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BETTER THAN NANOPARTICLES: ON THE USE OF SILVER NANOCLUSTERS FOR IONIZING RADIATION DOSIMETRY

NUNES, L. H. S.[1,†] and GUIDELLI, E. J.[1]

[1]Departmento de Física Médica, FFCLRP, Universidade de São Paulo, 14040-901 Ribeirao Preto, SP, Brazil
[†]luiz.santos.nunes@usp.br

Introduction: Radiolytic synthesis of nanomaterials, i.e., a synthesis that employs ionizing radiation as a catalyzer to grow nanoparticles, can be used for radiation dosimetry if we are able to quantify the amount of nanoparticles produced. Silver nanoparticles (AgNP) can be detected and quantified by their absorption band in the UV-vis region that results from the surface plasmon resonance (SPR) phenomena. However, the detection is usuallu limited to doses above some unites of gray, which is too high for medical dosimetry. In this work, we show for the first time that, by combining radiolyyic and microfluidic routes, silver nanoclusters (AgNC), i.e, cluster containing few atoms formed during an intermediate stage preceding the nanoparticle growth, can be use to detect doses of radiation below 0.75 Gy. Furthermore, the sensitivity in the low dose region obtained when using AgNCs is higher than the sensitivity obtained with AgNPs produced at higher doses.

Material and method: The synthesis is based on the citrate reduction of silver nitrate. Silver nitrate ($AgNO_3$) 2 mM and sodium citrate (Na_3Ct) 5% w/w were used to produce a precursor solution. The components were mixed, quickly heated to 100 °C for 1.5 min, and then quickly cooled to 5 °C with the aid of a microfluidic reactor built in our laboratory

After that, the samples were irradiated with an X-ray tube Magnum (48 kVp / 0.2 mA). They were irradiated with doses from 0 to 2.5 Gy, with dose rate equal to 2.054 Gy/min. After this step, the nanoclusters and/or nanoparticles are formed

The nanoparticles were characterized by UV-visible absorption spectroscopy (ABS) using an Ultrospec 2100 pro Spectrometer, and by fluorescence spectroscopy (FLS). on a Hitachi F700, with excitation on 240 nm.

Results: Figure 1 show that the absorbance of the samples increases with the absorbed dose. This is due the increased production of nanoparticles upon increasing the radiation dose. As a consequence, it is possible to find a region in which the response of the dosimeter is linear with dose, as shown on Figure 1. The results show that there are two regions of linearity, divided according the dose. The first one, from 0 to 750 mGy, has a great sensitivity ($9.2\cdot10^{-3}$ a.u./Gy) and linearity (R^2 = 98.22 %). Compared to the higher dose region ($6\cdot10^{-3}$ a.u./Gy and R^2 = 84.59 %).

According to the literature, AgNC, but not AgNP, present fluorescence emission when excited with UV light. Therefore, in order to verify the presence of silver nanoclusters in the samples irradiated with doses below 0.75 Gy, fluorescence spectra were recorded.

As show on Figure 2, the fluorescence intensity of an emission band around 390 nm increases with dose until 0.75 Gy and decreases after that. This suggests that, at low doses, AgNCs are formed and contributes for the increased absorbance. Above 0.75 Gy, the concentration of nanoclusters and Ag^0 is probably high enough to cause them to grow to nanoparticles, as evidenced by presence og the characteristic AgNP plasmon band together with the drcreased fluorescence of the AgNCs.

Conclusions: Due to the quick heating and cooling process, the radiomicrofluidic method developed here allows the use of AgNCs to detect lower doses of ionizing radiation

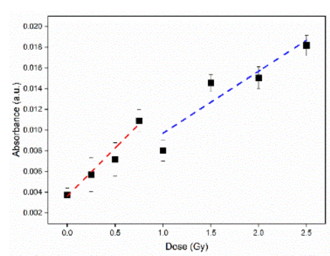

Figure 1: Absorbance of silver nanoclusters *versus* dose

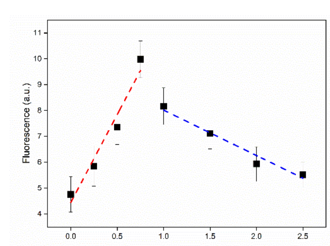

Figure 2: Fluorescence intensity of silver nanoclusters *versus* dose, showing their formation by radiation