CHARACTERIZATION OF NANOPARTICLES IN FLUIDS WITH QUARTZ CRYSTAL MICROBALANCE (QCM)

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Abstract: In this paper we study and develop a simple method to characterize nanoparticles in liquid media using Quartz Crystal Microbalances (QCM). For this we used five types of nanoparticles in ultra-pure water (deionized water): Ag, Au, Pd, Ti and Fe. The nanoparticles have the size of between 70 nm and 80 nm, and the concentration was about 20 mg/l (20 ppm).

Keywords: Quartz Crystal Microbalance, Nanoparticles, Nanocolloids

1. Introduction.

Nanoparticles, typically in the size range of 1-100 nm, are used increasingly in various applications; e.g., better catalysts, sorbents, optical or electronic materials, filter materials, and drug carriers. It is of interest to further optimize particular nanomaterial functions, as well as to avoid potential adverse effects of nanoparticles for human health and the environment. QCM offers a unique way of studying nanoparticle interactions both in liquid and gas phase. Engineered nanoparticles are prepared from all types of materials; metals, ceramics, polymers and carbon materials (e.g., graphene and carbon nanotubes) and also as composites of these materials. Both physical and chemical properties of nanoparticles may be different compared to bulk materials. Such size-dependent effects are usually stronger the smaller the particles are. Considering the fact that nanocolloids are difficult to investigate under normal conditions, we choose to use a Quartz Crystal Microbalance in order to remove the liquid and retain only the nanoparticles from the sensor surface for the further investigations.

The rate of mass change (slope of the sensor frequency) versus time plots are useful indicators of particle behavior during deposition on surfaces. Nanoparticle interactions with solid surfaces are of interest to learn about nanoparticle surface affinity, e.g. for filtering/removal of nanoparticles from water or air, for collecting samples for later characterization, or for preventing nanoparticle induced fouling.

In our study we used 0.5 mL from different colloidal samples: Ag, Au, Pd, Ti and Fe in pure water. After deposition nanoparticles on sensors we have been analyzed surfaces of sensors by Atomic Force Microscopy - AFM (Ntegra Prima by NT-MDT), Scanning

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Electron Microscopy - SEM (SU-70 by Hitachi) and Energy Dispersive X-Ray Spectrometer (UltraDry EDS) for characterization of clusters and isolated nanoparticles.

Nanoparticles were adsorbed uniformly over the entire sensor, but from place to place were formed clusters. Depending on the adsorbed element and the size of the nanoparticles, the formed clusters have different shapes. These shapes were investigated in order to determinate the mean size of nanoparticles.

Obtained AFM images were processed with Nova Px software. The purity of metal nano colloids is 99.99% of metal. The average size of these nanoparticles is: Ag - 80 nm (concentration 17 mg/l), Au - 70 nm (concentration 22 mg/l), Pd - 70 nm (concentration 25 mg/l), Ti - 76 nm (concentration 18 mg/l), Fe - 60 nm (concentration 21 mg/l). The particles of the colloidal solutions are electrostatically stabilized. The mean zeta potentials are between -53 mV and - 65 mV.

2. Theory

Sauerbrey was the first to recognize the potential usefulness of the Quartz Crystal Microbalance (QCM) technology and demonstrate the extremely sensitive nature of these piezoelectric devices towards mass changes at the surface of QCM electrodes [1]. The results of his work are embodied in the Sauerbrey equation, which relates the mass change per unit area at the QCM electrode surface to the observed change in oscillation frequency of the crystal. More recent developments have focused on tailoring electrode surface chemistry (i.e. specialized polymer and Nano-particles coatings) so that these devices can be applied as discriminating mass detectors for (1) specific gas detection, (2) environmental monitoring, (3) biosensing and (4) basic surface-molecule interaction studies. When the QCM comes in contact with a solution, there is a decrease in frequency that is dependent upon the viscosity and the density of the solution. A quantitative understanding of the resonator behavior is a prerequisite for proper interpretation of experimental results under total liquid immersion. This problem was first treated by Glassford, and later by Kanazawa and Gordon [2]. Kanazawa's treatment of the influence of the solution properties on the crystal witch permits the prediction of the change in resonance frequency which accompanies immersion of the crystal into a viscous medium.

$$\Delta f = -f_U^{1/2} \left(\frac{\rho_L \eta_L}{\pi \rho_q \mu_q} \right)^{1/2} \tag{1}$$

where f_U = frequency of oscillation of unloaded crystal, ρ_q = density of quartz = 2.648 g cm⁻³, μ_q = shear modulus of quartz = 2.947×10¹¹ g cm⁻¹ s⁻², ρ_L = density of the liquid in contact with the electrode, η_L = viscosity of the liquid in contact with the electrode.

