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Fractal structures of gold obtained by diffusion limited aggregation in alkali halide crystals

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Nanostructures of gold embedded in potassium chloride matrices were obtained after the doped crystals growth, by electrolytical colouring, and by thermal treatment. When the TEM images of the nanostructures were analyzed using fractal geometry it means was proved that the self assembling of the metallic structures is governed by the diffusion limited aggregation (DLA) mechanism. The values of the fractal dimension, which were in all cases between 1.7 and 1.9, calculated using two methods, sandbox and box-counting, proved the DLA mechanism.

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1. Introduction

The possibilities of nanotechnology applications in a large domain, from electronic to the medicine and life sciences, lead to an increasing interest in the field [1-5]. An important aspect of new products development and applications in nanotechnology is the understanding of self-aggregation phenomena. It is aimed practically to the shifting from the top-down mode, used nowadays in industrial production, to the bottom-up mode, a fabrication concept based on self-aggregation that mimics the biological phenomena using microscopical devices.

Our recent studies showed strong similarities between the aggregation of the colloidal particles in host crystalline matrices [6] and the aggregation phenomena of biological or metallic colloids in liquid media [7,8]. More than this formal similarity, by using of the fractal geometry in the analysis of resulting aggregates we evidentiated the fact that those two types of phenomena are alike in essential ways and that the formation processes are governed by the same laws.

The processes of obtaining of noninteger (or fractal) scale structures have attracted considerable attention and have been the subject of extensive experimental, numerical and theoretical studies [7-10] with the realization that scaling concepts may be applied to describe many features of the phenomena. These concepts have been successfully applied to the experimental investigation of several aqueous colloid systems [11-12]. The diffusion limited aggregation (DLA) model, in which infinitely diluted concentration of particles mimics Brownian motion by moving about randomly until attaching upon first contact with a central cluster is a particularly attractive realization of such growth processes.

Studies on silver nanoclusters obtained in alkali halide crystals by thermal treatments showed that the nanoclusters are obtained in spatially arranged structures [13]. It was found the same arrangement, without any isolated particles, for samples of KCl:Ag with Ag clusters obtained by thermal conversion of Ag^- -ions at 700, 645, 525 and 400 ^oC [14,15]. One of the main questions regarding the heavy metal nanoclusters obtained in alkali halide crystals is referring to the aggregation phenomena of those particles in structures, to how they are formed, as well as to some particular features of those structures. The aim of this paper is to present our studies on Au nanoclusters embbeded in KCl matrices formed during growth, electrolytical colouring or thermal treatments. The nanoclusters are of DLA type obtained in potassium chloride crystal, fact proved by the calculated values of the fractal dimensions.

2. Experimental

Doping of alkali halides with gold is a very difficult process. Single crystals of KCl doped with Au powder grown by Kyropoulos method in dry argon atmosphere do not incorporate any trace of Au^+-ions. It is possible to obtain KCl with Au^+-ions only by the Bridgman method in sealed quartz ampoules in argon and CCl_4 pressure starting from a mixture of dry KCl purified salt and very thin Au sheet powder. Before the KCl salt melts, CCl_4 is decomposed in carbon and Cl_2 which reacts with Au powder and forms AuCl vapors. The crystal obtained contains not only Au^+-ions, but also Au^--ions and Au clusters. Some of the crystals were transparent but colored due to the presence of Au clusters. Electrolytical coloring has been performed in air at 550 °C and 300V/cm. The reversal of the electric field polarity leads to removal of the F-centers from the samples.

For TEM imaging, small pieces ($2 \times 2 \times 1$ mm^3) of freshly cleaved crystals were placed on a carbon film covered microscope grid and carefully dissolved in distilled water. The amount of water was sufficient so after drying the grid on which the gold nanoclusters were placed, no traces of KCl salt remained on. Measurements of transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed with a PHILIPS CM 30 transmission electron microscope equipped with a goniometer stage, thus being possible the observation of the spatial arrangement. In all our experiments we used an accelerating voltage of 200 kV.

3. Results and discussion

The almost universally used parameter for characterizing the structure of aggregates as being fractals is their fractal dimension d_f which is a noninteger.

The "practical" problem is to determine the fractal dimension d_f of either a computer generated fractal or a digitized fractal picture. The two most useful methods are: boxcounting method and sandbox method. We built a computer program to calculate the fractal dimensions of our gold nanoclusters using both methods, with the following algorithms.

For the boxcounting method, we draw a grid on the image of our nanostructures that consist of S_i^2 squares, and determine the number of squares $N(S_i)$ needed to cover the entire fractal. Choosing finer and finer grids with $S_1^2<S_2^2<....<S_m^2$, we calculate the corresponding numbers of squares $N(S_1)...N(S_m)$ that are needed to cover the fractal. Knowing that $N(S_i)$ scales as

$$N(S_i) \approx S_i^{-d_f} \tag{1}$$

we obtain the fractal dimension by plotting $N(S_i)$ versus $1/S_i$ in a double logarithmic plot. The asymptotic slope, for large S, gives d_f.

