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## Tuning the size of silver deposits by templated electrodeposition using agarose gels

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**Abstract** Tuning the size of electrochemically deposited silver crystals is possible by using template layers of agarose gels of certain concentrations on platinum electrodes. The size of the silver crystals can be controlled in the range of 100 to 400 nm by choosing the appropriate agarose concentration. The obtained crystal sizes match very well with the size of the pores that have been reported in literature for the used agarose concentrations. This is also a good proof of the correctness of the earlier pore-size estimations applying other techniques.

**Keywords** Atomic force microscopy · Electrochemistry · Silver deposition · Templates

### Introduction

Much effort has been focussed in recent years on using templated electrodeposition for achieving control of the shape and size of structures in the nanometer range [1]. The size and shape of the empty space in the templates determine the size and shape of the deposits. Most templates of well-defined sizes and shapes, however, do not allow at all, or allow only to a small extent to tune the structures of the template. This is because most templates possess a rigid structure that cannot be deliberately altered. Agarose gels are well-known for their concentration-dependent pore structures, a property that is utilized especially in electrophoresis. Although the effect of agarose at various concentrations on the morphology of silver deposits has been intensively studied from a mechanistic point of view by

Arvia et al. [2–5], no attempt is known that uses agarose as a template for the preparation of silver grains in the range of a few hundred nanometers. Here, we report a templated silver deposition on platinum electrodes that have been covered with a thin layer of agarose gel to produce silver crystals of a specified size. It is very important to possess such a tool, because for the study of electrochemical conversions of solid particles, it is necessary to start with well-defined and pre-specified particles. We intended to achieve this goal especially to continue our studies of in situ atomic force microscopy (AFM) electrochemistry of solid state electrochemical reactions [6–10].