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Viscous coupling of the liquid medium to the oscillating crystal surface results not only in a decrease in the series resonant frequency but also in damping of the resonant oscillation - the viscous loss is manifested as an increase in series resonance resistance, R, of the QCM resonator.

Thus, *R* serves as an excellent independent measure of viscous loading by the medium (liquid or soft-film) at the crystal's surface. Δf and ΔR measurements are both routinely used as independent indicators of mass loading and viscosity at the crystal-liquid interface of the QCM resonator during chemical and electrochemical depositions in solution.

In a separate study, a Butterworth-Van Dyke equivalent circuit model was applied to derive a linear relationship between the change in series resonance resistance, Δ_R , of the quartz oscillator and $(\rho_L \eta_L)^{1/2}$ under liquid loading:

$$\Delta R = \left(\frac{n\omega_s L_u}{\pi}\right) \left(\frac{2\omega_s \rho_L \eta_L}{\rho_q \eta_q}\right)^{1/2}$$
(2)

Where: ΔR = change in series resonance resistance in Ω , n = number of sides in contact with liquid, ω_s = angular frequency at series resonance ($2\pi f_s$), L_u = inductance for the unperturbed (dry) resonator, usually in mH.

3. Experiment

We have choosed to use a Quartz Crystal Microbalance from Valahia State University of Targoviste (QCM-200 by Stanford Research Instruments). The sensor used is quartz with TiPt metal electrodes and 5 MHz frequency of resonance.

The method use is static method [3] in real time. After remove the liquid by evaporation we retain only the nanoparticles from the sensor surface for the further investigations [4-11].

The standard QCM System (from Stanford Research Systems-SRS) is a stand-alone instrument with a built-in frequency counter, resistance meter, personal computer and printer (figure 1). It includes controller, crystal oscillator electronics, crystal holder, and quartz crystals.

The QCM may be locked to a user supplied 10 MHz clock for ultra-stable frequency measurements. In addition, the QCM has an RS-232 interface and comes with both Windows and LabVIEW software providing real-time display, analysis and storage of our QCM data.

Supplementary, we have Ultra-stable Rubidium Frequency Standard with 2 ppb stability and 0.0001 Hz sensibilities. The ultra-precise temperature meter measure "*in situ*" temperature, between 4 K and 700 K with 0.1 K.



Fig. 1. a) QCM System; b) Quartz crystal holder and c) Diagram for operation.

After adsorbed nanoparticles we have been analyzed by Atomic Force Microscopy - AFM (Ntegra Prima by NT-MDT); Scanning Electron Microscopy - SEM (SU-70 by Hitachi) and Energy Dispersive X-Ray Spectrometer (UltraDry EDS).

3. Results and discussions

QCM is a simple method for analyzing, which combined with other analysis tools can provide important information's about the materials examined in liquid complex or in nanometer films. For every nanocolloids we obtained a graphic with specific energy prints. Nanoparticles were adsorbed uniformly over the entire sensor, but from place to place were formed clusters.

Depending on the adsorbed element and the size of the nanoparticles, the formed clusters have diffent shapes. These shapes were investigated in order to determinate the mean size of nanoparticles. Obtained AFM images were processed with Nova Px software.

In the figure 2 we represent the QCM fill diagram "Frequency shift versus time" and "Resistance versus time" for Ag nanocolloids in DI water. Solution with Ag nanocolloids (0.5 ml) was left to analyze up to full evaporation of water. Ag nanoparticles from solution were deposited on the sensor electrode knew clusters. The time of total analysis was around 16 hours.

The time between two analyses were made in the range of 0.1 seconds. In the first 8 hours of analysis (about 30,000 seconds) held an adsorption process and rejection of nanoparticles.

Then, the process followed with deposition of nanoparticles on the electrode. The sharp dramatically drop in frequency (increasing the mass of electrode). At the end of the process the entire quantity of nanoparticles in the fluid volume were deposited on the sensor electrode. Result of the variation in frequency indicates the amount of deposited metal that is consistent with the amount of nanoparticles in the initial volume of 0.5 ml.



Fig. 2. The QCM fill diagram "Frequency shift versus time" and "Resistance versus time" for Ag nanocolloids in DI water.

The figure 3 shows the behavior of nanoparticles in aqueous solution in the first 3 hours of analysis. Frequency curve is observed adsorption of liquid containing nanoparticles. Repeatability of curve is approximately 1 hour. In this period of time, the shift frequency is about 35 Hz and shift resistance is 12 Ω .



Fig. 3. The QCM shortened diagram "Frequency shift versus time" and "Resistance versus time" for Ag nanocolloids in DI water.

In the figure 4 we represent the image AFM and image SEM with final sensor. Ag molecules have been deposited in the form of clusters with diameters up to 500 nm.



