THE INFLUENCE OF PATTERNED MAGNETIC BEADS ON THE SELF-ASSEMBLY OF MAGNETIC NANOPARTICLES

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ABSTRACT

The assembly of nanostructures has critical importance for construction of higher structures to utilize the unique properties of nanoparticles (NPs). The future applications of nanotechnology mostly depend on directing the NPs on desired location or orientation in the proposed structure. Therefore, there is a need to understand the forces governing their self-assembly and approaches to control them. The magnetic nanoparticles (MNPs) also show unique properties and can be manipulated under the influence of a magnetic field. However, there is limited information on how to control their behavior in a well-controlled manner. In this study, the influence of the presence of magnetic layer of particles and their template structure on the controlled assembly of MNPs is investigated. Several unpatterned and patterned, hydrophobic and hydrophilic surfaces are prepared to assemble the magnetic beads (MBs) on these surfaces to investigate their influences on the assembly of MNPs that are composed of iron oxide (Fe_3O_4). Different surfaces with different patterns are successfully used and tested. It is found that the presence of a patterned surface between a magnetic field and the substrate that the MNPs are assembled on has an influence on the finally formed structure. It is also found that the assembly of the MNPs on surfaces is influenced by the solvent that the MNPs are dispersed in. This work may offer a new and simple approach for preparation of patterned and renewable surfaces, constructed from MNPs, which find use in many fields of science and technology.

ÖZET

Nanoparçacıkların kendilerine özgü özelliklerinden faydalanmak için nanoparçacıkların belirli yapılara derlenmesinin kritik önemi vardır. Nanoteknolojinin gelecek uygulamaları çoğunlukla önerilen yapı içerisindeki nanoparçacıkların istenilen lokasyon ve oryantasyona yönlendirmeye bağlıdır. Bu amaçla, nanoparçacıkların derlenmesini yöneten kuvvetleri ve kontrol edilmesi üzerine yaklaşımları anlamaya ihtiyaç vardır. Manyetik alan etkisi altında, manyetik nanoparçacıkların ayrıca kendilerine has özellikleri vardır ve üzerlerinde değişimler yapılabilir. Dahası, nanoparçacıkların davranışlarının nasıl iyi kontrol edileceği üzerine kısıtlı bilgi vardır. Bu çalışmada, manyetik parçacıklardan oluşan bir tabakanın ve alt ağ örüntünün manyetik parçacıkların kendiliğinden düzenlenmeleri üzerine etkisi araştırılmıştır. Çeşitli örüntülü ve örüntüsüz, hidrofilik ve hidrofobik yüzeyler, üzerlerine manyetik boncukların dizilmesinin manyetik nanoparçacıkların oluşturduğu yapılardaki etkisini görmek üzere hazırlanmıştır. Farklı örüntülerdeki farklı yüzeyler başarı ile hazırlanmış ve kullanılmıştır. Manyetik alan ve manyetik boncukların örüntülü diziliminin oluşturduğu yüzeylerin manyetik nanoparçacıklarca oluşturulan yüzeyler üzerinde etkisi olduğu görülmüştür. Ayrıca manyetik nanoparçacıkların oluşturduğu yapılarda nanoparçacıkların çözücülerinin de etkisi olduğu gözlemlenmiştir. Bu çalışma, bilim ve teknolojinin sayısız uygulama alanlarında kullanılabilecek, örüntülü ve yenilenebilir manyetik nanoparçacık yapılarının hazırlanması için basit ve yeni bir yöntem önermektedir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS / ABBREVIATIONS

F_m	Force acting on a magnetic nanoparticle
H	Magnetic field magnitude
$V_{particle}$	Volume of a nanoparticle
χ	Magnetic susceptibility
∇H	Magnetic field gradient
AFM	Atomic force microscopy
AgNP	Silver nanoparticle
AuNP	Gold nanoparticle
CD	Compact disc
CTAB	Cetyl trimethylammonium bromide
DNA	Deoxyribonucleic acid
EM	Electron microscopy
Emu	Electromagnet unit
MB-a	Amine functionalized magnetic beads
MB-c	Carboxyl functionalized magnetic beads
MBs	Magnetic beads
MNPs	Magnetic nanoparticles
MRI	Magnetic resonance imaging
NPs	Nanoparticles
PAH	Poly alkylamine hydrochloride
PDMS	Poly dimethyl siloxane
PET	Positron emission tomography
PSS	Poly sodium 4-styrene sulfonate
QDs	Quantum dots
RNA	Ribonucleic acid
SEM	Scanning electron microscopy
SERS	Surface enhanced raman spectroscopy
SPECT	Single photon emission computed tomography

T	Tesla
TEM	Transmission electron microscopy
TMA-POSS	Octa (tetramethylammonium)-polyhedral oligomeric silsesquioxane
XRD	X-ray diffractometer

1. INTRODUCTION

"Think a person that you know from your primary school class. After 20 years passes, when you saw her/him, you (I mean the memory department of your brain) will recognize her/him in about 1-2 minutes. What about the huge computers in our homes? There is no machine can do that in such a speed and, even say that it is a man or woman. If she/he wears a peruke, you will still recognize her/him when you come closer. If you are a bit further from the face; if the light changes, you will still recognize her/him. The little computer we carry in our head can easily do that. But the computers we build are not able to do that. Clearly, the number of program codes and any other elements in this bone box of mine are enormously greater than the number of elements in our huge, wonderful computers! But our mechanical computers are too big; the elements in this box are microscopic. If we wanted to make a computer that had all these marvelous extra qualitative abilities, we would have to make it perhaps, the size of the Pentagon..." this visionary speech of Richard P. Feynman in 1959 has been accepted as the risen of the concept nanotechnology [1]. Just because of the realization of "beauty of small" idea, scientists from various science branches has interested in this new and multidisciplinary area called nanotechnology, regarding the need in their main fields. In the giant world of the nanotechnology there is a need for physicist, chemists, biologist and many different disciplined engineers. Thus, nanotechnology tree has many sub-branches. One of them is called nanobiotechnology which combines the biology and engineering with the aim of nano and micro fabrication methods to build innovative, high speed and efficient devices to be used in biosystems and their applications.

The nanotechnology's main employees nanoparticles (NPs), which have extraordinary properties, have many workspaces such as sensing [2, 3], diagnosis [4], nanomedicine [5, 6] and electronics [7, 8]. The NPs have these superior properties due to quantum size effect. In order to benefit from these superior properties, there exist two problems that have to be struggled with. First is synthesizing the NPs in desired shape and size in reproducibly. Second is assembling the NPs in various desired patterns. In order to employ the NPs according to our needs, we have to control them. Synthesis problem is nearly solved by using many different synthesis procedures [9-13]. In assembling part of

the problems, there are some solutions namely; self-assembly at solid-liquid interface such as drying droplet [14-16], template assisted self-assembly [17, 18], programmed self-assembly [19-21]; self-assembly at liquid-liquid interface [22-25] and shape induced self-assembly [26-28]. All of them work for the particular aim.

In assembling part of the problem, one of the solutions is using templates during the assembly experiments. Templates behave as a guide for the NPs which are trying to be assembled. Thus, a new challenging area for the scientists has risen. How these templates can be obtained in such a simple, rapid and non-expensive way? Scientists working in various fields with this question mark, spend too many efforts for finding the simplest way of obtaining a template and using it for the further steps [29-31]. The responsibility of the templates which are trying to be obtained are not being only a guide in the assembly of NPs but also being responsible in fabrication of smaller scale microelectronic products, sensitive result giving substrates in molecular detections and many other applications. In our case, collaboration of the synthesized magnetic nanoparticles (MNPs), magnetic beads (MBs), convective-assembly method, commercially available compact disc (CD) and a simple magnet have presented an easy and exciting solution of way.

In this study, the aim is to offer a simple method for preparation of renewable surfaces which have nanoscale repetitive structures formed by MNPs. The project starts with a theoretical background on the techniques and topics mainly related to the experimental studies. General information on nanobiotechnology and its application areas, main nanostructures including MNPs, self-assembly method and used equipments are given briefly. In the next section, materials, chemicals and equipments used in experimental part are explained and schematically shown. All the experiments are also classified step by step and explained in the methods part of the thesis. In the experimental part of the study, MBs are characterized on hydrophilic and hydrophobic glass surfaces in the presence and absence of a positively charged surfactant, Cetyl trimethylammonium bromide (CTAB). Then, by using the MBs a nano-patterned template is prepared by using CD and convective-assembly method. Afterwards, by using the prepared surface in the presence and absence of magnetic field, the formation of structures by drying of synthesized MNPs which are suspended in various solvents were carried out. Moreover, the influence of patterned MBs existence, which forms nano-patterned template underneath

the dealing surface, is also established. In the results and discussion part of the thesis, the obtained experimental results and comments on the results are presented. In the last part, conclusions for the whole work are given.

2. THEORETICAL BACKGROUND

In this chapter, general information on nanobiotechnology and its application areas, its components including MNPs, self-assembly method, nano patterning techniques and some of the equipments used during the experiments are explained and presented briefly.

2.1. NANOBIOTECHNOLOGY AND ITS MAIN APPLICATIONS

Though top-down approach has been used for centuries in industry and even in Paleolithic age, Feynman created a question mark about "bottom-up approach" to the scientists who listen his famous and prescient speech in 1959. His speech of having "Small is beautiful" main idea has introduced the Nanotechnology term to the world, which is still on progress. The new and rapidly expanding science branch called "Nanotechnology" combines the classical science branches physics, chemistry, material science and engineering science. Despite its existence is in the overlapping area of many classical sciences, its components' behaviors do not suit classical Newton's Laws [1]. The nanostructures have high quantum efficiency, great scattering or absorbance cross sections, optical activity over biocompatible wavelengths, increased chemical or photochemical stability and many others beneficial properties [32]. The nano-scale structures used in nanotechnology are carbon nanotubes, quantum dots (QDs), several metal NPs and MNPs [33]. The nanotechnology is a shining new field because of its exciting miniaturization and ultra precision promises [1, 34]. Nanotechnology revolution's some striking offers are to pack more computational power into a sugar cube than exists in the today's world; to make inexpensive structural materials which are as lighter and stronger as a diamond (which fascinates the aerospace industry) and to make surgical tools and instruments of molecular size and precision [35].

The aim of the various scientists who, although have different major fields of study, work on nanotechnology is to control the morphology, structure and size of the nanomatters which they are dealing with. Controlling their behaviors and actions is the major challenge of improvements in nanotechnology studies [36]. The nanostructures with highly controlled properties bring extraordinary and advantageous applications to various

fields of science [32]. The overlapping of biology and nanotechnology branches is named as nanobiotechnology or bionanotechnology. The nanotechnology inspires from biology and provides useful devices for understanding the biological life [37]. In Figure 2.1, the interaction of the coworkers; biology and nanotechnology can be seen.

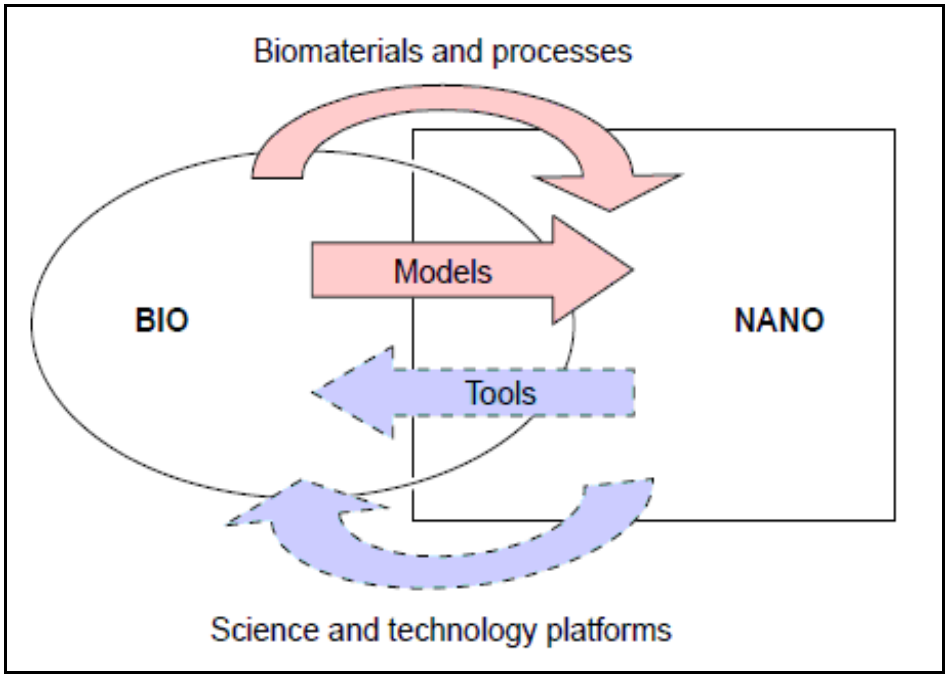

Figure 2.1. The interaction of biology and nanotechnology [37]

Since NPs have size similarity with biomolecules and also have other advantageous properties like having chemical stability and good optical activity over biocompatible wavelengths, the nanostructures are highly appropriate matters in biological systems. The NP-biomolecule hybrid behavior comes into being like companions in the over all biosystems. By modifying the nanostructures which will serve a desired purpose, semiconductor nanocrystals, core shells, janus NPs, NPs with various shapes (triangles, rods, spheres, cubes), biomolecule attached nanostructures can be obtained in various accurate ways. Those various types of nanostructures having hybrid structure with a biomolecule enhance the suitability of foreign substances, nanostructures, to the biological systems [32]. Moreover, those hybrid nanostructures can be used in diverse applications such as medicine, imaging, diagnosis, disease treatment and prevention, drug delivery, biosensing, electronics [32, 38].

Since nanostructures have ability to exist both on surface as well as in the inside of cells and have biomolecular interactions where they are, they have potential to diagnose disease and heal it directly in situ. It is also said that, some similar properties of the nanostructures and the natural biological molecules in nanometer size contribute to develop artificial nanostructures that sense and repair the needed section of the body [39-41].

In the study of Stylios et al., it has been reported that NPs and drugs in powder form, surrounded (or in other words hidden) with a biocompatible and biodegradable polymer shell or in 3D polymer matrix, can easily travel in bloodstreams without any rejection by the immune system. By directing these hidden agents to the needed part of the body, healing can be provided [39]. Dentistry will also receive its share from nanobiotechnology. Nano-dentistry will make possible nearly perfect oral health by using nano materials, biotechnology and nano robotics [32, 42-46]. Additionally, nanobiotechnology offers a choice to orthopedic applications with higher mechanical strength, improved bioactivity, and resorbability in improving the life quality of patients who suffer from bone related diseases. Owing to structure similarity of bone materials composed of organic and mineral phases with nanostructured materials which varies from 1 to 100 nm, nanobiotechnology will be an impressive solution for many cases in orthopedics [47-53]. In the study of Wagner et al. in 2006, it was reported that approximately 30 nanotechnology healing products have been approved for clinical uses [54].