For the sandbox method, we first choose one pixel in the fractal as an origin of n circles of radii $R_1<R_2<...<R_n$, where R_n is smaller than the radius of the fractal, and count the number of points (pixels) $P(R_j)$ within each circle. We plot $P(R_j)$ versus R_j in a double logarithmic scale and the slope of the curve, for large values of R_j, determines the fractal dimension.

There is a resemblance between gold aggregates in aqueous solutions obtained by Weitz and Oliveira [7] and our Au nanoclusters with a spatial arrangement in a solid matrix. Therefore, we used their structures to "calibrate" our program. For Weitz and Oliveira's gold aggregates (reported $d_f \approx 1.75$) using our program we found by boxcounting method a value of d_f=1.749 and by sandbox method a value of d_f=1.75.

In the TEM images, the nanoclusters are digitally selected in order to reduce the errors in our calculated values of the fractal dimensions. We used TEM images with magnifications of x10.500, x21.000 and x120.000.

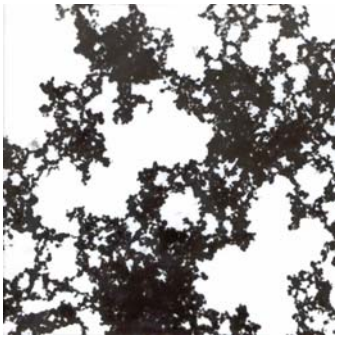


Fig. 1. TEM image of Au nanoclusters obtained in a KCl:Au crystal directly after crystal growth (×10.5k magnification).

Typical TEM image of gold nanoclusters obtained in an alkali halide matrix is shown in Fig. 1. The Au nanoclusters were obtained directly by the KCl:Au crystal growth.

Using our computer program we calculated the fractal dimensions for the gold nanostrctures in KCl crystal formed directly after crystal growth and the plots are presented in Fig. 2. Thus, we obtained a value of d_f=1.85 for both the sandbox method and the boxcounting method. This value proves that the aggregation is initiated and carried through by the crystal growth and the gold nanostructures were formed by diffusion limited aggregation (DLA).

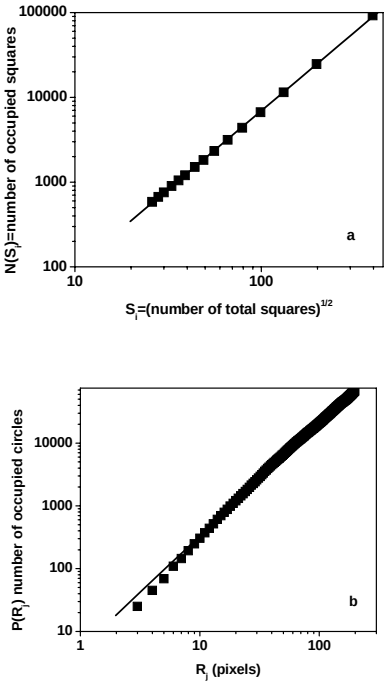


Fig. 2. Results obtained on the TEM image in Fig. 1: (a) log-log plot of $N(S_i)$ number of occupied squares on the grid, vs. S_i=(number of total squares)$^{1/2}$; (b) log-log plot of $P(R_j)$, number of occupied pixels in the circles, vs. R_j, the radius of the circles.

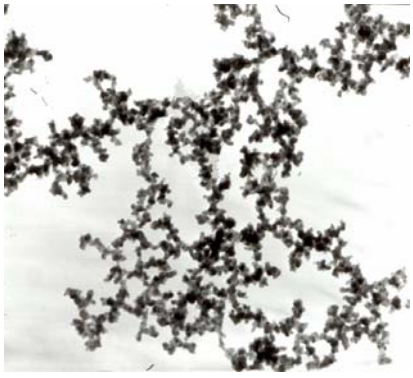
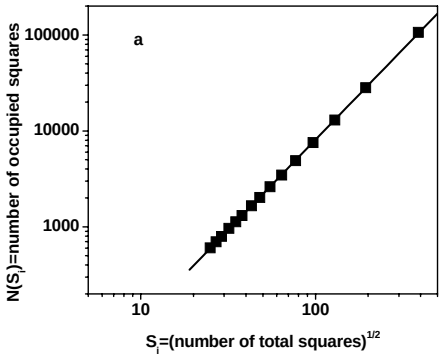


Fig. 3. TEM image of Au nanoclusters obtained in a KCl:Au crystal by electrolytical coloring at 550 °C. The initial magnification of the TEM image is of × 120 k.

In Fig. 3 is shown a TEM image of the gold nanoclusters obtained by electrolytical colouring in a KCl:Au crystal, before the digital selection of the fractal. Some of the gold fractals obtained by electrolytical coloring have the aspect of snow flakes, clearly suggesting the fractal character of the nanostructures.

Log-log representations for fractal dimensions' calculations on Au nanoclusters obtained in KCl after an electrolytical colouring, shown in Fig. 4, lead to the values d_f=1.88 for the boxcounting method and of d_f=1.89 for the sandbox method for the fractal dimensions.



