Rotating magnetic field assisted formation of highly ordered two-dimensional magnetic bead arrays

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***Abstract*—The authors present a method for the formation of highly ordered two-dimensional arrays of magnetic beads based on dipolar particle interactions in rotating magnetic fields. Growth mechanisms of the arrays inside the carrier liquid are presented. After evaporation of the carrier liquid, the resulting bead monolayers on silicon substrates are analyzed with respect to size and defect structure.**

Keywords- magnetic bead arrays; formation of bead monolayers; rotating magnetic fields

I. INTRODUCTION

Magnetic beads and nanoparticles are promising candidates for various lab-on-a-chip applications [1-3]. Their magnetic moments allow for the manipulation by external magnetic gradient fields [4, 5]. Detection of magnetic beads or nanoparticles may be achieved by the use of magnetoresistive sensors due to their magnetic stray field [6]. When combined with appropriate functional groups on the surfaces, the individual magnetic bead or particle may act as markers for biological or chemical analytes. For these applications, low particle concentrations have to be applied in order to prevent particle coupling based on dipolar interactions.

If superparamagnetic beads are suspended in a liquid and immersed in a homogeneous external magnetic field, a torque acts on their magnetic moment vector favoring parallel alignment with the external field orientation. Since the external magnetic field is homogeneous, no magnetic force is acting on the particle ensemble. However, in the case of high particle concentrations, the inhomogeneous magnetic stray field of neighboring particles leads to an attractive force, which entails the formation of one-dimensional agglomerates [7]. These one-dimensional assemblies may be used as, e.g. static components in on-chip sandwich immunoassays [8] or as dynamic components in micropumps driven by magnetic gradient fields [9]. Magnetic assemblies may also be influenced by rotating magnetic fields allowing for stable rotations depending on the applied field frequency [10]. Higher rotation frequencies of the external magnetic field lead to higher shear stresses along the bead chains due to the hydrodynamic interaction with the carrier liquid. At higher shear stresses the probability for chain collapse is enhanced [11]. Therefore, two dimensional assemblies of magnetic beads may be formed. This work will focus on the growth of such two-dimensional bead arrays and analyzes the size of resulting monolayers after evaporation of the carrier liquid.

In this contribution we describe the experimental techniques to generate magnetic bead assemblies based on dipolar particle interactions in rotating magnetic fields. Furthermore, the resulting monolayers are analyzed with respect to symmetry, growth modes and sizes of the resulting monolayers in dependence of the particle concentration.

II. EXPERIMENTAL

Superparamagnetic microbeads Dynabeads M-270 SA [12] were used in the experiments. These microbeads have a radius of 1.4 µm with a standard deviation below 2% and are coated with a streptavidin functionalization. The iron content of these beads is 14%. In order to avoid salt crystallization after liquid evaporation, the buffer of the stock solution was exchanged with deionized water by subsequent centrifugation and resuspension. Two different suspensions at 0.2 and 1.0 mg/ml were prepared. The rotating magnetic field was created by a magnetic stirrer RCT classic (IKA, Germany) at a maximum field strength of 330 Oe. At this field strength a linear response of the magnetization in dependence of the external magnetic field is expected according to the magnetic characterization of the beads [13]. Assemblies were performed on a silicon wafer, which was cleaned with acetone and ethanol prior to spotting the solutions. Optical microscopy images were collected with a Keyence VHX-600 during formation of the agglomerates and after liquid evaporation. Rotation frequencies of 400, 800 and 1200 rounds per minute (rpm) are applied.

The microscopy data is evaluated with respect to agglomerate sizes based on the analysis of pixels at a defined color value within a certain area. The expected error of this counting method is about 2.43% when compared to manual counting of magnetic beads. Furthermore, the defect concentrations are obtained by manual counting of one-

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dimensional and two-dimensional defects within the bead arrays.