Nanobiotechnology is also used in imaging systems. The importance of imaging in disease detection, therapy decision and surgery is obviously apparent. Table 2.1 shows the used drug delivery systems, techniques, imaging agents, and limitations of use in imaging systems. The techniques used in imaging systems are namely, single photon emission computed tomography (SPECT), positron emission tomography (PET), magnetic resonance imaging (MRI), fluorescence microscopy, computed tomography and ultrasound [55, 56]

Table 2.1. Nanoscale systems for imaging [55]

Drug delivery systems	Stage of development	Technique	Contrast agent / imaging agent / radio label	Limitation of use
Liposomes	preclinical	SPECT MRI PET	Gadolinium	Preparation steps have to be carefully controlled to achieve reproducible properties such as size and entrapment efficiency
QDs / nanocrystals	preclinical	Optical / fluorescence	QDs QDs-micelles QD-conjugates	Further safety studies are required because QDs are very stable
MNPs	clinical / preclinical	MRI	Fe_3O_4-dextran Fe_3O_4-polyacrylamide Fe_3O_4-insulin	Toxicity may occur due to cellular internalization and membrane disruption.

The newly born area nano diagnostic uses nanobiotechnology in molecular diagnosis. Improved speed of detection, greater sensitivity, reduced cost and decreased invasiveness are the promises to bioelectronics and biomedical devices by nanotechnology revolution [57].

One of the major aims in nanotechnology is miniaturization of both medical and electronical devices. Smart nanostructures are interfaced with silicon or other substrates for the designs. These structures may be chemically synthesized molecules, supra molecules, biologically active recognition centers or biomolecular functional units. The smart biomolecular materials present the potential to be tailored on the atomic scale with controlled electrical, dielectric, optical, magnetic, mechanical, chemical or thermal properties for potential applications such as in electronic, photonic, magnetic, mechanical and molecular recognition devices [7]. Figure 2.2 shows the being applied strategies with varying nanostructures in the field of bioelectronics.

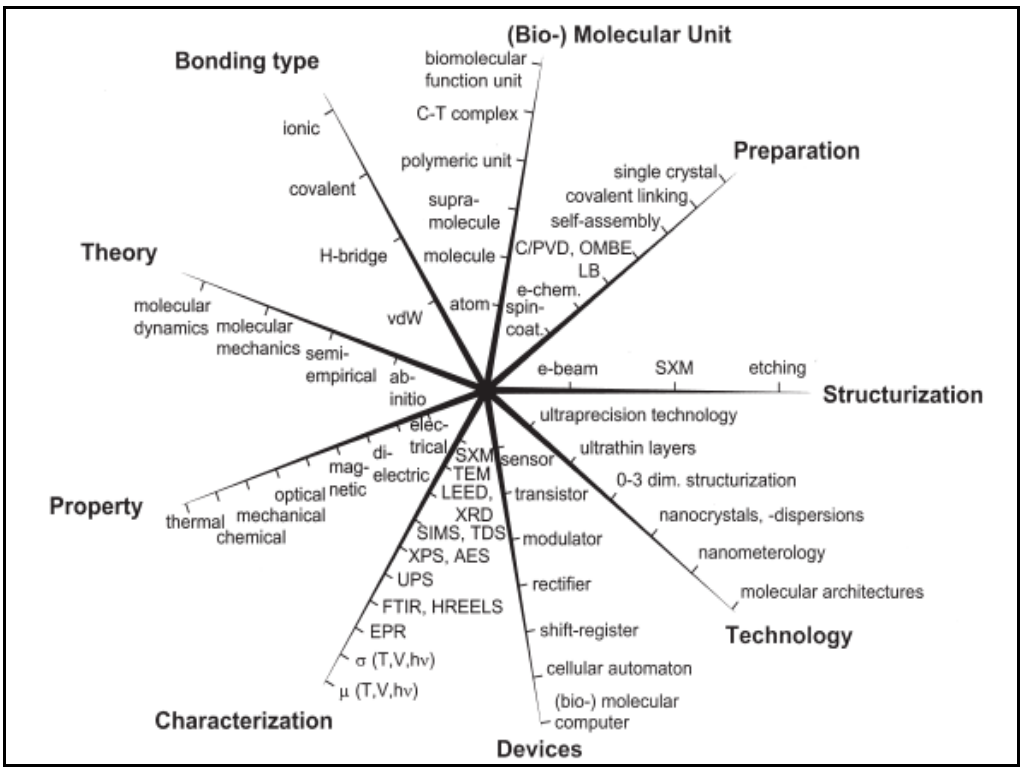

Figure 2.2. Various aspects of treating nanostructures based on biomolecular materials [7]

2.2. NANOSTRUCTURES

In this section, a brief summary of properties of selected nano structures used in nanotechnology applications is presented.

QDs are nanocrystals having size in 1-10 nm range with extraordinary photochemical and photo-physical properties. Owing to their odd properties they are used in place of common organic dyes and fluorescent proteins. QDs are also semiconductor. Depending on the size, the QDs emit light in different colors when they are excited at appropriate wavelengths. Generally, smaller particle emit a shorter wavelength of light than next larger size. Figure 2.3 shows suspensions of QDs in various sizes and injected QDs which show tumors in different sizes in a mouse. The reason of being perfect reagents for in vivo imaging at molecular and cellular levels is their high stability, increased and stable fluorescence capability and multicolor fluorescence emission. This is why they are the highly preferred nanostructure in vivo cancer studies [56]. The crucial challenge of QDs

usage in further developments is their encapsulation by a biocompatible layer and the need to avoid non-specific adsorption [37, 58].

Figure 2.3. QDs emitting different color of lights due to their varying sizes and a mouse that was injected with varied size QDs thus multicolor tumor targets can be detected and tracked [59, 60]

Chemistry and physics of gold NPs (AuNPs) have various sub disciplines in the domain of colloids and surfaces. The remarkable optical properties of small AuNPs, their size dependent electrochemistry, and their high chemical stability are the reasons of their use in self-assembly, bio-labeling, catalysis, electron transfer theories, phase transfer, deoxyribonucleic acid (DNA) melting and assays and crystal growth studies. The protected AuNPs that have shell of thiolate ligands express good stability towards aggregation and exhibit a good platform for chemical manipulations and attachments. AuNPs are used in applications varying from photonic device fabrications to charge storage systems [61].

NPs are covered or protected by, shells of ligands depending on the synthesis procedure. The chemical surrounding the NP attached during the synthesis can be exchanged by other desired functionalized ligands for any aim. AuNPs provide ability to make manipulations on the surface. Moreover, when the biocompatibility of the AuNPs has been taken into consideration, the reason of being mostly selected as outer material can obviously be understood [61]. There are numerous reports about the AuNPs modifications and their applications in sensing, medicine and biomedicine [62-66].

The surface chemistry of NPs can easily be functionalized for targeting and delivery. For example, in the study of Fuente et al., the biocompatibility of glucose derivatives functionalized MNPs coated with Au over cell viability of human fibroblasts were investigated [67].

Silver NPs (AgNPs) can be synthesized with several methods such as chemical reduction, photochemical methods, ultrasonic-assisted reduction, electrochemical method, irradiating reduction and biochemical methods [68-76]. AgNPs are used mainly due to their plasmonic and antibacterial properties. The plasmonic properties have made the AgNPs very popular in sensing applications. Ag nanostructures which are prepared by nano sphere lithography can also be used in chemical and biological sensing [77, 78].

In addition to AuNPs, AgNPs are widely used as substrates for surface-enhanced Raman scattering (SERS) that is a vibrational spectroscopic technique experienced on noble metal nanostructures [76, 77, 79-82]. AgNPs have been extensively used for the utility of SERS in biological applications. [83-86].

In Figure 2.4, AuNPs and AgNPs in colloidal form and in various sizes are presented.

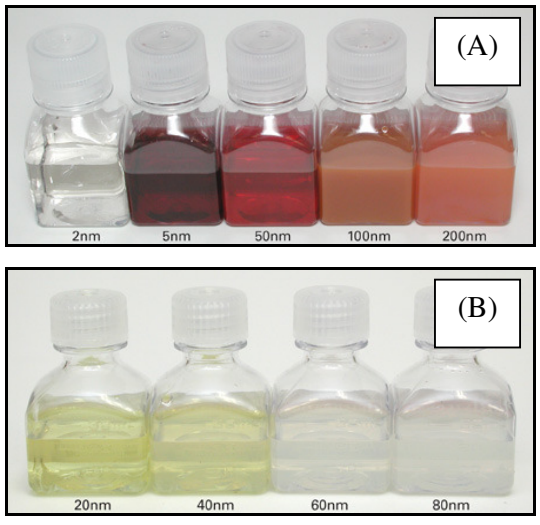

Figure 2.4. The colloidal suspension of AuNPs (A) and AgNPs (B) in various sizes [87]

Carbon nanotubes are other promising nanostructures due to their good optical, electrical, magnetic, chemical and thermal properties. There are single wall and multi wall carbon nanotubes. Figure 2.5 shows multi wall carbon nanotubes with various diameters. Single wall carbon nanotube is in the form of cylindrical graphene sheet with a diameter of 0.7-10 nm. The aspect ratio (length/diameter) of the cylinders can be as large as 10^4 - 10^5. Carbon nanotubes have wide application areas such as chemical and biological separation, purification, catalysis, energy storage, composites for coating, filling and structural materials, probes, sensors, actuators for molecular imaging, sensing, logic devices, nanoelectronic devices, field emission devices for X-ray instruments and flat panel display. Their low weight, small size, high performance provides remarkable advantages in their applications [88-91].

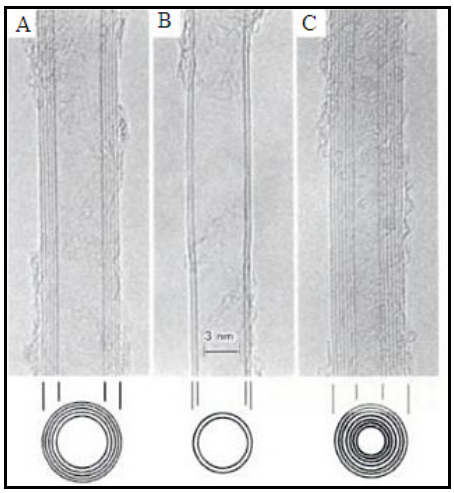

Figure 2.5. The TEM image of multi-wall carbon nanotubes with various inner and outer diameters (A) with 5 shells (B) with 2 shells (C) with 7 shells [88]

MNPs are one of the most fascinating nanostructures with promising applications in nanobiotechnology due to their unique ability to be guided and functionalized by an external magnetic field. The MNPs have wide application areas including magnetic fluids, catalysis, biotechnology/biomedicine, MRI, data storage and environmental remediation. MNPs can be synthesized in various composition and phases like iron oxides as Fe_3O_4 and g-Fe_2O_3; pure metals as Fe and Co, spinal type ferro magnets as $MgFe_2O_4$, $MnFe_2O_4$ and $CoFe_2O_4$ and alloys as $CoPt_3$ and FePt by using different methods like co-precipitation,

thermal decomposition and/or reduction, micelle synthesis, laser pyrolysis and hydrothermal synthesis methods. Table 2.2 summarizes the four main synthesis methods of MNPs by considering their advantages and disadvantages. After synthesis, functionalization of them has promises in vast areas like bio-labeling, bioseperation and catalysis [92].

Table 2.2. Summary comparison of the MNP synthesis methods [92]

Synthesis method	Reaction temp (ºC)	Reaction period	Solvent	Surface capping agent	Size distribution (shape control)	Yield
Co-precipitation (Very simple, ambient conditions)	20-90	min	water	needed, added during or after reaction	relatively narrow (not good)	high / scalable
Thermal decomposition (Complicated, inert atmosphere)	100-320	hours-days	organic compound	needed, added during reaction	very narrow (very good)	high / scalable
Microemulsion (Complicated, ambient conditions)	20-50	hours	organic compound	needed, added during reaction	relatively narrow (good)	low
Hydrothermal synthesis (Simple, high pressure)	220	hours, days	water-ethanol	needed, added during reaction	very narrow (very good)	medium

In 1960s, NASA research center discovered the unique and controllable behavior of the magnetic fluids in the presence of magnetic field. The NP solutions of these fluids are known as ferro-fluids. They have wide application area in industry such as dampening vibration in audio loudspeakers, behaving as liquid O-rings in rotating shaft seals, and they are used in high-speed computer disk drives to eliminate impurities. They also have many potential applications in biomedical, environmental, and engineering fields such as DNA and ribonucleic acid (RNA) purification, cell separation, MRI, guided drug delivery, magnetic hyperthermia cancer therapy, tissue engineering, cell tracking, bioseperation and biosensors [93-97].

Table 2.3 shows some general properties of nanostructures and their representative applications.

Table 2.3. Characteristics, ligands and representative applications for some of the nanostructures [79]

Core material	Characteristics	Ligands	Applications
Au	Optical absorption, fluorescence and fluorescence quenching, stability	Thiol, disulfide, phosphine, amine	Biomolecular recognition, delivery, sensing
Ag	Surface enhanced fluorescence	Thiol	Sensing
CdSe	Luminescence, photo-stability	Thiol, phosphidine, pyridine	Imaging, sensing
Fe_2O_3	Magnetic property	Diol, dopamine derivative, amine	MR imaging, biomolecule purification

MNPs are composed of magnetic elements like iron, nickel, cobalt and their oxides [95]. Magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3) are the main forms of the iron oxides available in nature [98]. In MNPs applications, magnetite, Fe_3O_4, is the mostly promising form of all, due to its biocompatibility and high superparamagnetic properties and high magnetic susceptibility [99]. Magnetite NPs can be synthesized by mixing Fe (II) and Fe (III) salts at a specific ratio [100]. Magnetite has a cubic inverse spinal structure with oxygen and forms a face-centered-cubic closed packing [101].

The MNPs are to be coated with a surfactant to prevent aggregation. The surfactants must fulfill their essential role even in the presence of magnetic field. They must overcome the intermolecular forces between NPs. A typical ferro-fluid contains 5 per cent MNPs, 10 per cent surfactant, and 85 per cent carrier fluid by volume [97].

There exist many studies in the literature about MNPs functionalization and their promising applications. In the study of Maceira et al., Fe_3O_4 MNPs are synthesized and coated with a silica shell that were functionalized with AuNPs afterwards, by using

electrostatic interactions. Then, these gold-coated magnetic silica spheres showed strong resonance absorption in the visible and near-infrared range and can be controlled by using magnetic field which is a very promising biomedical application [102]. In the study of Rotello et al., Fe_3O_4 MNPs synthesized in toluene solution were transferred to the aqueous solution under stirring with octa (tetramethylammonium)-polyhedral oligomeric silsesquioxane (TMA-POSS). Also, they proposed that this TMA-POSS exchange can be applied to the oleic acid stabilized Fe_3O_4 MNPs and oleic acid, oleylamine, or hexadecanediol stabilized FePt NPs [103]. Obtaining water soluble NPs is vital due to their stability in biologically relevant pH ranges and salt concentrations [92].

Because the size of MNPs ranges from few nanometers to tens of nanometers, they can be comparable to and interact with proteins, antibody, DNA, RNA and other biomolecules [93, 94,104,105].

Magnetic fluids have a novel response in the presence of magnetic fields. Figure 2.6 shows the response of MNPs in a magnetic fluid in the presence of magnetic field. Superparamagnetism is a form of magnetism which occurs only when external magnetic field is applied on. Magnetic field presence forms a net magnetization value which makes MNPs aligns along with existing magnetic field. Totally, net magnetization drops to zero in the absence of external magnetic field [106].

