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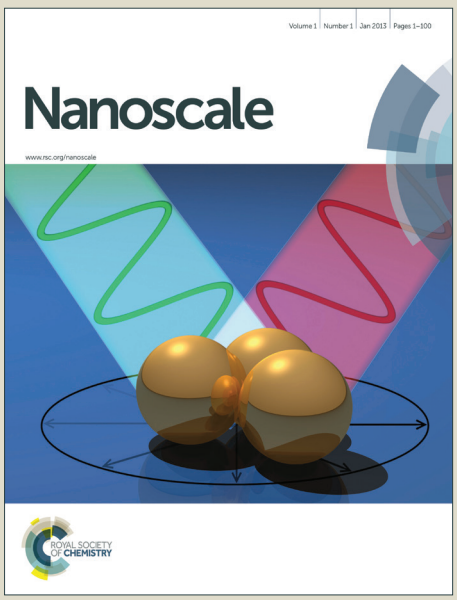

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A comment on the article on EPR in silver/alanine nanocomposites for radiation detection by Guidelli et al. in Nanoscale 4, 2012

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This comment refers to an interesting article published in Nanoscale by Guidelli et al.[1] on use of silver/alanine nanocomposites as radiation detectors in EPR dosimetry. Similar approaches to sensitize alanine dosimeters was reported also by Ciesielski et al.[2] or Marrale et al.[3,4], who used such additives as boron or gadolinium to increase sensitivity of the detectors to thermal neutrons (due to the high cross section of those elements for neutron capture) and to high energy photons (due to the high photon interaction coefficients of gadolinium). The addition of silver nanoparticles, as described by Guidelli et al., also leads to an increase in sensitivity of alanine dosimeters to ionizing photon beams, in particular at lower photon energies, where photoelectric effect is strongly present in the radiation interactions with matter. However, despite of important and comprehensive data provided by the authors, which characterize physical parameters of their silver/alanine dosimeters, such as spectrophotometric spectra, results of XRD and DLS, analysis of TEM images, their results and conclusions regarding EPR measurements require some corrections and comments. The key parameter investigated by the authors, is dose enhancement factor (DEF), which reflects the gain in sensitivity to radiation of the silver-enriched detectors over the regular, pure-alanine detectors. The authors compare theoretically predicted DEFs with those measured experimentally by comparison of EPR signals induced in the silver-enriched and regular dosimeters. They found, that the measured DEFs were higher than those predicted theoretically and attributed this discrepancy to the fact, that the their theoretical calculations were done for the effective energy (90 keV) of the X-rays generated at 180 kV voltage, instead of integrating the radiation response over whole energy spectrum. The presence of lower energy photons, for which the photoelectric absorption in silver is higher, in authors opinion was responsible for experimental DEFs of higher values, than the theoretically predicted ones. Below, I present my comments starting from pointing out a simple mistake done by the authors in their calculations. Namely, despite the fact, that they describe the theoretical DEF as ratio of mass absorption coefficients of the silver-enriched alanine to pure alanine (eq. 1 in their article), in their calculations they used mass attenuation coefficients. Figure 1 is showing comparison of the mass absorption and mass attenuation coefficients calculated on the basis of the NIST data used also by the authors, for the same range of percentage of silver in alanine. As can be easily noticed, the DEF plot in the inset in Fig. 5b in the article by Guidelli et al. is in fact identical with the plot marked by open-circles in Fig. 1 presented here, which is for ratio of mass attenuation coefficients. The ratios of mass absorption coefficients, shown by the open diamonds in Fig. 1, are much higher and, what is important for the final interpretation of the experimental results, are also higher than the DEF values experimentally obtained by Guidelli et al. (filled circles in Fig. 1)

Another comment refers to the authors' definitions of theoretical and experimental DEFs. In my opinion, the experimental DEF defined by the authors, is biased by an artefact caused by the normalization of the EPR signals to the dosimeters' total masses. The dosimetric signal comes only from alanine, so, it is proportional not to the total mass (alanine and silver) of a measured sample, but to the mass of alanine alone. To compare the experimental DEFs, as defined by the authors, with theoretical predictions (i.e. the ratio of mass attenuation coefficients), the latter ones should be corrected downward by a factor reflecting the percentage of alanine in the total mass of the detectors. This effect was accounted for in Ref. 2 by correcting upward the experimental enhancement factors, or in works of Marralle at al. [4] by making dosimeters with the same amount of alanine regardless of the gadolinium content. Theoretically predicted DEFs, properly corrected to the content of alanine in the dosimeters, are presented by the solid line (filled diamonds) in Fig.1. Finally, the experimental DEFs measured by Guidelli et al., turn out to be significantly lower than the mass-corrected ratios of mass absorption coefficients – for 10 % silver content in a nanocomposite the measured DEF is only about 55 % of the theoretical one (compare the data in Fig.1 here and in Fig.5b in Guidelli et al). This observation is opposite to the statements of Guidelli et al., who reported higher values of the experimental DEFs and attributed this to underestimation of effects from low energy photons in the X-ray spectrum which, apparently, were not properly reflected in their calculations based on the effective energy of the beam.