Fig. 4. AFM and SEM images of sensor with Ag nanoparticles after total liquid evaporation.

In the figures 5, 6 and 7 we present results of analyzes QCM with Au nanocolloids (0.5 ml), which was left to analyze up to full evaporation of water. The time of total analysis was around 24 hours. The time between two analyses were made in the range of 1 second. In the first 10 hours of analysis (about 36,000 seconds) held an adsorption process and rejection of nanoparticles. Then, the process followed with deposition of nanoparticles on the electrode. The sharp dramatically drop in frequency (increasing the mass of electrode). At the end of the process the entire quantity of nanoparticles in the fluid volume were deposited on the sensor electrode. Result of the variation in frequency indicates the amount of deposited metal that is consistent with the amount of nanoparticles in the initial volume of 0.5 ml. The figure 50 shows the behavior of nanoparticles in aqueous solution in the first 2 hours of analysis. Repeatability of curve is approximately 1 hour. In this period of time, the shift frequency is about 250 Hz and shift resistance is 90 Ω .



and "Resistance versus time" for Au nanocolloids in DI water.



Fig. 6. The QCM shortened diagram "Frequency shift versus time" and "Resistance versus time" for Au nanocolloids in DI water.

In the figure 7 we represent the image AFM and image SEM with final sensor. Au molecules have been deposited in the form of clusters with diameters up to 300 nm. The clusters with strong bonds are formed on the TiAu electrode. Occupied sensor surface gold has increased substantially. Such a sensor can be used as for the determination of cyanide in the liquid.



Fig, 7. AFM and SEM images of sensor with Au nanoparticles after total liquid evaporation.

In the figure 8 and 9 it present solution with Pd nanocolloids (0.5 ml) was left to analyze up to full evaporation of water. The time of total analysis was around 16 hours. The time between two analyses were made in the range of 0.1 seconds. In the first 8 hours of analysis (about 30,000 seconds) held an adsorption process and rejection of nanoparticles. Then, the process followed with deposition of nanoparticles on the electrode. The sharp dramatically drop in frequency (increasing the mass of electrode). At the end of the process the entire quantity of nanoparticles in the fluid volume were deposited on the sensor electrode.

Result of the variation in frequency indicates the amount of deposited metal that is consistent with the amount of nanoparticles in the initial volume of 0.5 ml.



The figure 9 shows the behavior of nanoparticles in aqueous solution in the first 3 hours of analysis. Frequency curve is observed adsorption of liquid containing nanoparticles. Repeatability of curve is approximately 1 hour. In this period of time, the shift frequency is about 80 Hz and shift resistance is 20 Ω .





In the figure 10 we represent the image AFM and image SEM with final sensor. Pd molecules have been deposited in the form of clusters with diameters up to 250 nm.



Fig. 10. AFM and SEM images of sensor with Pd nanoparticles after total liquid evaporation.

Solution with Ti nanocolloids (0.5 ml) was left to analyze up to full evaporation of water (figure 11). Ti nanoparticles from solution were deposited on the sensor electrode knew clusters. The time of total analysis was around 3 hours. The time between two analyses were made in the range of 0.1 seconds. In the first 3600 seconds of analysis held an adsorption process and rejection of nanoparticles. Then, the process followed with deposition of nanoparticles on the electrode. The sharp dramatically drop in frequency (increasing the mass of electrode). At the end of the process the entire quantity of nanoparticles in the fluid volume were deposited on the sensor electrode. Result of the variation in frequency indicates the amount of deposited metal that is consistent with the amount of nanoparticles in the initial volume of 0.5 ml. The figure 12 shows the behavior of nanoparticles in aqueous solution in the first 3600 seconds of analysis. Frequency curve is observed adsorption of liquid containing nanoparticles. The shift frequency is about 40 Hz and shift resistance is 15 Ω .



Fig. 11. The QCM fill diagram "Frequency shift versus time" and "Resistance versus time" for Ti nanocolloids in DI water.





Fig. 12. The QCM shortened diagram "Frequency shift versus time" and "Resistance versus time" for Ti nanocolloids in DI water.

In the figure 13 we represent the image AFM and image SEM with final sensor. Ti molecules have been deposited in the form of clusters with diameters up to 5000 nm. The clusters formed are not crowded.



Fig. 13. AFM and SEM images of sensor with Ti nanoparticles after total liquid evaporation.

Nanoparticles of iron in pure water behave differently from the other QCM analysis studied nanoparticles (Ag, Au, Pd and Ti). In the figure 14 shows the QCM fill diagram "Frequency shift versus time" and "Resistance versus time" for Fe nanocolloids in DI water. After 3 hours frequency falls dramatically (about 1000 Hz).