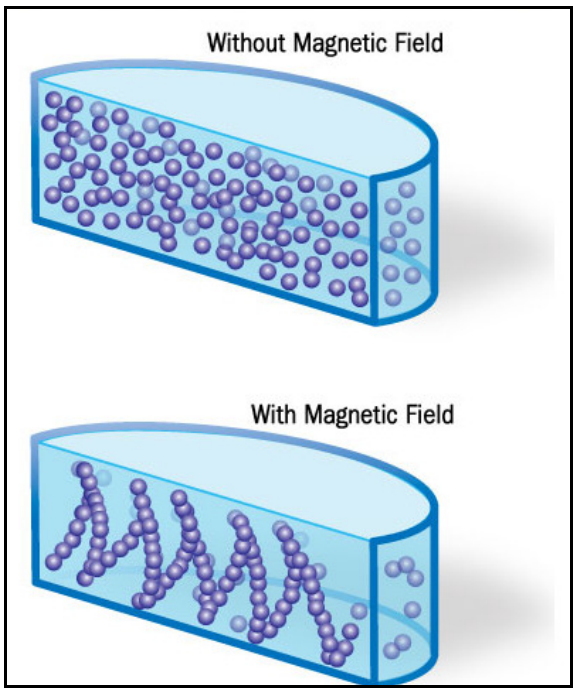

Figure 2.6. The response of MNPs to the presence and absence of magnetic field [106]

$$F_m = V_{particle} * \chi * \mu_0 * H * \nabla H \quad (2.1)$$

Equation 2.1 shows the Kelvin force. In Equation 2.1, $V_{particle}$ shows the volume of the MNP, χ shows susceptibility of MNP, μ_0 shows the vacuum permeability, H shows the magnitude of magnetic field and ∇H shows the magnetic field gradient. The F_m parameter shows the force exerted by a magnetic field to a MNP. As it is seen in the equation, the volume of the single MNP, its magnetic susceptibility, created magnetic field's magnitude and gradient are the parameters affecting the force acting on each particle [107, 108].

2.3. TECHNIQUES USED IN NANOSTRUCTURE CHARACTERIZATION

As it is said "seeing is believing", the most important aspect of the nanostructure characterization is the verification of the targeted structure. Therefore, several microscopic techniques have been utilized. The most important techniques pertaining to this study are briefly outlined.

The resolution limit of light microscope ranges from 0.4 µm to 0.7 µm (from violet to deep red). Therefore, bacteria and mitochondria which are about 1 µm wide can be seen by using light microscope. For further details of much smaller objects, light microscope does not satisfy the need. By using electrons or scanning tiny probes, instead of light, limit of resolution reached can be very small, e.g., 0.004 nm with 100 kV electrons. The practical resolving power of most modern electron microscopes (EMs) is 0.1 nm or 1 Å [109].

The atomic force microscopy (AFM) gives information about the topography of the specimen in 3D. The mechanism of AFM can be associated to a blind man having a walking stick. As walking stick gives information about the road's hills and downs, the sharp tip/probe of AFM having a radius approximately 1-2 nm gives information about the surface of the specimen. The tip goes up and down with respect to the surface topography with cantilever. The movement of the cantilever is transferred to the photodiode by the laser pointing on the cantilever and scattering towards to photodiode. The working principle of AFM is presented in Figure 2.7.

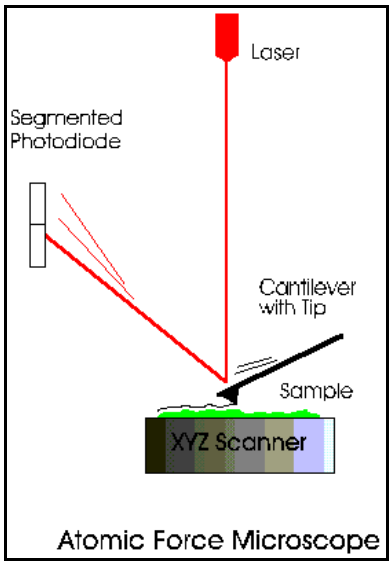

Figure 2.7. The mechanism of AFM [110]

Scanning electron microscope (SEM) uses electrons instead of light or a probe to form an image. Since SEM has many advantages over traditional microscope as having

large depth of field, higher resolution, controlling the degree of magnification. The SEM gives information about microscopic details of the surface of the specimen in 1D. A sample that will be studied by using SEM should be conductive. Therefore, by using coating device, a thin gold layer is coated on the top of the sample. The gold layer-coating helps to obtain better images. In SEM, electron gun sends extremely focused beam of electrons towards to the specimen surface. The SEM image is formed by the signal of the reflected electrons. It presents intense images where zero signals are displayed as black, intermediate signals as shades of grey and maximum signal as white. The SEM uses the backscattered or emitted electrons from the specimen surface [109]. Figure 2.8 shows a cartoon view of SEM.

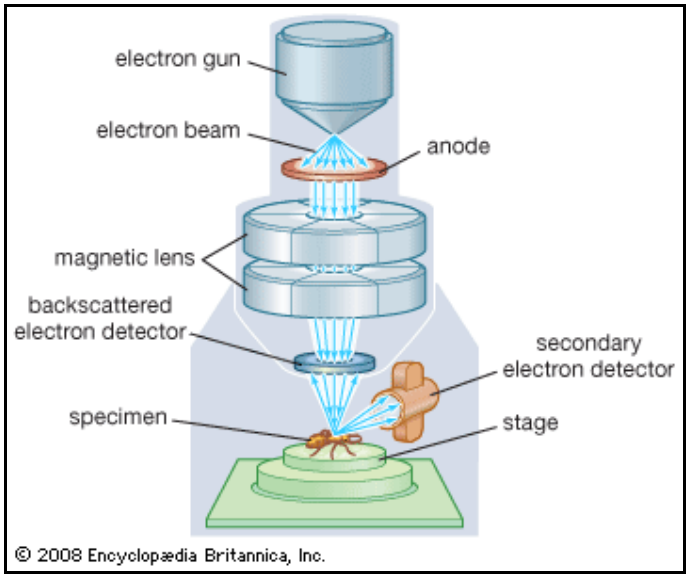

Figure 2.8. The schematic illustration of SEM [113]

The resolution obtained by using light microscope is approximately higher than 200 nm (wavelength of green light= 500 nm) with magnifications up to 3000 times. On the other hand, SEM provides resolution of less than 5 nm (wavelength of 30 kV electrons=0.007 nm) with magnifications up to 1 million times [109]. In Figure 2.9, the comparison of light microscope and EM can be observed.

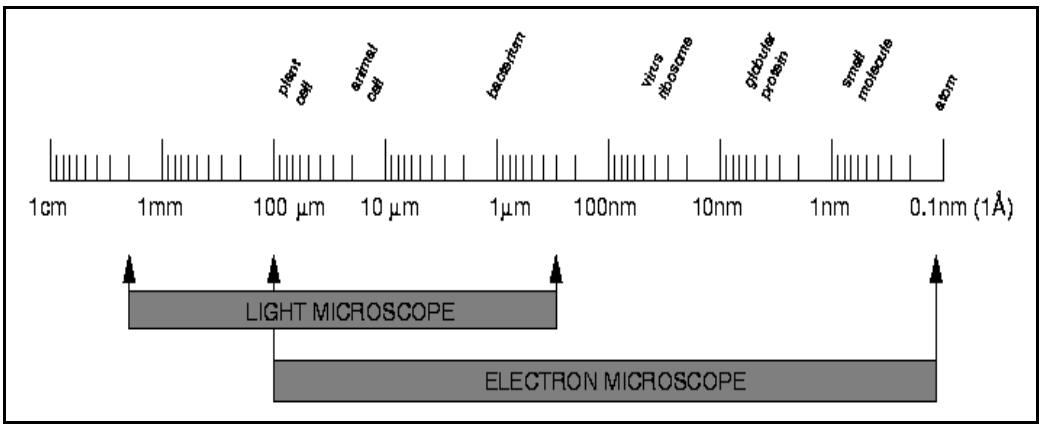

Figure 2.9. The visible region for EMs and light microscopes [111]

Since air molecules may cause scattering of electrons by collisions, the EM need high vacuum conditions during the analysis. One of the disadvantages of using EMs is related to the high-vacuum need. Biological specimens can not be viewed in vivo due to the high vacuum. Therefore, some pre-experimental fixation and preservation procedures are applied for biological specimens [111-113].

Transmission electron microscopy (TEM) uses the electrons, which have passed through the specimen, to form an image, whereas SEM uses the backscattered or emitted electrons from the specimen surface. The preparations before SEM analysis are easier and quicker with respect to TEM analysis. By using TEM, much higher magnifications from SEM can be obtained. TEM gives information about the inside of the specimen with the help of the electrons passing through the sample. High-vacuum condition is also necessary in TEM analysis. The specimen is scanned with electron of beams whose diameter can be adjusted. Electron beams coming from the electron gun hits and enters to the specimen and the quantity of electrons exiting from the specimen is measured by an electron detector. At the end, the image is transferred to the computer screen [111]. Figure 2.10 summarizes the mechanisms of light microscope, TEM and SEM.

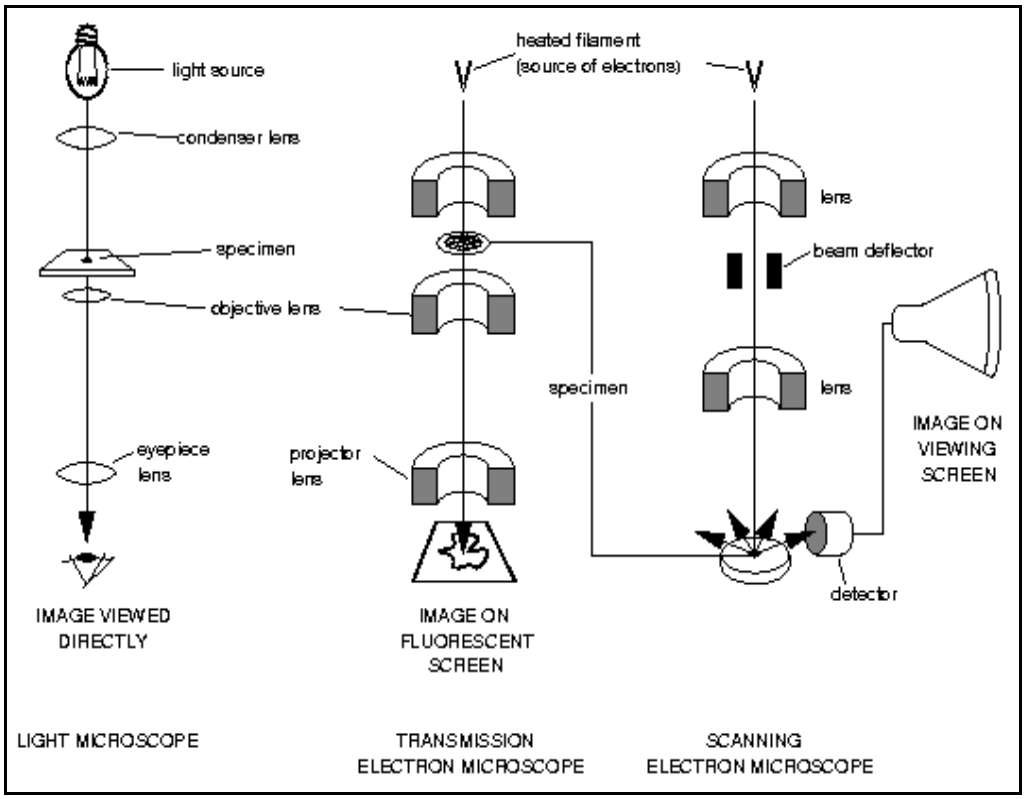

Figure 2.10. The principal of a light microscope, TEM and SEM [112]

2.4. SELF-ASSEMBLY

To benefit from the superior properties of nanostructures, two problems have to be coped with. The first is synthesizing the NPs in desired shape and size in an accurate way. The second is assembling the particles in various desired patterns. To employ the NPs according to our needs we need to have ability to control the shapes and sizes of NPs and assemble NPs in desired patterns. The problem of synthesis is nearly solved by using different procedures [2, 4, 8, 114-121]. In assembling part, there are some solutions. These are: self-assembly at solid-liquid interface such as drying droplet [9-13, 122-126], template assisted self-assembly [127-131], programmed self-assembly [16, 14, 132-141] self-assembly at liquid-liquid interface [142-146] and shape induced self-assembly [17, 18, 147-151].

Also, there are two different approaches in assembly of nanostructures. These are top-down approach and bottom-up approach. Since Paleolithic age, people use top-down approach in industry and many other fields. In top-down approaches, which were used in Paleolithic ages, big particles are minimized into smaller scales in order to be used for further steps. On the other hand, in bottom-up approaches, small particles are obtained or synthesized and used to build higher structures [125, 126]. Figure 2.11 shows the difference of bottom-up and top-down approaches.

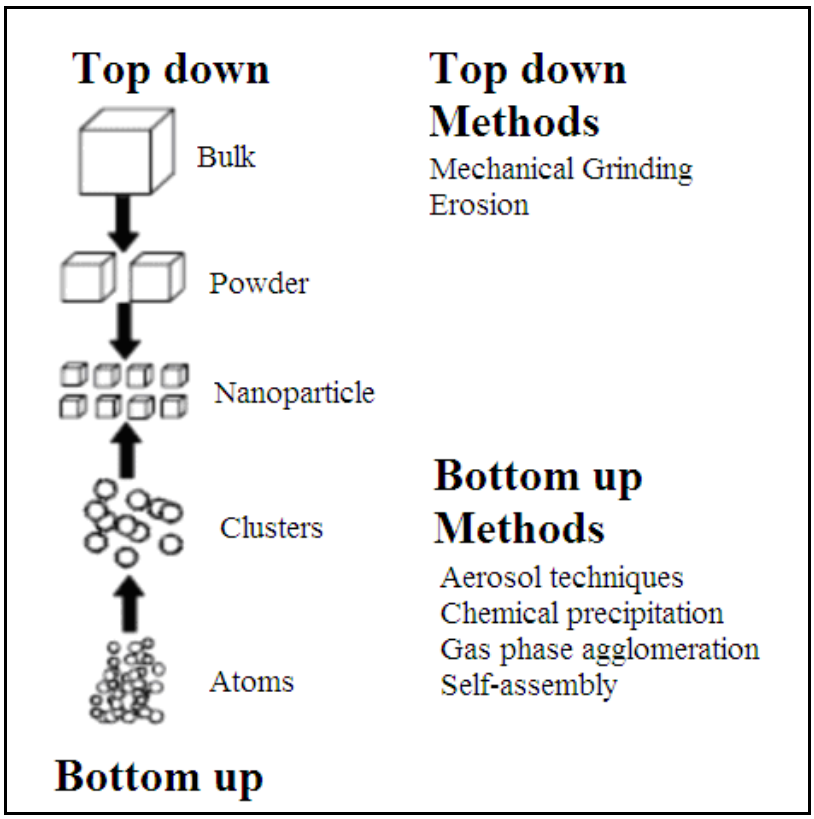

Figure 2.11. The schematic representation of bottom-up and top-down approaches for NPs synthesis [152]

The bottom-up approach that was introduced in Feynman's speech in 1959, is being used nowadays especially in preparing nanostructured surfaces. Lithography and micro contact printing techniques are the examples of top-down approach used in nanostructured surface preparation studies [125, 126]. Since those techniques are troublesome and expensive, usage of nanostructures in bottom-up approach based techniques have been

emerged. The NPs' surface properties play influential role in bottom up approach based techniques. The surface chemistry determines the solution properties that the NPs are suspended in. The surface property of the NP is determined by the synthesis method or it can be altered with a chemical attachment or physical adsorption of wanted molecules [9-13, 122-124].

