend to stick at the M_xO_y/H_2O interface. The surface charge density (σ) at the M_xO_y/H_2O interface has been calculated using the following expression [10]:

$$\sigma = 2\Sigma_{\ell}\Sigma_n(2\ell + 1)f_{\text{FD}}(E_{n,\ell}) \int |\psi_{n,\ell}(r)|^2 dr, \quad (1)$$

where f_{FD} is the Fermi–Dirac distribution function.

Fig. 2 illustrates the surface charge density versus pH, for M_xO_y nanoparticles ($L_W = 4$ nm, $V_0 = 600$ meV, and $T = 300$ K). Different nanoparticle sizes as well as different band offset values in Fig. 2 lead to different graphs for the surface charge density versus pH. We first note the excellent agreement between the range of the calculated surface charge density and the data available in the literature [11]. Second, the close similarity of the curve with the titration curves of aqueous charged colloids [12]. As shown in Fig. 3, the surface charge density first increases as the QD size

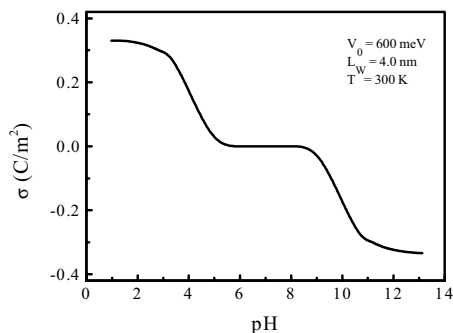


Fig. 2. Calculated surface charge density versus pH.

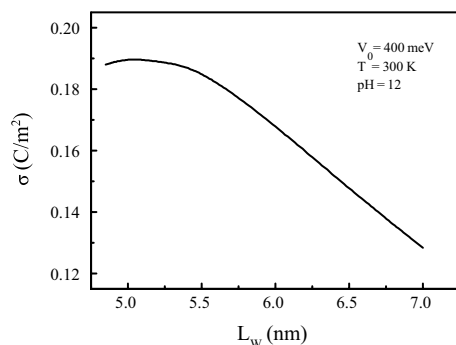


Fig. 3. Calculated surface charge density versus particle size.

decreases from higher values, reaching a peak value at a well-defined QD size, following a decrease as the QD size approaches zero. Furthermore, the curve peak in Fig. 3 shifts to higher QD sizes as the pH value decreases [13].

In summary, a new approach to calculate the surface charge density in semiconductor metal-oxide QDs dispersed as aqueous colloids, as a function of the pH and dot size, is presented. Surface charge density in the range of $\pm 0.4 C/m^2$ was obtained for spherical nanoparticles in the pH range 1–13. The range of the calculated surface charge density as well as the shape of the σ versus pH curve are in excellent agreement with the data reported in the literature.

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