III. RESULTS AND DISCUSSION

After spotting the microbead solutions, the rotational magnetic field entails the formation of two-dimensional agglomerates due to stray field interaction. In Fig. 1 a typical resulting cluster is shown. The in-plane rotating magnetic field strongly favors the growth of two-dimensional agglomerates over three-dimensional assemblies. From Fig. 1(a) we can identify a hexagonal symmetry for the agglomerates which is also reproduced in the fast Fourier transform (FFT) image of Fig. 1(a) as presented in Fig. 1(b). The Voronoi tessellation of Fig. 1(a) is shown in Fig. 1(c), where Voronoi cells with 4, 5, 6 and 7 neighbors are dyed in yellow, red, white and green, respectively. The Voronoi tessellation also shows the high degree of hexagonal ordering inside the clusters, but additionally reproduces the frustration along the edge of the cluster and the two vacancies in the middle of the cluster shown in Fig. 1(a). The formation of clusters can be described as a two step process. In the first step collapsing chains form agglomeration seeds, comparable to nucleation in nanoparticle synthesis [14]. In the second step, these nuclei grow at the cost of chains and single particles. Chain addition to previously formed clusters corresponds to a slow growth mode which entails the formation of highly ordered arrays with low defect concentration. Besides, also merging of clusters can be observed, which is exemplarily shown in a series of microscopy images in Fig. 2. Neighboring clusters merge due to attractive magnetic forces. The rotating magnetic field entails reordering processes along the cluster-cluster interface in order to obtain a stable magnetic configuration. However, due to the larger areas of broken symmetry along the boundaries, the merging of clusters may lead to a higher concentration in the bead arrays when compared to the growth based on chain addition. During evaporation of the carrier liquid superstructures are transferred to the substrate.

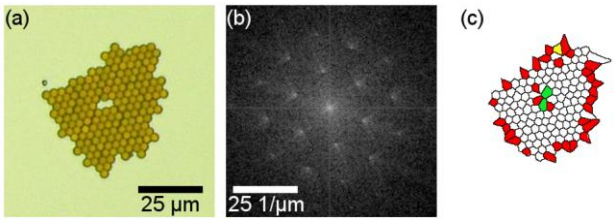

Figure 1. Optical microscopy image of a highly ordered two-dimensional assembly under the influence of a magnetic field rotating at 400 rpm (a). FFT of (a) showing the hexagonal symmetry of the assemblies and the high degree of ordering (b). Voronoi tessellation of (a) where cells with 4-, 5-, 6- and 7-fold symmetry are dyed in yellow, red, white and green, respectively.

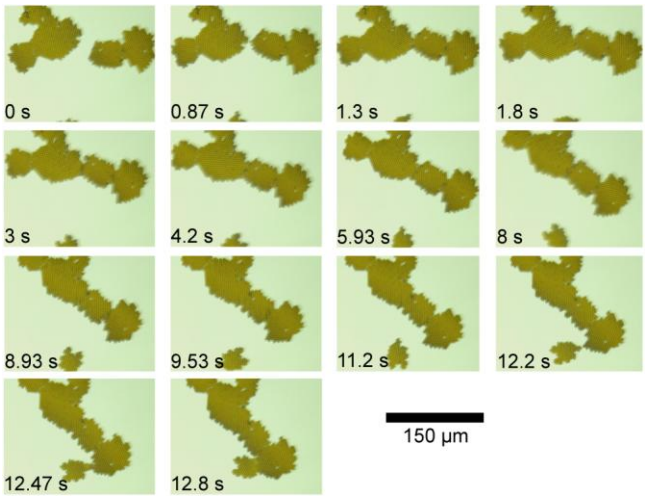

Figure 2. Series of optical microscopy images showing the merging of previously formed clusters under the influence of a rotating magnetic field at a frequency of 400 rpm.

The resulting structures are exemplarily shown in Fig. 3 for the case of three subsequent
spotting procedures of a 1 mg/ml bead solution. If no magnetic field is applied (Fig. 3(a)), a randomly dispersed pattern of superstructures and single particles is obtained, which shows no visible ordering. The FFT of the image also reproduces this finding: no sharp peaks can be observed in the FFT pattern (Inset of Fig. 3(a)). In contrast, the sample which was prepared under the influence of a rotating magnetic field with a frequency of 400 rpm clearly shows hexagonal ordering (Fig. 3(b)) in the microscopy image and the corresponding FFT pattern (Inset of Fig. 3(b)). Fig. 3(b) shows one cluster with low particle coverage in the second layer. An analysis of the second layer growth shows that the second layer coverage of clusters assembled under the influence of a rotating magnetic field is below 5%. The quantitative evaluation of the cluster sizes for different experimental parameters is depicted in Fig. 4(a). The inset of Fig. 4(a) shows the agglomerate sizes without the influence of the magnetic field. For both of the investigated concentrations, an increase in the cluster size by applying a rotating magnetic field when compared to the reference sample (inset) is obtained. The iterative supply of bead solution in order to enhance the effective bead concentration on the substrate may lead to a shift of the cluster sizes to higher particle numbers. This particular aspect of the cluster growth mechanism resembles the behavior of nanoparticles in the growth regime of Ostwald ripening [15]. The assembly of few larger particle arrays is favored over the formation of many small clusters. According to our experiments, the rotation frequency of the magnetic field does not influence the size of the resulting agglomerates. However, the defect concentrations show a dependence on