2.4.1. Self-Assembly at Solid-Liquid Interface

Most of the NPs self-assembles in their solutions or suspensions on any solid surfaces, upon evaporation of the solvent of droplet. During the drying of the droplets, some physical, chemical or magnetic forces can be applied on. This section explains the self-assembly of NPs at the interface of solid and liquid media in three subsections, namely: self-assembly from a drying droplet, template assisted self-assembly and programmed self-assembly.

2.4.1.1. Self-Assembly from a Drying Droplet

As the solvent is evaporated from the droplet of suspension, the weak forces become dominant among the NPs, therefore self-assembly occurs. Before the evaporation process starts, the particles disperse well in the suspension. The evaporation process occurs on the surface of the droplet. As the droplet starts to evaporate, the concentration increases. The reason for self-assembly of NPs during evaporation process lies on the fact that the evaporation of solvent is faster than the diffusion rate of NP during this increase of concentration.

The phenomenon was reported by Denkov and coworkers. They explained the driving mechanism for the formation of irreversible packing NPs by thermodynamics of non-equilibrium processes of aggregating NPs [16, 134]. By using this method, easy, simple and cheap way of preparing nanostructured surfaces can be achieved. Several surfaces can be obtained by using gold, silver or polystyrene NPs. Furthermore, using various morphologies of NPs and NPs in various solvents may result obtaining diverse surfaces.

2.4.1.2. Template Assisted Self-Assembly

Template assisted self-assembly or in other words directed self-assembly of NPs is another powerful and well-established technique [17, 18]. The template is obtained by a physical or chemical application such as e-beam lithography, light lithography, a co-polymer and chemical functionalization. Then, the NPs can be directed physically into the holes, groves or wells by using coating techniques such as convective-assembly, dip- and spin coating [147, 148] or, the NPs can be directed chemically into the holes, groves or wells through weak interactions such as hydrogen bonding or hydrophobic interactions attached to the functionalized areas. In the study of Lu et al, a method based on wrinkles formed on the polymer Poly dimethyl siloxane (PDMS) was reported. The spray of poly sodium 4-styrene sulfonate and poly alkylamine hydrochloride (PAH-PSS) created a thin film onto the PDMS and by applying a stretch-retraction process wrinkles were obtained. The formed groves were filled with colloidal particles by dip-coating process. This lithography-free method was quite well ordered and defect-free [150].

Another promising way of template assisting self-assembly was stated as using block copolymers due to low cost and their extended areas of having highly resolved defect free patterns. Craig and et al. have reported an approach for well ordered square arrays of sub-20nm features without using chemical pattern on the surfaces [153]. However, the same group reported that A-B-C triblock polymers have more complex structures in comparison to A-B diblock polymers which result in the enhancement of physical properties and broaden the processing window; the use of different blend of polymers such as A-B/B-C and A-B/C-D alloys could be advantageous [154, 156].

2.4.1.3. Programmed Self-Assembly

DNA is used as a guide to assemble the NPs to generate periodic assembly on surfaces. By using DNA as a platform, the metal NPs [21, 157-159] and proteins [160-164] can be assembled into complex forms. There are vast studies on the area [157, 159, 165-175].

2.4.2. Self-Assembly at Liquid-Liquid Interface

Thin film formation at the interface of two different immiscible solutions had already been observed [22, 176]. Then, the idea of having defect-free assembly of NPs at the interface has risen [177]. Pieranski claimed that decreased total free energy at the interface is the reason for the assembly of NPs [178]. However, particle size, interaction between particles and particle-liquid interactions are the other parameters having effect on the thin film formation at the interface [178-180].

2.4.3. Shape Induced Self-Assembly

Another approach is named as shape induced self-assembly. The NPs that have different shapes have different facets. Also they have different affinities for the ligands, this can be used as an advantage for the assembly of NPs [181-189] There are many studies on the combination of NPs with different shapes by adding another NP to the different facets [190-192].

2.5. NANOPATTERNING

Since patterning is principally important in many areas of modern science and technology, there are various methods for pattern preparation which can be classified into three groups: generation of patterns, replication of patterns and three dimensional patterning. The applications of patterning are in integrated circuits, information storage devices, biochips, photonic band gap crystals, micro-optical components, and diffractive optical elements. The process of patterning is commonly referred to as lithography. With respect to the application, the requirements for a successful lithographic process can vary. The most appropriate lithographic technique is selected with respect to the needed pattern sizes. Figure 2.12 shows the different lithographic methods and obtained sizes [193].

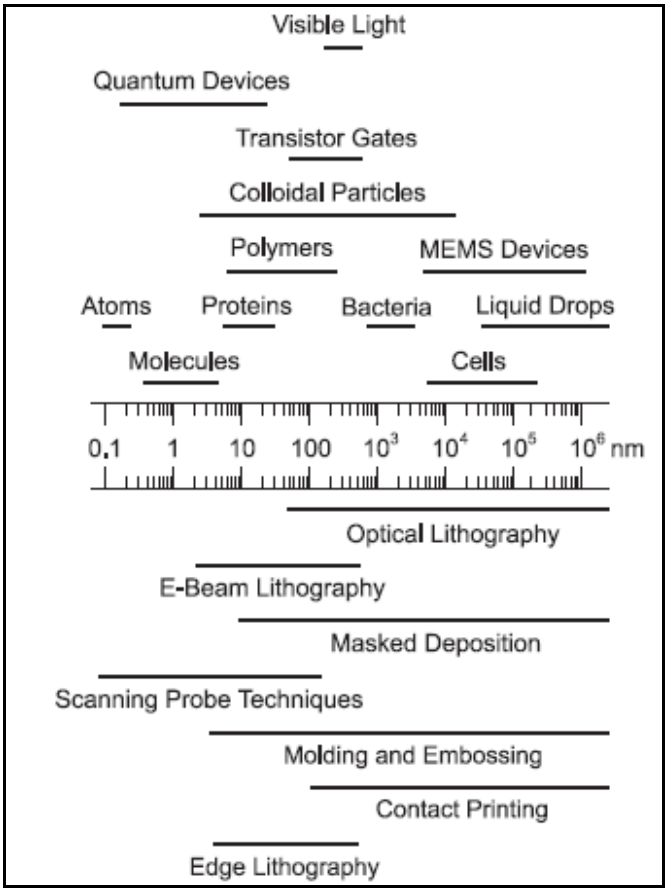

Figure 2.12. Lithographic methods and their results in terms of size [194]

Generation of pattern can be made by various writing processes. Figure 2.13 shows the different writing processes for patterning, writing with a rigid stylus (A), writing with a beam of energetic particles (B), writing with an electric field (C), writing with a magnetic field (D) [194-202].

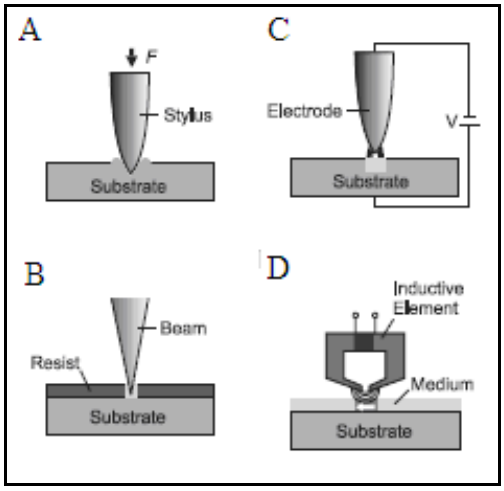

Figure 2.13. Writing processes for patterning [194]

In Figure 2.13 a rigid stylus is used to write a pattern by applying a physical force on stylus (A); energetic particles like photons or electrons is used to form changes on a resist material (B); an electrode is used to apply an electric field to the substrate (C); an inductive element on a recording head is used to generate domains with uniform magnetization directions in a thin layer of ferromagnetic material (D) are shown.

Also, self-assembly may be used for patterning by using appropriate building blocks. Nanosphere lithography is one of the main self-assembly based patterning techniques. Nanosphere lithography uses nanoscale sphere assembled particles. After applying soft lithography method, a nano-patterned substrate is obtained. For the aim of soft lithography PDMS stamp is used [203-208].

Furthermore, replication of patterns is another method for nanopatterning. The main idea of replication is duplicating the proper pattern having substrate. By this aim, photolithography or optical lithography (uses photons), etching, replication with a master (known as soft lithography) are some known techniques [209- 218].

Figure 2.14 shows the mostly used replication pattern techniques by using a master.

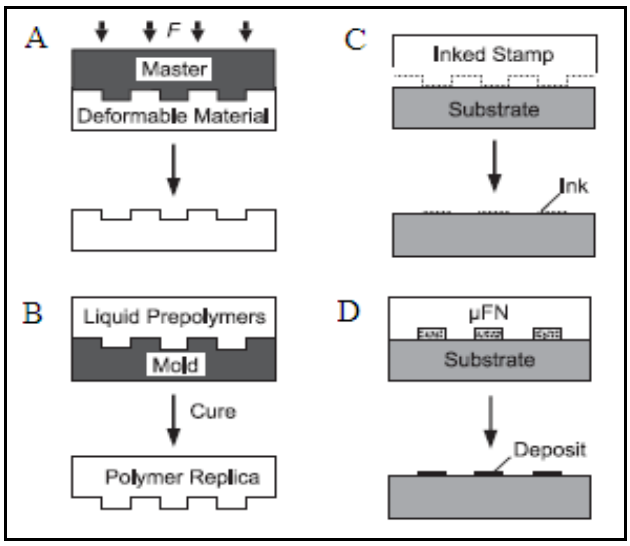

Figure 2.14. Replication pattern techniques by using a master; under mechanical forces (A), replica molding of liquid pre-polymer which is cured to polymerize into solid rigid form (B), micro contact printing (C) and micro fluidic patterning (D) [209]

In order to obtain three dimensional patternings, electron beam writing [219], layer by layer fabrication [220], self-assembly [221, 222] and molding techniques are used [30, 223]. Also it is observed that biological nature offer astonishing variety of sophisticated nanostructures which are difficult to obtain with other technological methodologies. Thus, biotemplating in other words bionanofabrication area has emerged. Biotemplating can be categorized into three subgroups depending on the basis of the origin of the biological template employed as; microorganisms (organisms, diatoms, viruses, bacteria...), design based biomacromolecular building blocks (natural or synthetic lipids, peptides, DNA oligonucleotides) and proteins. Biotemplating looks for replicating the morphological characteristics of a biological specie or use biological specie for guiding to form a pattern [30].

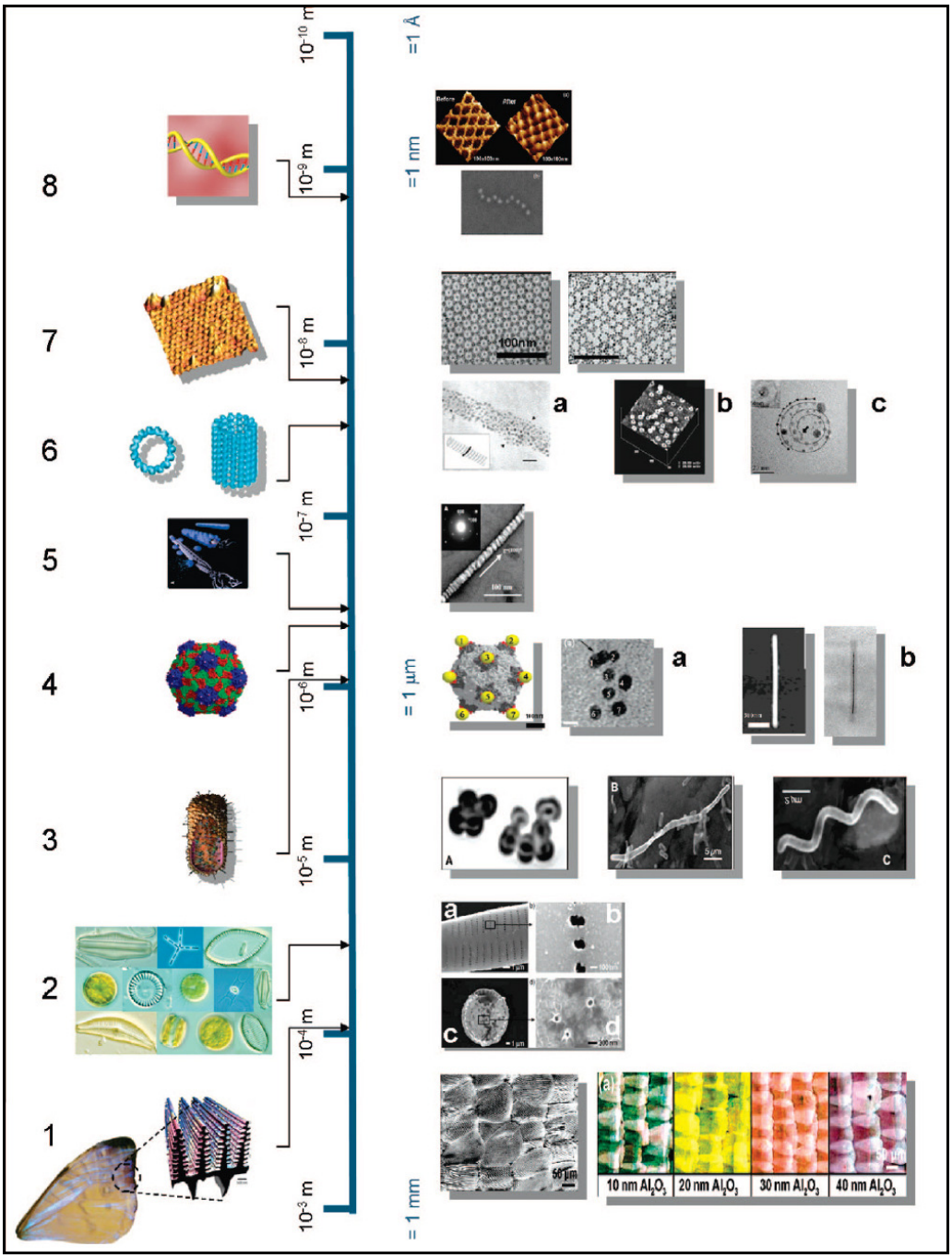

Figure 2.15. The overview of biological templates [30]

The Figure 2.15 summarizes the biological templates in wide range. On the left side of the figure biological structures in schematic representation is shown, whereas on the right side of the figure corresponding template structures synthesized are displayed. The (1) shows a butterfly wing and SEM image of alumina template and optical images of their

tunable photonic properties, (2) shows diatoms and SEM images of Synedra and Thalassiosira frustules coated with silver, (3) shows bacteria and microscope images of metalized microspheres from *D. Radiodurans*, microfilaments from *E.coli* and micro coils from *R.rubrum*, (4a) shows AuNP bound cowpea mosaic virus (4b) shows AFM image of the tobacco mosaic virus and TEM image of a 3nm diameter Ni nanowire cast within the inner channel, (5) shows M13 bacteriophage virus and Dark-field diffraction contrast image of a ZnS viral nanowire with specific crystallographic ordering, (6a) shows TEM image of Pd NPs on a microtubule, (6b) shows AFM image of tubulin structures and (6c) shows TEM image of AgNPs on tubulin spirals, (7) shows S-layer proteins (from *D. radiodurans*) and TEM image of the native and QD-functionalized S-layer from *D.radiodurans*, (8) shows AFM image of a self-assembled DNA "grid" functionalized with Au nanoclusters (SEM) [30].