### Experimental

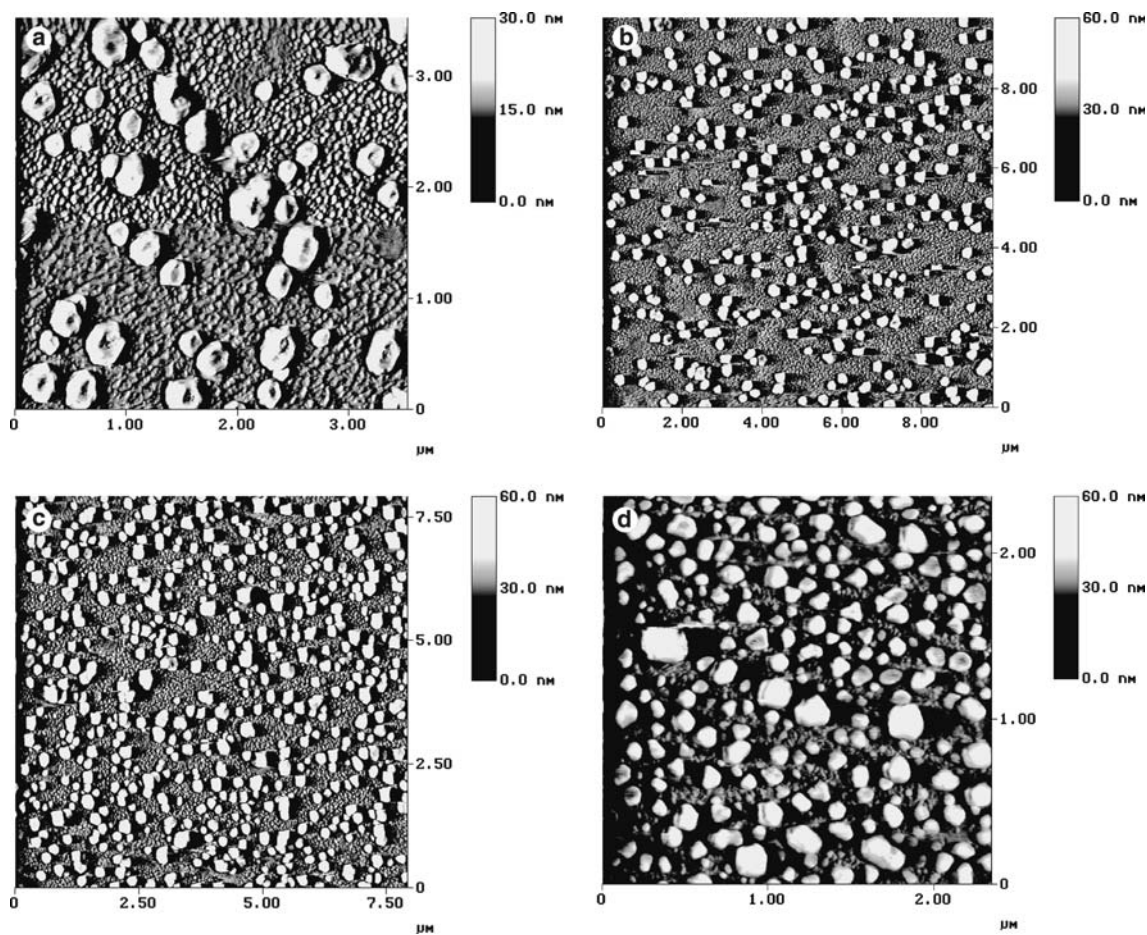
#### Equipment and chemicals

The AFM images were recorded with the AFM/STM of Digital Instruments (Hardware: NanoScope Version 1.0, Software: NanoScope E Version 4.23r3). Silver deposition was performed using the Autolab PGSTAT 20, EcoChemie, Netherland and a VA-Stand 663, Methrom, Switzerland. The platinum electrodes were purchased from Schröder GmbH, Lienen, Germany. Silver nitrate and agarose (all p.a.) were from Merck, Darmstadt, Germany.

#### Preparation of agarose gel-covered platinum electrodes

Weighted amounts of agarose powder were added to bidistilled water at room temperature and the suspension was stirred for some time with the help of a magnetic bar. Then, the suspension was slowly heated upto 95°C. During the heating, the suspension was stirred very slowly and carefully to avoid the formation of gas bubbles. The solution was kept at 95°C until it had a clear appearance. Twenty-five microlitres of the agarose solution was transferred onto a platinum

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**Fig. 1** Atomic force micrographs of silver deposits on platinum electrodes for template gels with 0.25% (a), 0.5% (b), 0.75% (c), and 1% (d) agarose (note the different scales)

electrode (the special AFM electrodes from Schröer GmbH) with the help of a syringe. The solution spread and, after having attained room temperature, the gel covered a circular area of  $0.8 \text{ cm}^2$ . The thickness of the layer was  $30 \text{ }\mu\text{m}$ .

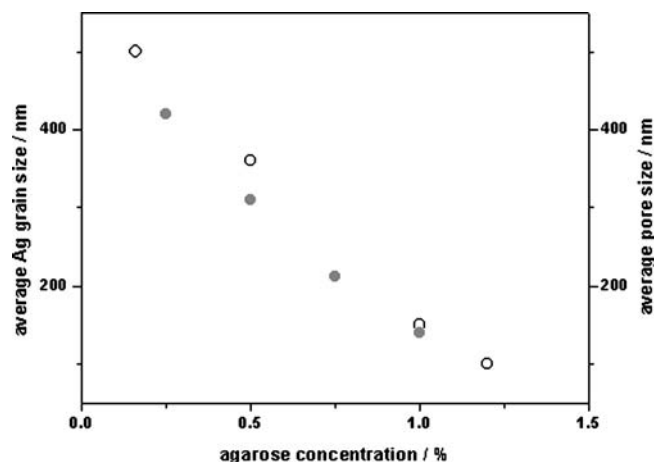
#### Electrochemical silver plating and preparation of electrodes for AFM imaging

For the silver deposition, a solution containing  $10^{-4} \text{ mol L}^{-1} \text{ AgNO}_3$  and  $0.1 \text{ mol L}^{-1} \text{ KNO}_3$  was used. The gel-covered electrodes were contacted with a crocodile clip on one edge and transferred to the electrochemical cell. The electrode was kept in the electrolyte for 1 min before a reduction potential of  $-150 \text{ mV vs. Ag/AgCl}$  ( $3 \text{ M KCl}$ ) was applied for 1 s. Then the electrode was put into bidistilled boiling water for 5 min. This was followed by immersing the electrode in fresh bidistilled water and keeping it there for another 5 min. This procedure was repeated at least three times to clean the surface of all agarose gel. Finally the electrode was dried at  $80^\circ\text{C}$  for 10 min in a drying oven. After cooling down the electrodes to room temperature, they were

transferred to the AFM to image the generated silver grains.