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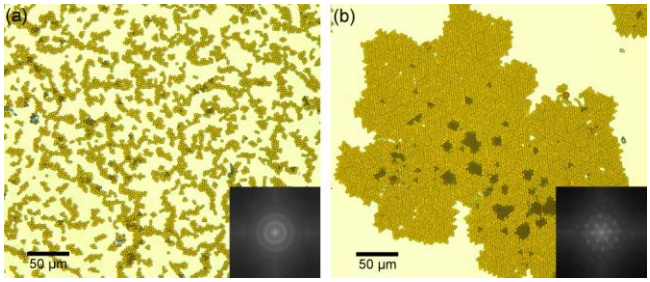

Figure 3. Optical microscopy images of the resulting particle layers after liquid evaporation. If no rotating magnetic field is applied, the beads show a randomly dispersed pattern (a), which is also reproduced in the corresponding FFT of the image (inset). Under the influence of a rotating magnetic field, particles assemble in two-dimensional arrays (b) with a high degree of hexagonal ordering, which is also visible in the FFT pattern (inset).

the field frequency as shown in Fig. 4(c). In Fig. 4(b) an example for a one-dimensional defect structure within the bead arrays is shown. The concentration of one-dimensional and two-dimensional defects increases with increasing rotation frequency of the external magnetic field. This behavior may be attributed to a difference in the time scales of magnetic and geometric reorganization processes. While remagnetization occurs on a nanosecond timescale [16], the geometrical reordering of particles cannot follow the fast magnetodynamics inhibiting the geometric reordering.

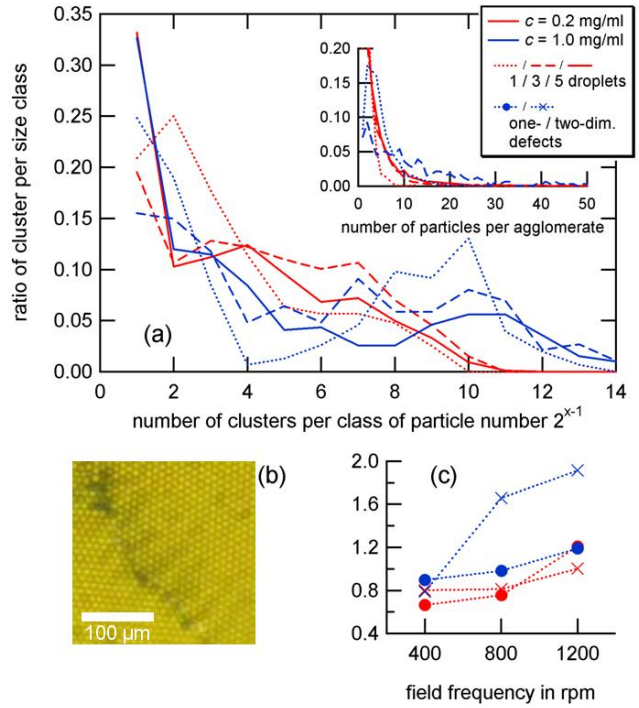

Figure 4. Evaluation of cluster growth for concentrations of 0.2 mg/ml and 1 mg/ml and 1, 3 and 5 iterative replenishments (a). The inset shows the results without applying a magnetic field. A one-dimensional defect structure of a particle clusters prepared under the influence of a rotating magnetic field (b). The defect concentration of one- and two-dimensional defect structures increases with increasing the rotation frequency (c).

Conclusions and Outlook

We have shown that highly ordered two-dimensional arrays consisting of superparamagnetic beads can be prepared by applying a rotating magnetic field. The properties, such as one- and two-dimensional defect concentrations, can be controlled by the field frequency. The magnetic field entails a high degree of hexagonal ordering and leads to the formation of larger clusters when compared to the reference samples that were prepared without a magnetic field.

The ability to assemble these highly ordered objects on demand by switching on a magnetic field may lead to the design of novel microfluidic devices based on the reconfigurability of the particle arrays. Especially the possibility to assemble bead arrays with specific surface functionalization in certain regions of lab-on-a-chip devices may be of major interest in future works.

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