Bionanotemplating approach is potentially more cost and time efficient and it offers the chance of having topographically repetitive structures when it is compared to other nanopatterning techniques. Although bionanopatterning has these advantages, it has also some limitations like lack of purified biological species that is needed to be used in large scale fabrications. Moreover, not being fully informed on biological species' exact mechanisms in forming the pattern is also another disadvantage [30].

3. MATERIALS

PDMS is a polymer used in soft lithography experiments and purchased from Dow Corning in USA. The chemical CTAB was purchased from Merck in Germany. Potassium dichromate ($K_2Cr_2O_7$) was purchased from Fluka in Switzerland. Sulfuric acid (H_2SO_4) was purchased from Riedel de Haen in Germany. Dichloromethylsilane (CH_3SiHCl_2) was purchased Aldrich in Germany. Regular glass slides were purchased from Pearl in China. The CD having Princo brand was selected. The Fe_3O_4 MNPs have been synthesized by Tuğçe Özdemir who is a master student of the Chemical Engineering department in Yeditepe University. The MNPs have been synthesized by organic phase synthesis explained in the study of Sun et al. [224]. The diameter of MNPs was approximately 6-10 nm and they were characterized by TEM. The MBs were purchased from AdemTech in France.

The purchased MBs were two types: amine functionalized (MB-a) and carboxyl functionalized (MB-c). Table 3.1 shows the properties of MBs. The MBs were mono dispersed and superparamagnetic beads. They were composed of magnetic core encapsulated by a hydrophilic polymer shell. The surface of bead was activated with amine or carboxylic acid functionality.

Table 3.1. The properties of the MBs

	MB-a	MB-c
Mean diameter (nm)	510 ±20	510 ±20
Weight per cent	1.0±0.1	5.0±0.1
Solid content (mg/mL)	10	50
Particle number (per mL)	$6.02*10^{10}$	$3.6*10^{11}$
Specific surface area (m^2/g)	5	5
Fe_3O_4 content (per cent)	70	70
Magnetization at saturation (emu/g)	40	40

In order to use MB-c and MB-a in same concentration, with respect to their solid contents, they were diluted with water. After dilution, both MB-c and MB-a have had 1 mg/mL solid contents. In other words, MB-c and MB-a suspensions have 0.1 weight per cent solid contents.

AFM Park Systems XE-100 instrument was used in the experiments. The AFM characterization studies were done by using non-contact AFM tip. Also, two different SEM instruments were used in order to obtain images in higher resolution: XL30 ESEM-FEG/EDAX system at Boğaziçi University and Carl Zeiss Evo 40 Instrument at Yeditepe University. The convective-assembly setup that was used for the assembly of MBs composed of moving stage equipment, which was purchased from PI in Germany.

4. METHODS

4.1. PREPARATION OF SURFACES

4.1.1 Preparation of Hydrophilic and Hydrophobic Unpatterned Surfaces

In this section, preparation of hydrophilic and hydrophobic glass slides is explained. This was done to observe the drying pattern behaviors of MBs on both hydrophilic and hydrophobic surfaces.

In the preparation of hydrophilic glass slides, 10 g of $K_2Cr_2O_7$ was dissolved in enough H_2SO_4, to obtain H_2CrO_4, which is also known as a good glassware cleaning solution. The regular glass slides were submerged in the H_2CrO_4 solution for one day. Since the regular glass slides possess hydroxyl groups on their surfaces, they are naturally hydrophilic at varying degrees depending on the manufacturing processes. However, washing with the chromic acid improves the hydrophilicity of the glass slides.

The hydrophobic surfaces used in the study were prepared by coating the surface of ordinary cleaned glass surface with CH_3SiHCl_2. A set-up seen in Figure 4.1 was used for coating the glass surfaces with this hydrophobic material. Since CH_3SiHCl_2 is volatile at room temperature, it can easily stick to glass surfaces in vapor phase. The glass slide is exposed to its vapor in a closed container. Therefore, a thin organic film on the glass surface is formed. In Figure 4.1, the pipette used to drop a few droplets into the beaker (A), the glass slide lie parallel to the bottom of the beaker (B), the smaller beaker (C), the protector beaker which prevents the evaporating chemical to escape (D) are seen.

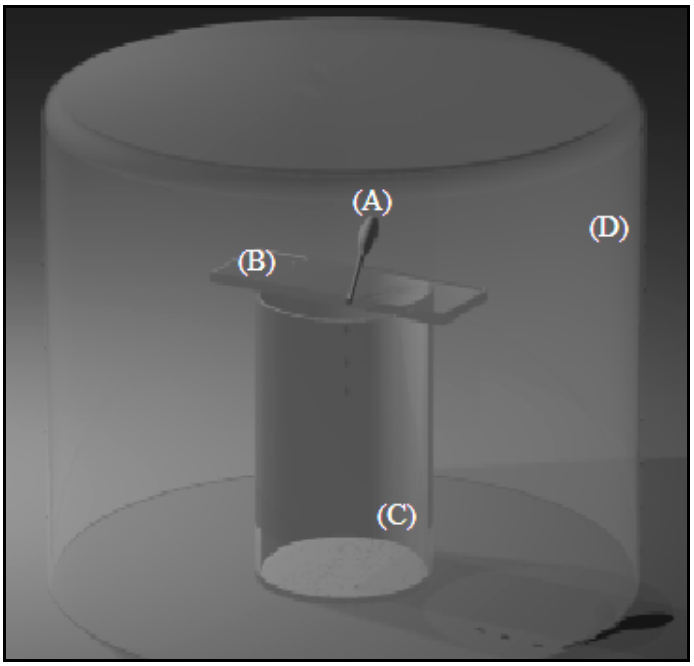

Figure 4.1. The scheme of hydrophobic glass slide preparation

4.1.2. Preparation of Hydrophilic and Hydrophobic Patterned Surfaces

Three different surfaces were used: CD surface, aluminum foil which was removed from CD surface and PDMS surface which is the mold of CD surface. Then, these three surfaces were used for the directed assembly of MBs. In this part of the study, the influence of the surface hydrophilicity and hydrophobicity on the directed assembly of MBs was investigated.

The hydrophobic polymer PDMS was used in template preparation. Slygard 184 silicone elastomer kit was used for PDMS preparation. The kit consists of curing agent and silicone elastomer, which were mixed in the ratio of 1:10, respectively. The fluid polymer was poured onto the substrate that was required to make the mold of it. Because of the hydrophobic nature of air, bubbles were formed on the PDMS. The PDMS-poured-substrate was placed into the desiccator for 10-15 minutes to remove the air bubbles. Finally, the substrate was polymerized in a 70ºC oven for 50-60 minutes. When polymerization process was over, the solid PDMS was peeled off gently by using a bistoury.

CD was used as a template in the experiments. The aluminum foil on the CD was peeled off carefully by a bistoury, Figure 4.2 shows a piece of CD (A), bistoury that is used for peeling process (B), the peeled off aluminum foil (C) and aluminum foil peeled off-CD (D) image. Then, the PDMS mold of CD and PDMS mold of the aluminum foil were used as two different pattern-having-hydrophobic-surfaces. However, aluminum foil peeled-off-CD and the aluminum foil itself were also tested as pattern-having-surfaces which have hydrophilic nature. The CD and aluminum foil were characterized by both SEM and AFM.

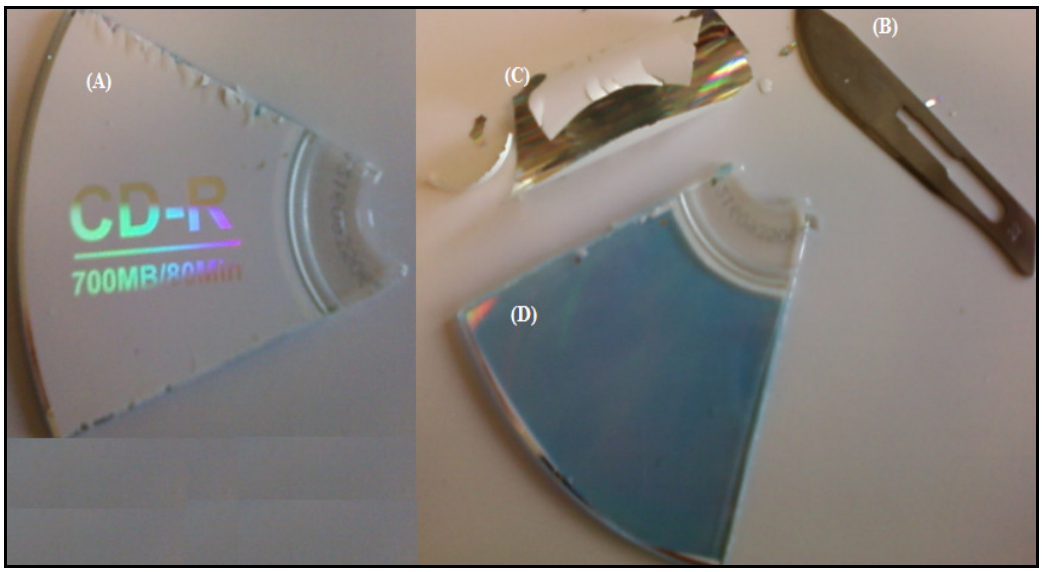

Figure 4.2. The images of a piece of CD (A), bistoury (B), the peeled of aluminum foil (C) and aluminum foil peeled off-CD (D)

4.2. ASSEMBLY OF MBs ON SURFACES

4.2.1. Assembly from a Drying Droplet

A 5 µL suspension of known MB concentration was placed on the prepared surface with the help of a micropipette. This was done with suspensions of MBs in two different solid contents. Also, in the presence of magnetic field drying behavior of MBs were characterized. Figure 4.3 shows drying droplet experiment with magnetic field “on”. The drying patterns were characterized by using SEM.

Figure 4.3. Magnet applied on CD having MNP droplet on

4.2.2. Convective-Assembly

The convective-assembly setup is seen on Figure 4.4. This technique is used as explained in the study of Denkov et al. [225]. A cleaned glass slide or CD surface was fixed on the moving stage. A clean glass slide was placed on top of the fixed glass slide or CD with an angle of 30º. The glass slide is held by a clamp at this particular angle. The solution containing NPs that is to be assembled is spotted at the junction point of two slides. As the stage moves forward, the solution at the junction point is spreaded on the clean glass slide or CD surface. As the suspension of NPs is spread, the solvent starts to evaporate, leaving the NPs to assemble on the surface according to the surface morphology (If there are any channels on the surface, the NPs will fill those channels).

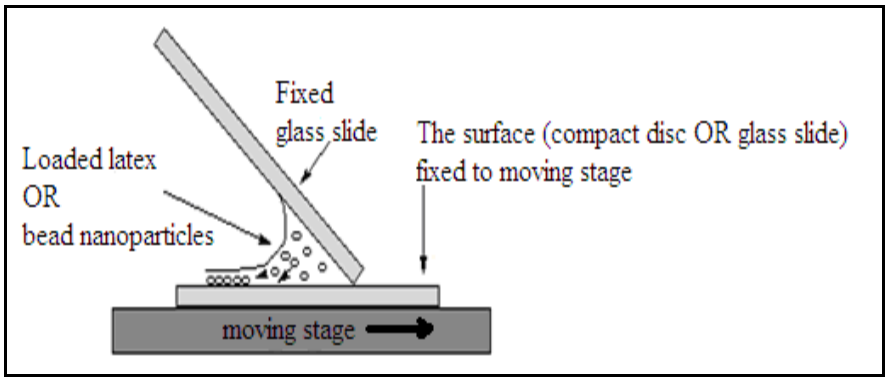

Figure 4.4. The convective-assembly set up

The parameters affecting the convective-assembly method are the stage velocity, loaded suspension volume and concentration of the suspension and the angle of the two glass slides. Therefore, the stage velocity, suspension concentration and volume were the optimization parameters of the experiments, to completely fill the micro channels of the templates used. Optimal conditions were found as 7 μm/s of stage velocity, 20 μL of MB-c solution with 0.1 weight per cent. Room temperature and humidity, which affects the evaporation of solution between the glass slides, were assumed to have no effect.

4.3. CHANGING THE SURFACE CHARGE OF MBs

The interactions of particles to be assembled on surfaces may also influence the assembly process. Therefore, the surface charge effects of MBs on their assembly were also investigated. In order to change the charge of the MB surface, positively charged surfactant CTAB was used. Carboxyl functional group attached negatively charged MBs and amino functional group attached positively charged MBs were treated with CTAB. The diluted bead suspensions were treated with CTAB to coat the surface of the carboxylated MBs to increase their surface hydrophobicity. The carboxyl groups on the surface of the beads are expected to make ionic interaction with positive head groups of CTAB molecules and generate a hydrophobic surface, which is compatible with hydrophobic glass surfaces. The suspensions of MBs were dropped on hydrophilic and hydrophobic glass slides separately to test the success of the assembly. The characterization of patterns formed on hydrophilic and hydrophobic surfaces were carried out by using SEM.

4.4. MAGNETIC FIELD STUDIES

In this section, the presence of a patterned surface between a magnetic field and the substrate that the MNPs were assembled on was investigated. Figure 4.5, demonstrates the experimental procedure up to the magnetic field studies. The prepared surface, with beads assembled into the microchannels, was coated with a thin film of PDMS as shown in Figure 4.5 (C). Then, the MNPs were dropped on the PDMS in the absence and presence of magnetic field that was created by a hand held magnet. The MNP structures formed were characterized by using SEM. Another prepared surface which has MBs layer

underneath the PDMS has also been used for comparison. The influence of solvent types on forming MNPs structures was also studied. The resulting surfaces were characterized by using SEM.