## Results and discussion

Figure 1 shows AFM images of the silver deposits on platinum electrodes that have been covered by layers of gels with different agarose concentrations. The images show very clearly how the agarose concentration affects the size of silver deposits. Figure 2 depicts the dependence of average crystal size as a function of the agarose concentration. The figure also contains pore-size data from literature reported for such gels. The agreement with most of the literature data is very satisfactory. Obviously, the silver deposits thus obtained can be regarded as imprints of the pores of agarose and hence, these results substantially support the correctness of previous pore size determinations. Such studies have been performed by small-angle neutron scattering [11], by AFM of the gels [12, 13], and by measuring the mobility of different probe molecules [14, 15]. In the two reports of direct AFM of the surface of agarose

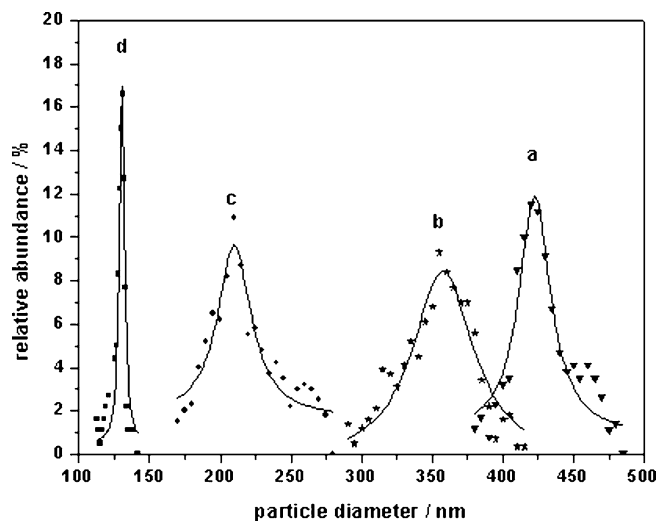


**Fig. 2** Plot of average grain sizes as determined from AFM images versus agarose concentration. The open circles are pore sizes of the agarose reported in literature [12, 13]

gels, considerably larger pore sizes have been reported than those obtained by other methods. The direct AFM can image only the surface structure of the gel as hills and valleys. One may have certain doubts as to what extent these hills and valleys really correspond to the pore structure. Another aspect to be considered is that even if the valleys in these direct AFM images depict the pores, are these also the pores that are accessible for molecules by diffusion? In our silver imprinting technique, the silver deposits can occur only at those places of pores that are accessible for the silver ions by diffusion. The relatively small silver ions ( $r = 113$  pm) can diffuse through any pores of the agarose gel and their diffusion will be only hindered by the walls of the agarose meshes, i.e., by the molecules constituting the gel. Whereas direct AFM can image any open pore on the surface, the silver imprints image only the pores accessible for diffusion.

Figure 3 depicts pore-size distributions derived from an evaluation of the grain sizes of the silver imprints obtained for three different agarose concentrations. The distribution is very narrow for the highest agarose concentration and thus for the smallest silver grains. For smaller agarose concentrations, and thus larger silver grains, the distributions are considerably broader, which is in agreement with previously reported data on the distribution of the pore sizes in agarose gels.

An important question to be asked is, to what extent the deposition time influences the grain size of the silver crystals, because this could in principle bias the results: fortunately, the deposition time had only a small effect on the grain size. There were no differences between 0.5, 1, 1.5 and 2 s of deposition time. Only if the potential was applied for more than 5 s, was the surface of the electrode covered completely with large (edge length 100  $\mu\text{m}$  and more) silver crystals, and hence measurements by AFM were not possible anymore.



**Fig. 3** Distribution of grain sizes as determined by AFM images for different agarose concentrations: 0.25% (a), 0.5% (b), 0.75% (c), and 1% (d)

## Conclusions

The present study proves the correctness of previous pore-size determinations of agarose gels, and it provides a new technique to tune the size of silver deposits on electrodes by using agarose gels as templates. The results obtained indicate that the silver deposits are imprints of the open pore structure of the agarose gel.

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