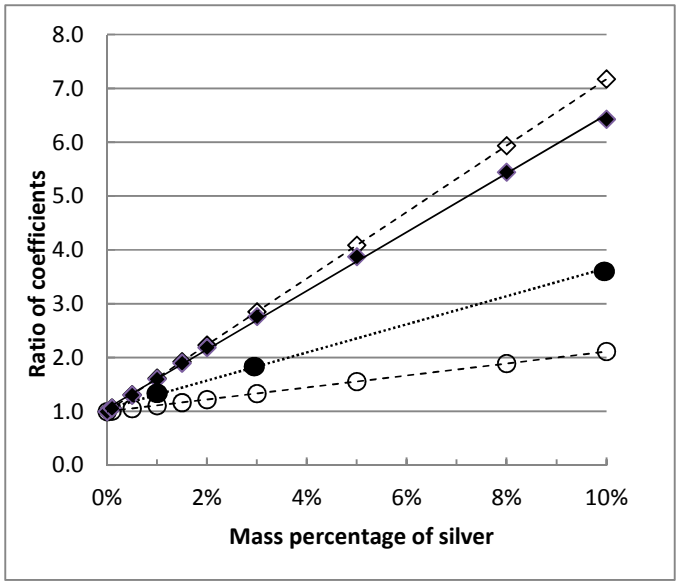

Fig. 1. The ratio of mass absorption (open diamonds) and mass attenuation (open circles) coefficients of the silver nanocomposites and pure alanine for various silver content. The filled diamonds show the theoretically predicted DEFs corrected to actual mass percentages of alanine in the nanocomposites. The filled circles and the dotted line present approximately experimental DEFs from article of Guidelli et al.

In the light of presented here remarks, the role of self-absorption of secondary electrons in silver nanoparticles, mentioned by Guidelli et al., seems to be crucial and, at least partially, can explain the lower experimental DEFs than the calculated ones. To verify this hypothesis a simple estimation can be done on the basis of the data provided by the authors: the size of silver nanoparticles was about 30 nm, 280 nm and over 1 μm for dosimeters with silver content from 0.01% to 0.1%, 0.5 % and from 1% to 10 %, respectively. On the basis of these numbers, one can estimate average distance between spherical nanoparticles distributed uniformly in alanine matrix. The nanoparticles' size and the distance between them can be compared to average range of secondary electrons produced in silver, calculated for their average energy in silver and in alanine. The average energy of secondary electrons for 90 keV photons can be estimated from the photon interaction data to be 64.8 keV. Results of such analysis are presented in Tab 1. As can be concluded from the data in Tab.1, the effect of self-

absorption of secondary electrons can be responsible for deposition of significant fraction of the electrons' energy in silver instead of alanine. The fraction of energy deposited by electrons generated in a nanoparticle inside the same nanoparticle can be approximated by the average fraction of their whole trajectories' within that nanoparticle. For the largest nanoparticles (at the largest Ag content), the fraction of self-absorbed energy shouldn't be greater than ratio of the nanoparticles' diameter to CSDA range of secondary electrons, i.e. 2 μm/12 μm = 17% (in fact, an average path length through a sphere is smaller than its diameter); for the smallest nanoparticles it is negligible (0.03 μm /12 μm = 0.25%). The effect of self-absorption by a neighboring nanoparticles, as illustrated in Fig. 5d of the article by Guidelli et al., is much more significant, because the average distance between the nanoparticles is several times smaller than the range of secondary electrons in alanine (Tab.1).

Table 1. Average distance between nanoparticles for various silver content in the dosimeters. The size for Ag content between 1 % and 10 % was reported to be "larger than 1 μm, therefore in those simulations for 10 % Ag content the distance is calculated for 1 μm and 2 μm sizes, for comparison. The last two rows show CSDA ranges for secondary electrons produced in silver for their average energy 64.8 keV.

Ag content in dosimeters	diameter of a nanoparticle (μm)	average distance between nanoparticles (μm)
0.1 %	0.03	0.5
0.5 %	0.28	2.6
1%	1	7.4
10 %	1	3.3
10 %	2	6.6
CSDA (μm) in Ag	*12*	
CSDA (μm) in Alanine	*50*	

In conclusion, the actual discrepancy between the theoretical DEFs and experimentally obtained DEFs in alanine-silver detectors, indeed can be explained by the effects of self-absorption in silver. Nevertheless, it is also probable, that a certain decrease in amplitude of EPR signals in samples containing conductive, metallic additives, can be caused by a drop in detection sensitivity of the EPR spectrometer due to increased, non-resonant loses in the cavity (a drop in its Q value due to the increased sample's conductivity). It can be expected, that a use of an inside-cavity standard sample (like the popular Mn^{2+} standard), measured simultaneously with the alanine dosimeters, can answer any doubts regarding possible effects of variations in the Q-factor on the measured DEFs.

References

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