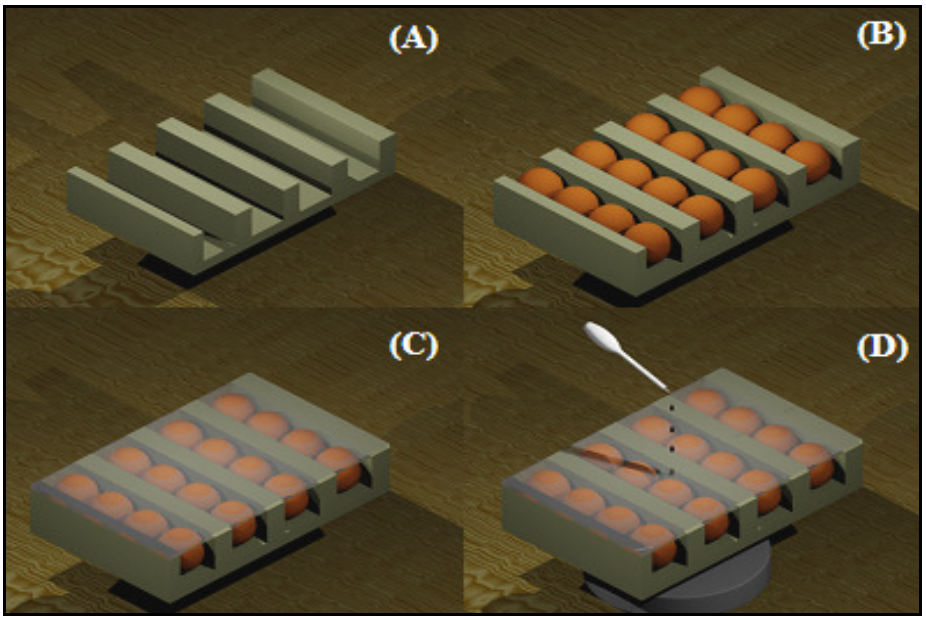

Figure 4.5. The cartoon view of the overall experiments: the CD template having microchannels (A), the assembled beads into the microchannels (B), covered substrate with a thin film of PDMS (C), dropping MNPs under the magnetic field (D)

5. RESULTS and DISCUSSION

The self-assembly of NPs are governed by many weak interactions. These interactions are not controlled well and they are complex. On the other hand, it is possible to control certain parameters such as surface properties of NPs and of the surface where the assembly is targeted. Therefore, the surface properties of MBs and surfaces are investigated by altering their hydrophilicity and hydrophobicity.

5.1. HYDROPHILIC AND HYDROPHOBIC UNPATTERNED SURFACES

In this section, two types of MBs were used: MB-c and MB-a. Their drying behaviors were tested on hydrophilic and hydrophobic glass slides.

The hydrophobic and hydrophilic glass surfaces were prepared as explained in section 4.1.1. Figure 5.1 and 5.2 show both types of MBs, MB-c and MB-a, on hydrophilic and hydrophilic surfaces, respectively. As seen in these figures, while both types of MBs are well dispersed on hydrophilic surfaces, they tend to form small aggregates on hydrophobic surfaces. The effect of addition CTAB into the MB suspension to change the surface properties of MBs was also investigated. Since CTAB has a positively charged head group and a hydrophobic tail, adding a certain amount of CTAB into the MB suspension should influence the polarity on the MB surface. The attempt to change the surface properties by adding CTAB caused serious morphological changes to the MB-c. The response of the MB-a to the addition of CTAB was the same. Figure 5.3 and 5.4 show the morphological change of beads in the presence of CTAB on both hydrophilic and hydrophobic surfaces, respectively.

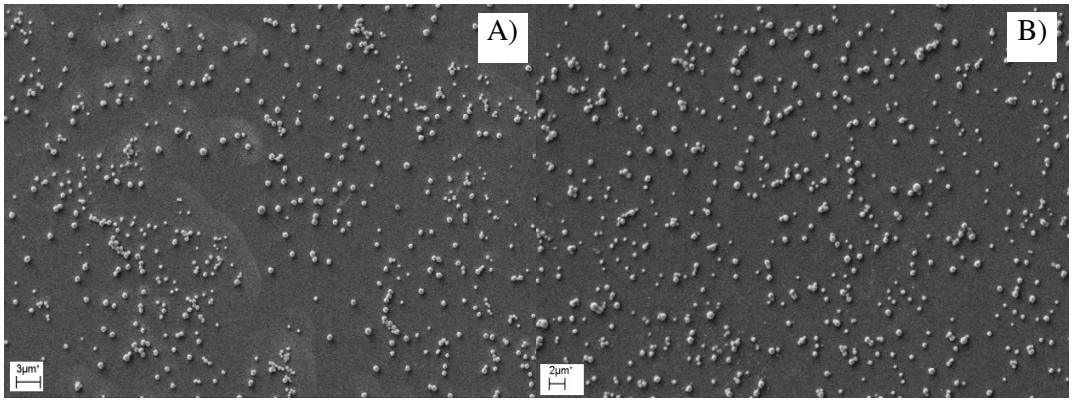

Figure 5.1. The SEM images of MB-a (A) and MB-c (B), on hydrophilic glass slide

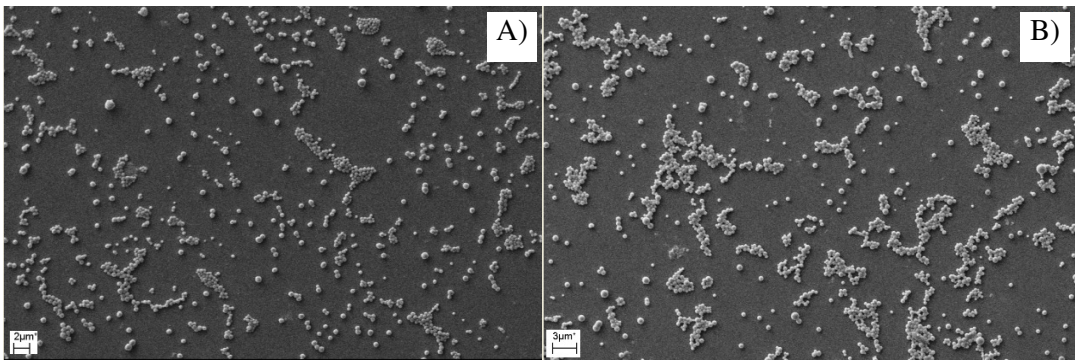

Figure 5.2. The SEM images of MB-a (A) and MB-c (B), both on hydrophobic glass slide

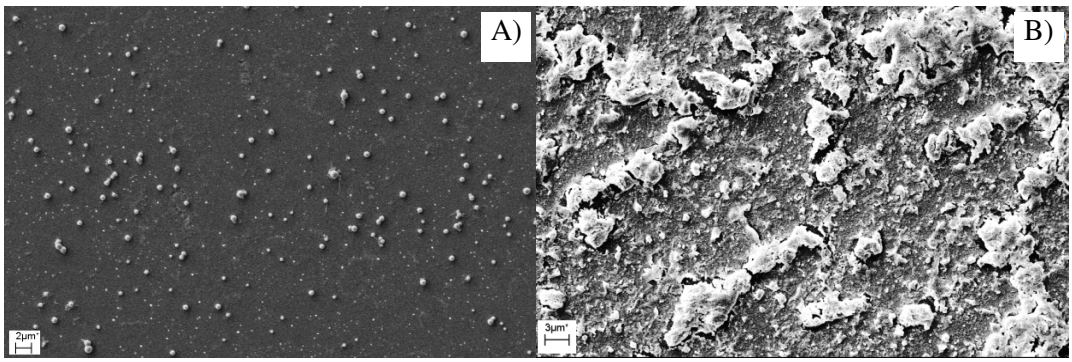

Figure 5.3. The SEM images of beads MB-a (A) and MB-c (B) both with addition of CTAB on hydrophilic glass slide

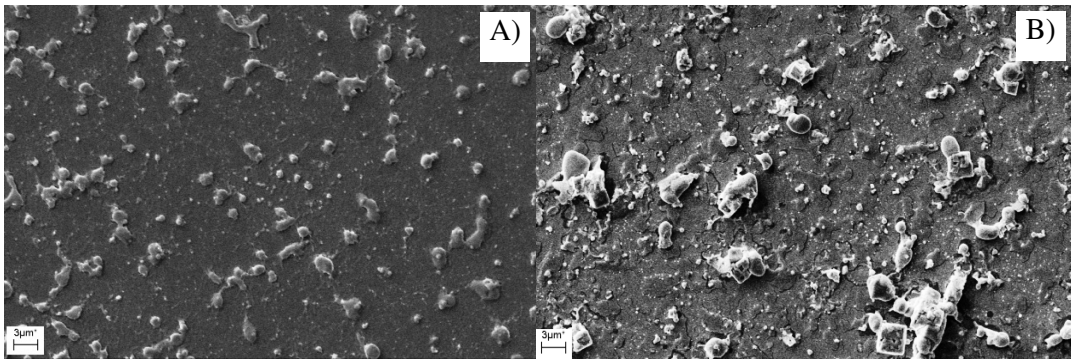

Figure 5.4. The SEM images of beads MB-a (A) and MB-c (B), both with addition of CTAB on hydrophobic glass slide

Overall, it has been observed that CTAB addition has caused the morphological changes on the MBs, and MBs were observed to undergo undesired aggregation on hydrophobic surfaces. On the other hand, on hydrophilic glass slide, MBs did not show any tendency to aggregate and no morphological change was observed. As seen in Figure 5.1, there was not any significant difference in the behavior of MB-a and MB-c on the hydrophilic glass surfaces. For this study, either MB-c or MB-a could have been used and MB-c was chosen to proceed with.

5.2. HYDROPHILIC AND HYDROPHOBIC PATTERNED SURFACES

A commercially available CD was used as both a patterned surface and a template to prepare the patterned surface with different chemical properties. When the aluminum foil on the surface of a CD is removed, the pattern on the polymeric body or the aluminum foil can be used for the directed assembly of MBs into the patterned surface. Both parts of the CD can provide surfaces with different hydrophilic or hydrophobic character. In order to generate a complete hydrophobic patterned surface, PDMS based soft-lithography was employed. The AFM image of the surface pattern of PDMS generated using a CD is seen on Figure 5.5. The red cursor in the Figure 5.5 shows the height of each microchannel. The green cursor shows the distance of two hills on a microchannel. The MBs are proposed to fix into the microchannels. The distance between two hills is estimated as approximately 1.55 µm.

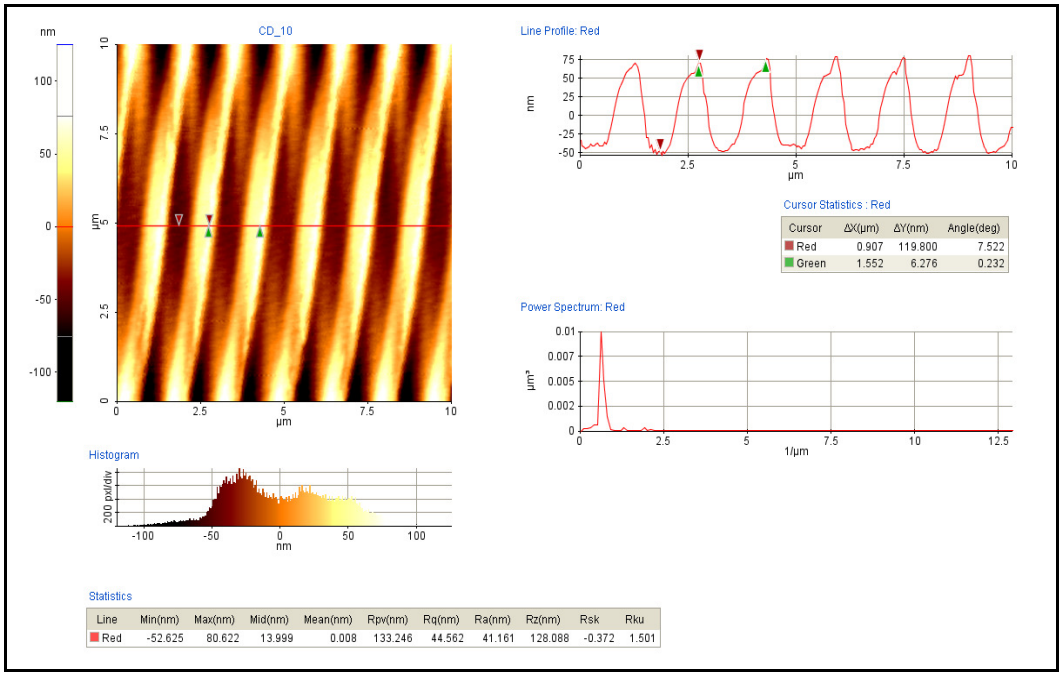

Figure 5.5. The AFM image of PDMS that has the pattern of CD

Also, the aluminum foil which protects the CD pattern was characterized by SEM. It has been observed that aluminum foil has a pattern complementary for the CD pattern. The aluminum foil has the same pattern with the PDMS after applying soft lithography method

to the CD. The only difference of soft lithography product of PDMS and the aluminum foil is their degree of hydrophobicity. PDMS shows hydrophobic behavior whereas the aluminum foil shows the hydrophilic behavior. This difference has been used to test their performance for the directed assembly.

5.3. ASSEMBLY OF MBs ON THE SURFACES

5.3.1. Assembly from a Drying Droplet

The behavior of the beads on both CD surface and aluminum surface was studied with drop casting method. The MBs suspensions were used in two different concentrations. The MBs were dropped on the surfaces and allowed to dry, then characterized by using SEM. Varying concentrations of MB suspensions were tested for optimal filling of the micro-channels. The possibility of assembly of MBs into the microchannels of CD and aluminum foil were investigated by using 0.01 and 0.1 weight per cents MB-c and MB-a droplets. As can be observed from Figures 5.6, 5.7, 5.8 and 5.9, the assembly of beads into the microchannels was not successfully obtained using the mentioned concentrations and templates.

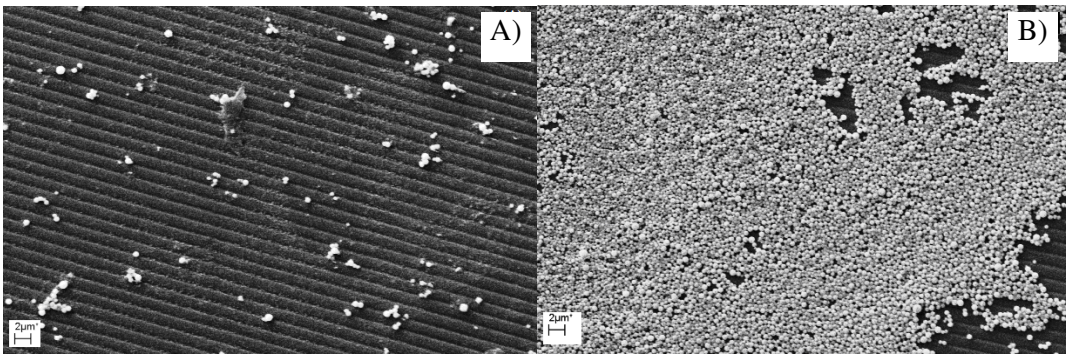

Figure 5.6. The SEM image of 0.01 (A) and. 0.1 weight per cent of MB-a's drying pattern (B) on CD

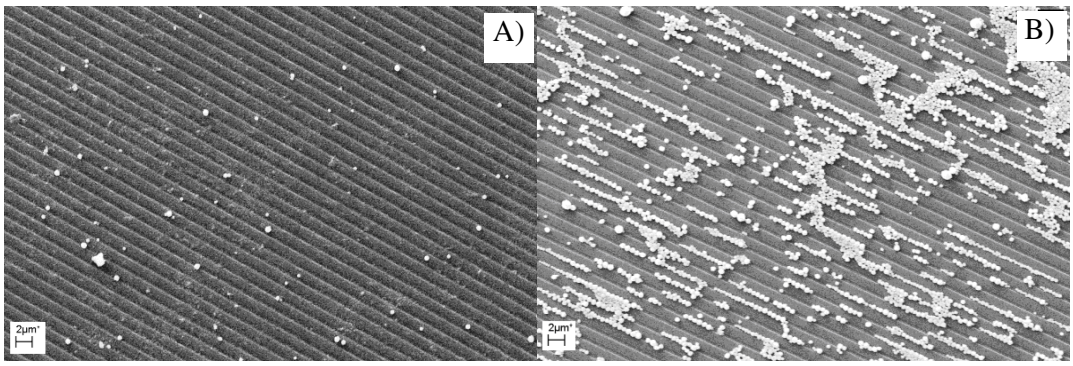

Figure 5.7. The SEM image of 0.01 (A) and 0.1 weight per cent of MB-c's drying pattern (B) on CD