In the first 2 ours Fe nanoparticles are adsorbed on surface sensor. The figure 15 shows the behavior of nanoparticles in aqueous solution in the first 9000 seconds of analysis. Frequency curve is observed adsorption of liquid containing nanoparticles. The shift frequency is about 100 Hz and shift resistance is 50 Ω .



Fig. 14.The QCM fill diagram "Frequency shift versus time" and "Resistance versus time" for Fe nanocolloids in DI water.



Fig. 15. The QCM shortened diagram "Frequency shift versus time" and "Resistance versus time" for Fe nanocolloids in DI water.

In the figure 16 we represent the image AFM and image SEM with final sensor. Fe molecules have been deposited in the form of clusters with diameters up to 10000 nm. The clusters formed are not crowded.



Fig. 16. AFM and SEM images of sensor with Fe nanoparticles after total liquid evaporation.

In the figure 17 and 18 we cumulate the graphics from QCM for Ag, Au, Pd and Ti nanoparticles: figure 17 represent the QCM fill diagram "Frequency shift versus time" for Ag, Au, Pd (left)and Ti (right) nanocolloids in DI water and figure 18 represent the QCM shortened diagram "Frequency shift versus time for" for Ag, Au, Pd (left) and Ti (right) nanocolloids in DI water. Except Ti and Fe nanoparticles rest nanoparticles behave identically to analyze QCM. The graphs show the same periodicity in time, with different amplitude of frequency and of resistivity. QCM can used method deposition be as of of a nanoparticles/nanoclusters on the surface of sensors.



Fig. 17. The QCM fill diagram "Frequency shift versus time" for Ag, Au, Pd (left) and Ti (right) nanocolloids in DI water.



Fig.18. The QCM shortened diagram "Frequency shift versus time for" for Ag, Au, Pd (left) and Ti (right) nanocolloids in DI water.

Also for a second determination of NP cluster shapes and chemical composition the sensors were studied with Scanning Electron Microscope coupled with Energy Dispersive X-Ray Spectrometer. The results of this study are shown below as SEM images and also as an elemental composition table where can be observed the concentration values for each NP sample. Beside the expected elements (Si, O - from quartz; Ti, Pt - from sensor metallization and the nanocolloidal element) were discovered a number of other elements (impurities) like: N, Na and S, that represent the subject for the future studies.

Elements	Ti	Fe	Pd	Ag	Au
C [%]	13.07±0.09	11.65±0.24	6.80±0.79	nd	10.09±0.16
N [%]	nd	nd	nd	nd	3.06±0.22
O [%]	16.91±0.15	22.28±0.34	8.19±0.16	4.62±0.12	8.57±0.19
Na [%]	3.85±0.02	nd	0.45±0.02	nd	2.20±0.04
Si [%]	8.71±0.03	8.47±0.07	14.39±0.05	5.63±0.05	11.45±0.06
S [%]	0.20±0.03	nd	0.29±0.05	nd	nd
Ti [%]	4.53±0.03	2.41±0.05	3.55±0.03	2.91±0.05	3.25±0.06
Ag [%]	nd	nd	nd	8.19±0.21	nd
Pd [%]	nd	nd	2.29±0.07	nd	nd
Fe [%]	nd	4.83±0.15	nd	nd	nd
Pt [%]	52.72±0.38	50.37±1.19	64.05±0.44	78.65±0.34	52.88±1.00
Au [%]	nd	nd	nd	nd	8.50±0.51

Table of elemental composition by Energy Dispersive X-Ray Spectrometer (EDS)

In conclusion each fluid shows an energetic imprint that depends on: the content and quantity of materials, media size and shape of particles, their affinity for the electrode material of sensor. In our study we have been succesfully combined four techniques in order to characterize the dimension and shape of nanoparticles (QCM, AFM, SEM and EDS). Also, the results give us new informations regarding the adsorption on sensor surface, furthermore we discovered new elements involved in the process.

6. Conclusions

The widespread use of the quartz crystal microbalance (QCM) can be attributed to its excellent sensitivity to the properties of liquid and soft solid materials with which it is brought into contact. This sensitivity arises from the coupling between the mechanical, shear oscillation of the crystal and its electrical response at frequencies close to resonance. This coupling depends on the details of the shear wave propagation into the material with which the QCM is in contact. For most liquid and soft viscoelastic materials, the decay length of this shear wave is on the order of 100 nm; so in these cases, the QCM is truly a surface-sensitive technique. This surface sensitivity is responsible for a wide range of applications in biology and electrochemistry, where the QCM is often used to sense material that is absorbed to the crystal surface from solution. The material property that determines the response of the QCM is the complex acoustic impedance of the loading material. In many cases, the acoustic impedance varies with the distance from the crystal surface, and models accounting for this depth dependence must be utilized in order to interpret the data.

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