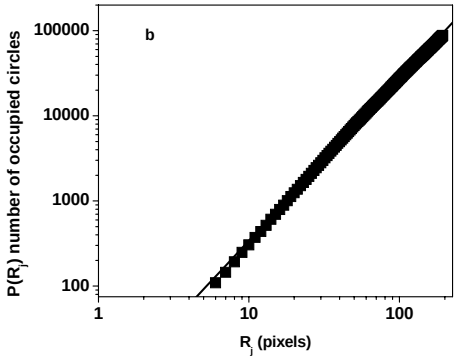


Fig. 4. The log-log plots for the TEM image presented in Fig. 3: (a) boxcounting method - $N(S_i)$ number of occupied squares on the grid, vs. S_i=(number of total squares)$^{1/2}$; (b) sandbox method - $P(R_j)$, number of occupied pixels in the circles, vs. R_j, the radius of the circles.

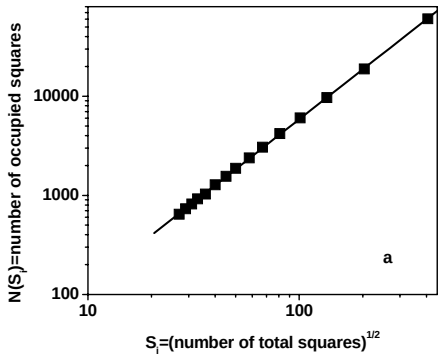
When a KCl:Au sample coloured electrolytically is subdued to a thermal treatment, the appearance of the gold nanoparticles is not changing, as it can be observed in Fig. 5. There is a change in the nanoparticles dimensions but the total aspect of the nanostructures remains the same.

We want to emphasize that the TEM technique has not altered the arrangement of the Au nanoclusters.

TEM measurements using the goniometer stage of the electron microscope proved that the gold nanoparticles were arranged in tridimensional structures.

The packing for the samples studied after thermal treatments are similar with the ones for crystal growth and electrolitical colouring, fact proved by the calculated values of the fractal dimensions. Log-log representations of fractal dimensions' values on Au nanoclusters obtained in KCl are presented in Fig. 6. For the sample studied after the thermal treatment, presented in Fig. 5, we found the fractal dimension of the gold nanoclusters d_f=1.71 using the boxcounting method and d_f=1.75 using the sandbox method.

Fig. 5. TEM image of Au nanoclusters obtained in a KCl:Au crystal after a thermal treatment at 650 °C (initial magnification ×21k).



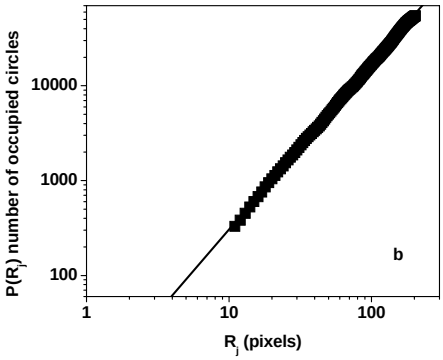


Fig. 6. (a) Log-log plot for boxcounting method of $N(S_i)$, number of occupied squares on the grid, vs. S_i=(number of total squares)$^{1/2}$; (b) log-log plot for sandbox method of $P(R_j)$, number of occupied pixels in the circles, vs. R_j, the radius of the circles.

The calculated values of the fractal dimensions for the gold nanoclusters obtained in doped KCl crystals are typical for DLA processes. The aggregation is initiated and carried through by growth, coloring or thermal treatment and the clusters were produced by DLA. The values of the fractal dimensions are close, as expected for nanoclusters of the same metal embedded in the same crystalline matrix. The errors related to the computer program were, for all the calculated values, of ± 0.01. The differences obtained in the calculated values of the fractal dimensions, though small, are due to the different obtaining methods, the fact that we used different TEM image magnifications and the fact that we evaluated tridimensional structures using their bidimensional images. Using bidimensional projections of the structures is nevertheless a reliable method of investigation of the fractal character of our nanoclusters. Comparative studies made on aqueous solutions showed that electron microscopy gives the same results as the light scattering technique of investigation [8].

4. Conclusions

We have succeeded in obtaining nanocrystals of Au structured like fractals in KCl crystals directly from growth, by electrolytical coloring, and by thermal treatment. These nanocrystalswere shown to be of fractal-like type when fractal dimensions were evaluated. Depending upon the method in which the fractal structures were obtained, the fractal dimensions of the Au nanoclusters were found to be between 1.71 and 1.89.

The values found for the fractal dimensions clearly show that the Au nanoclusters are structured in a DLA manner. Despite the fact that we used bidimensional pictures to characterize three-dimensional structures, typical d_f values for diffusion limited cluster aggregation (DLCA) were found. The diffusion aggregation mechanism can explain the short times in which the formation of metal nanoclusters in alkali halide crystals takes place. The calculated fractal dimension differs with the method in which the nanoclusters are produced.

Acknowledgements

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