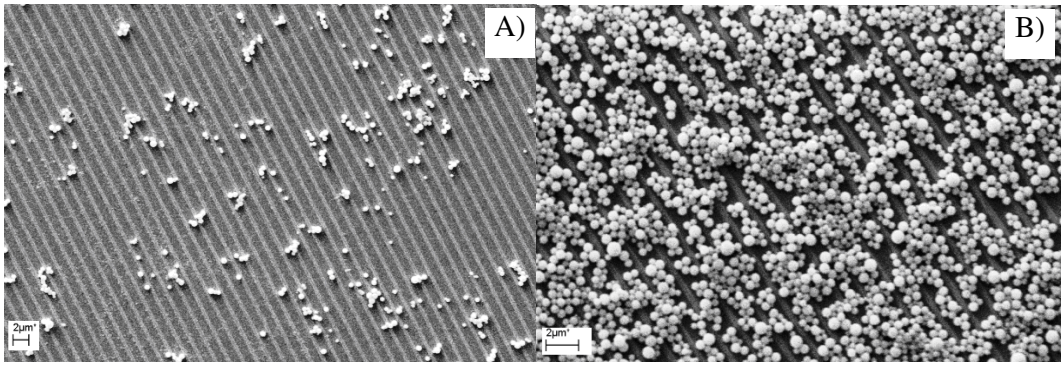

Figure 5.8. The SEM image of 0.01 (A) and 0.1 weight per cent of MB-a's drying pattern (B) on aluminum foil

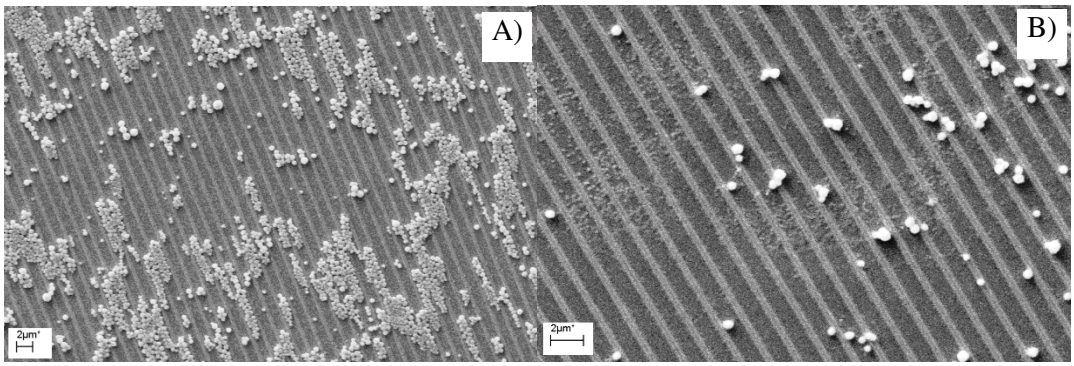

Figure 5.9. The SEM image of 0.01 (A) and 0.1 weight per cent of MB-c's drying pattern (B) on aluminum foil

After the beads were dropped onto the surfaces, magnetic field was applied on during drying. The beads were expected to assemble into the microchannels. Unfortunately, it could not be obtained by this approach. The drying droplets in the presence of magnetic field were observed by using SEM. As can be observed from Figure 4.3, when droplet was dropped on the CD, the particles in the suspension aggregated in the centre of the droplet due to the presence of the magnet. SEM characterization was done at two different sections of the sample. Figure 5.10 shows the edge (A) and the centre (B) of 0.01 weight per cent suspension of bead droplet on the CD in the presence of magnetic field.

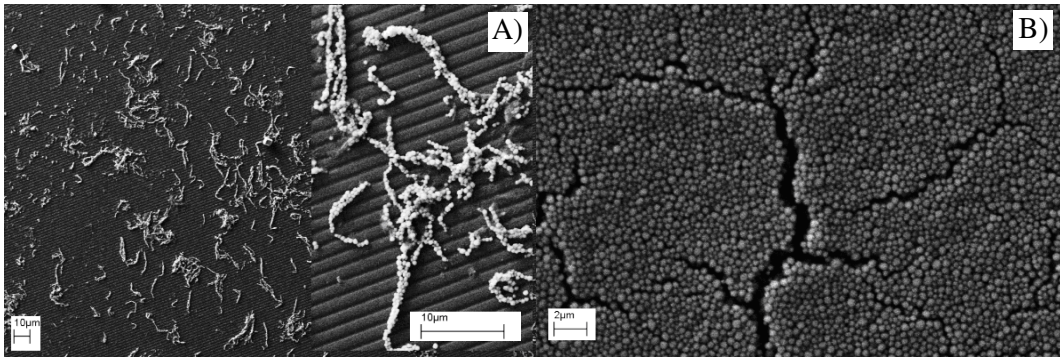

Figure 5.10. The SEM image of drying droplet of 0.01 weight per cent suspension of MBs on the CD in the presence of magnetic field (A), the SEM image from centre of same sample's droplet (B)

It was concluded that, beads did not assemble into the microchannels of CD or aluminum foil in any concentration by the applied approaches above.

5.3.2. Convective-Assembly

Due to having unsatisfactory results from drop casting study, another approach was carried out. In this approach, CD microchannels were filled with MBs by convective-assembly method. The convective-assembly method was explained in the section 4.2.2. Due to having successful performances in previous studies of using the method in assembling AgNPs into the microwells, the convective-assembly method was employed [144, 145].

Three surfaces, CD surface, its complementary aluminum foil surface, and the patterned PDMS surfaces, were used in convective-assembly experiments.

The pattern of CD had been transferred to the PDMS by soft lithography method. The obtained mold was of hydrophobic nature. The mold was used with convective-assembly method in order to fill the MB-c into the microchannels to form a pattern. Two different stage velocities were tried. Figure 5.11 shows the result of convective-assembly of 20 µL MB-c solution with 0.1 weight per cent on PDMS mold of CD with 1 µm/s and 5 µm/s stage velocity.

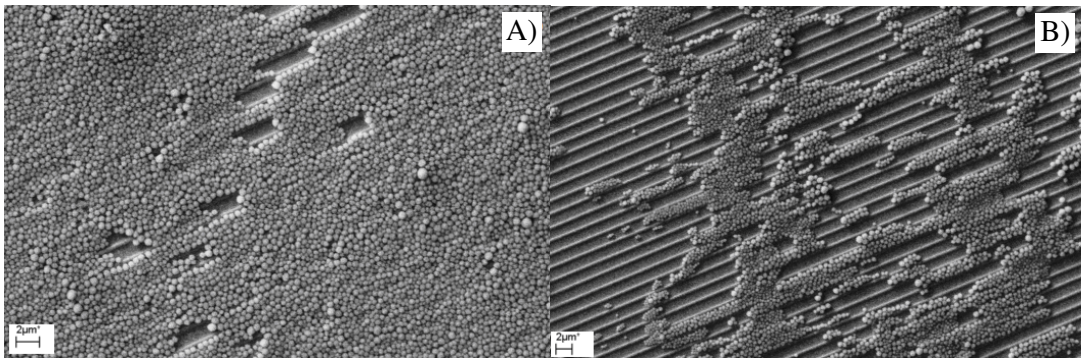

Figure 5.11. The convective-assembly of MB-c on PDMS mold of CD surface with 1 µm/s (A) and with 5 µm/s (B) stage velocity

In Figure 5.11, it was realized that the distance between the microchannels of CD patterned PDMS was too small. On regions of the image where the beads were assembled in the microchannels, assembly resembled a monolayer and the pattern did not play any role.

After finding that the pattern on the PDMS surface cannot be filled with MBs, CD and its complementary aluminum foil were used instead of using PDMS molds of CD samples. CD and the aluminum foil provided hydrophilic surfaces. When droplets of MBs were dropped on CD surface and aluminum foil, it was observed that contact angle of droplet was smaller on the aluminum foil. This visual observation proved that hydrophilicity of aluminum foil surface was higher than that of the CD surface.

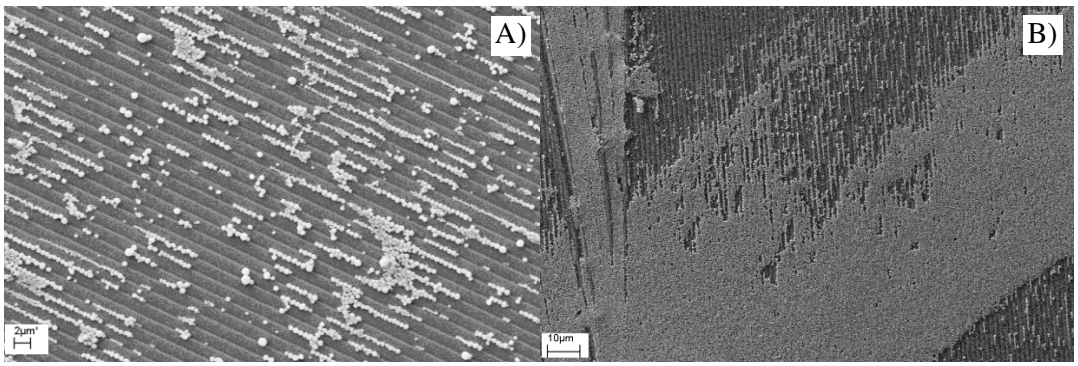

Figure 5.12. The SEM image of 40 µL suspension with 0.1 weight per cent of MB-c (A) and MB-a (B) 1 µm/s stage velocity on CD

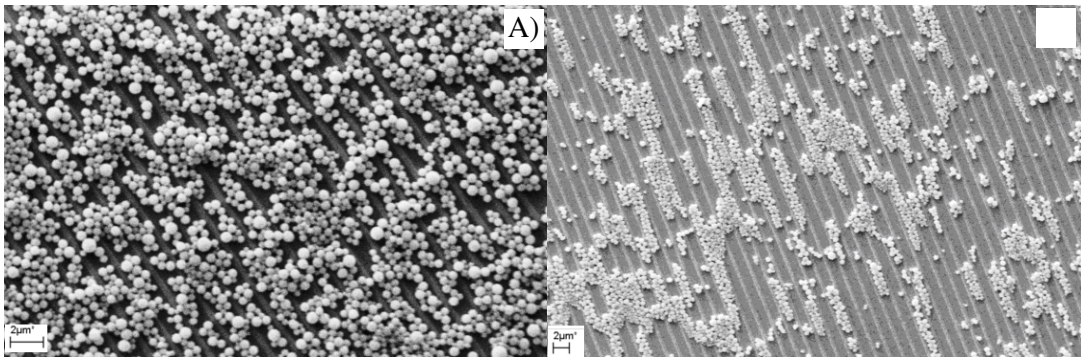

Figure 5.13. The SEM image of 40 µL suspension with 0.1 weight per cent of MB-c (A) and MB-a (B) 1 µm/s stage velocity on aluminum foil

Figure 5.12 and 5.13 show the difference of MBs assembly on CD surface and aluminum foil surface. Figure 5.13 shows the difference of MB-a and MB-c distribution on aluminum foil surface (the complementary of CD pattern) with all other parameters constant. As seen, in Figure 5.12, MB-c and CD surface was a better surface for the filling of the microchannels of CD.

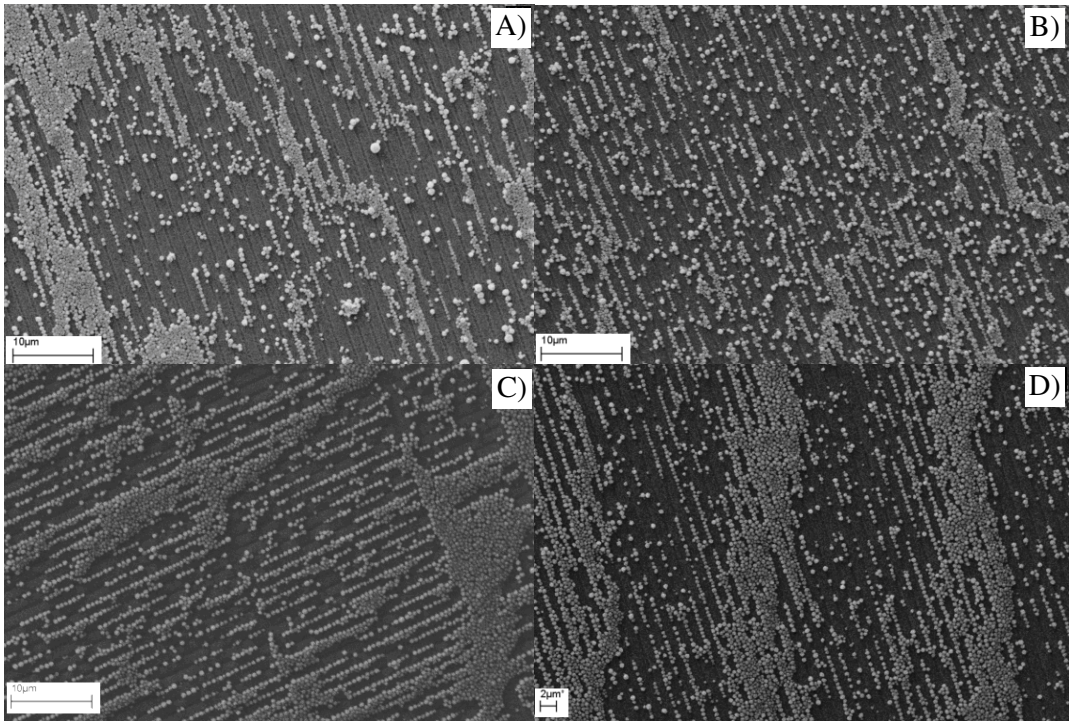

Figure 5.14. The SEM image of distribution for 40 µL suspension of MB-c with 0.1 weight per cent and 1 µm/s (A), 5 µm/s (B), 7 µm/s (C) and 10 µm/s (D) stage velocity

The next step was selecting the optimum stage velocity value. For this aim, different values of stage velocity experiments were performed and the distribution of beads to the microwells were characterized by using SEM. Figures 5.14 shows the stage velocity effects on MB-c distribution on CD microchannels.

The optimum distribution was observed with 7 µm/s trial in Figure 5.14 (C). The next parameter was the loading volume of bead solution. By considering the result represented in Figure 5.14, it was understood that 40 µL of bead solution was a bit excess and so causing the formation of aggregations on the surface. Therefore, lower volumes were employed. Figure 5.15 shows the SEM images of the CD surfaces loaded with 30 µL and 20 µL of bead solutions, respectively.

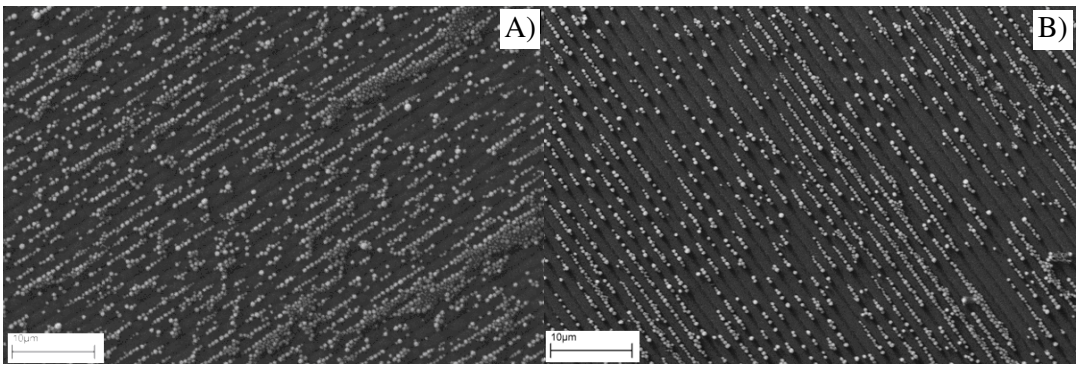

Figure 5.15. The SEM image of 30 µL (A) and 20 µL (B) MB-c distribution having 0.1 weight per cent and 7 µm/s stage velocity

The optimum conditions for distribution of beads into the microchannels of CD itself were observed with 20 µL loading volume of 0.1 weight per cent of MB-c and 7 µm/s stage velocity.

The final step was to coat the patterned surface with a PDMS thin film to immobilize the MBs between CD surface and the MNPs and to investigate their behavior under the influence of a magnetic field.

5.4. ASSEMBLY OF MNPs UNDER THE INFLUENCE OF MAGNETIC FIELD

In the next step, Fe_3O_4 MNPs were used in following drop casting studies in order to obtain higher structures in the presence of magnetic field. The Fe_3O_4 MNPs suspension in water and non-polar solvents namely, hexane, heptane and decane were dropped on the PDMS surface in the presence and absence of magnetic field. The presence of beads and absence of beads underneath the PDMS were also observed to see the role of assembled beads. In the presence of magnetic field, it was observed that beads under the PDMS had enhanced the magnetic forces applied on the MNPs on the PDMS.

In the experiments, magnetic field was applied by using a disc shaped Neodymium magnet, generating a magnetic field of 0.1 T on the surface. By referring to equation 2.1, the force acting on a MNP was related to the following parameters. The susceptibility was related to the material of the particles which was Fe_3O_4. The NPs diameters had been

characterized in TEM and observed that size distribution was narrow. Therefore, the volume of the MNPs was known and assumed to be constant. The remaining parameters affecting the force acting on a MNP were the magnitude of the applied magnetic field and the magnetic field gradient. By changing the values of the magnetic field and magnetic field gradient, force acting on a MNP could have been altered. In the experiments, magnetic field was created by the magnet in the magnitude of 0.1 T. Without an interference to the existing magnetic field gradient, MNPs were dropped on the PDMS surface and their drying behavior were characterized by using SEM. It has been seen that any novel structures of MNPs has not been formed with this magnetic field. By using polymer coated MBs between the PDMS and the prepared surface, magnetic field gradient was enhanced. This enhancement of magnetic field gradient resulting in the increase on the force applied on the MNPs caused the formation of interesting and repetitive structures of MNPs. In the experiments, the MNPs were suspended in various solvents, hexane, heptane, decane and water. The experiments showed that the solvent variation also have an influence on pattern formations.

The MNPs suspended in water were dried on PDMS surface either with or without MBs. Since PDMS was hydrophobic, the droplet of MNPs suspended in water did not show any analyzable results. The use of hydrophilic solvent (H_2O) onto a hydrophobic surface PDMS may cause the observed results. Figure 5.16 shows that water was not a suitable solvent to perform drying experiment on these hydrophobic PDMS surfaces. The difference of structural MNPs formation on the beads and on PDMS alone can be observed in Figure 5.16 (A) and 5.16 (B).

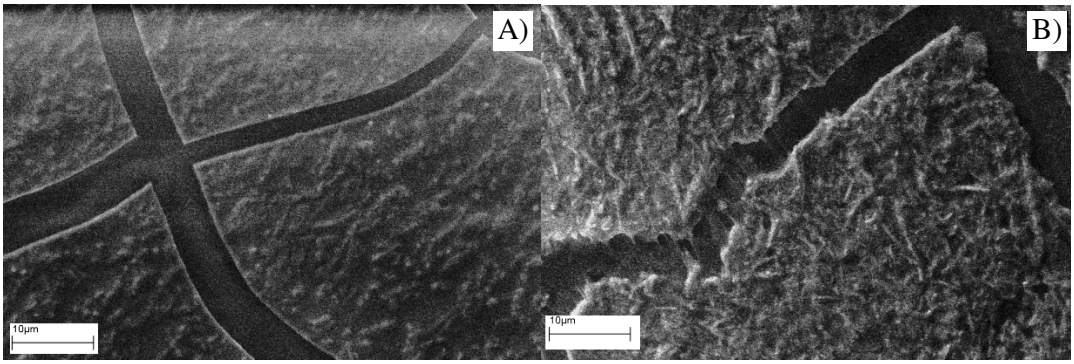

Figure 5.16. The structures formed after drying of MNPs suspended in water on the beads assembly underneath the PDMS (A) and on PDMS alone (B) in the presence of magnetic field

Since MNPs suspended in water results were not analyzable, MNPs suspended in non-polar solvents (hexane, heptane, and decane) were synthesized. The droplet of MNPs in non-polar solvents was used in the next set of experiments. Vapor pressures of hexane, heptane and decane are given as 130 mm Hg at 20 ºC, 40 mm Hg at 20 ºC, and 1.4 mm Hg at 25 ºC [226]. Figures 5.17 and 5.18 show the formed structures of MNPs suspended in hexane with and without the MBs. Since high vapor pressures shows more volatility, it is possible that the evaporation of hexane was too fast for MNP structures to form even in the presence of beads or applied magnetic field. The effect of presence of MBs assembly under the PDMS on MNPs suspended in hexane can be observed in Figure 5.17 and 5.18.

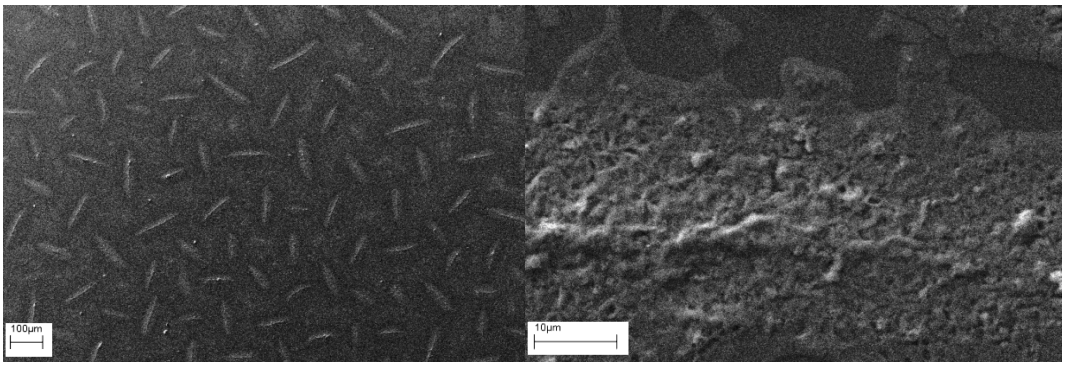

Figure 5.17. The structures formed after drying of MNPs suspended in hexane on the beads assembly underneath the PDMS in the presence of magnetic field

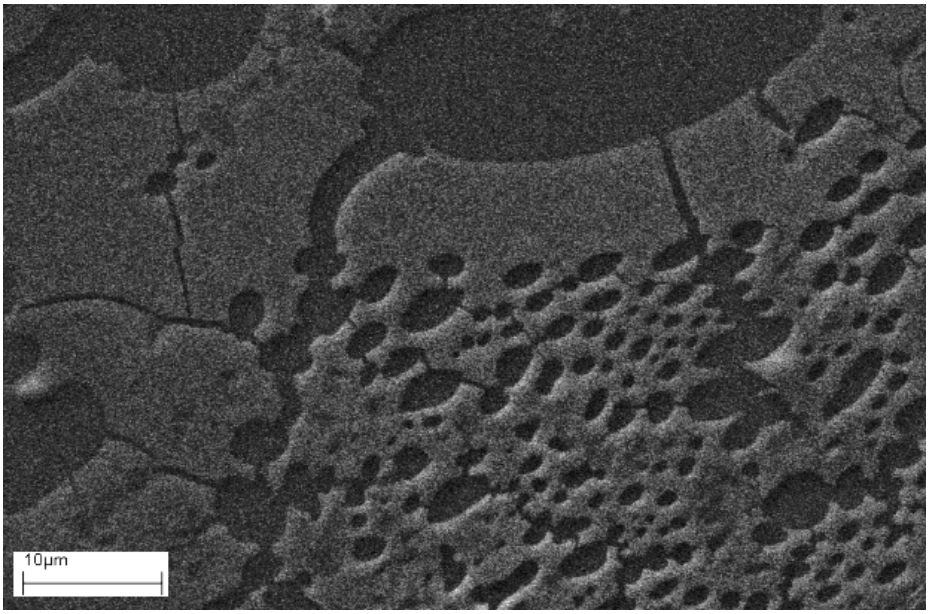

Figure 5.18 The structures formed after drying of MNPs suspended in the hexane on the PDMS alone in the presence of magnetic field

Since MNPs suspended in hexane has given hints to possible interesting results, other non-polar organic solvents with relatively lower volatilities were used for further trials. Heptane and decane were the next two solvents. Their relatively low volatilities which allowed the MNPs sufficient time to dry under the influence of the magnetic force, which resulted in the formation of MNP structures.

Figure 5.19 shows the MNPs suspended in heptane drying pattern while having beads assembly under the PDMS and in the presence of magnetic field. On the other hand, in the Figure 5.20 (A) and (B) the effect of the presence of magnetic field was observed in the assembly of the MBs presence. By comparing the two cases, it can be said that the presence of assembled beads made a clear change in the formation of drying patterns in the presence of magnetic field. The importance of assembled beads was due to the enhancement of the force acting on the particle when an external magnetic field was applied on.

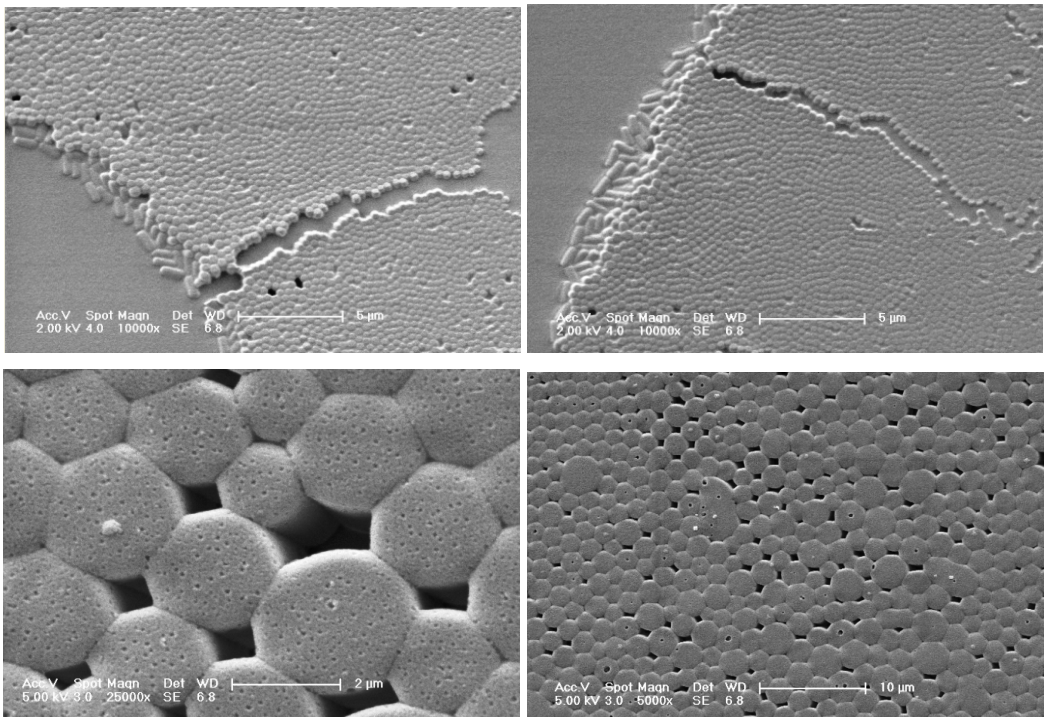

Figure 5.19. The structures formed after drying of MNPs suspended in the heptane on the beads assembly underneath the PDMS in the presence of magnetic field

In the presence and absence of magnetic field, droplets of MNP suspensions in organic solvents were dried on the PDMS that had assembled beads underneath. In the presence of magnetic field interesting and repetitive patterns of MNPs were observed. Figure 5.21 show the patterns of MNPs suspended in decane in the absence of magnetic field. Any structures of MNP have not been observed in the absence of magnetic field. Figures 5.19 and 5.22 show when magnetic field was present patterns of MNPs suspended in heptane and decane, respectively. It was clear that the presence of magnetic field enhanced the pattern formations of MNPs on the PDMS surfaces.

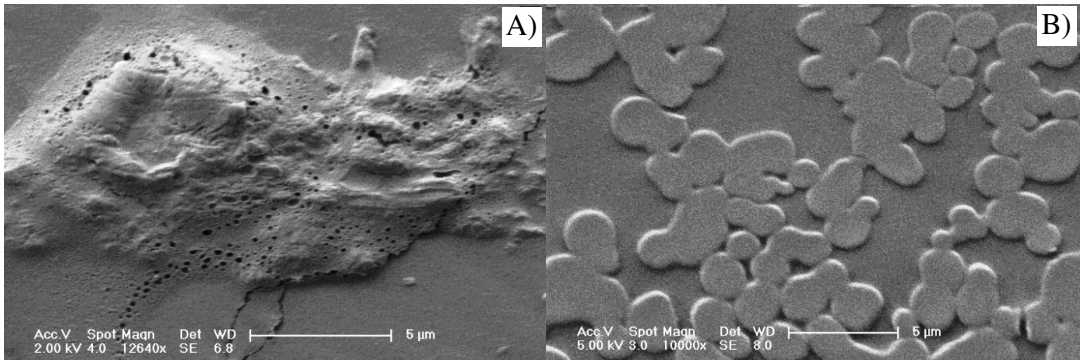

Figure 5.20. The structures formed after drying of MNPs suspended in heptane in the absence of magnetic field (A) and in the presence of magnetic field (B) on the assembly of MBs

As the effect of assembled beads existence under the PDMS had been tested, magnetic field effect on pattern formation was also observed. Figure 5.20 (A) and 5.20 (B) show the structure of MNPs suspended in heptane in the absence and presence of magnetic field, respectively.

More unusual and interesting results were obtained by other solvent, decane, trials. The results obtained from heptane in the presence of magnetic field and beads assembly were interesting and novel, whereas results obtained from decane trials were more interesting. Figure 5.21 shows the MNPs suspended in decane drying patterns in the absence of magnetic field. Although the existence of MBs assembly under the PDMS, there were no promising drying patterns of the MNPs suspended in decane.

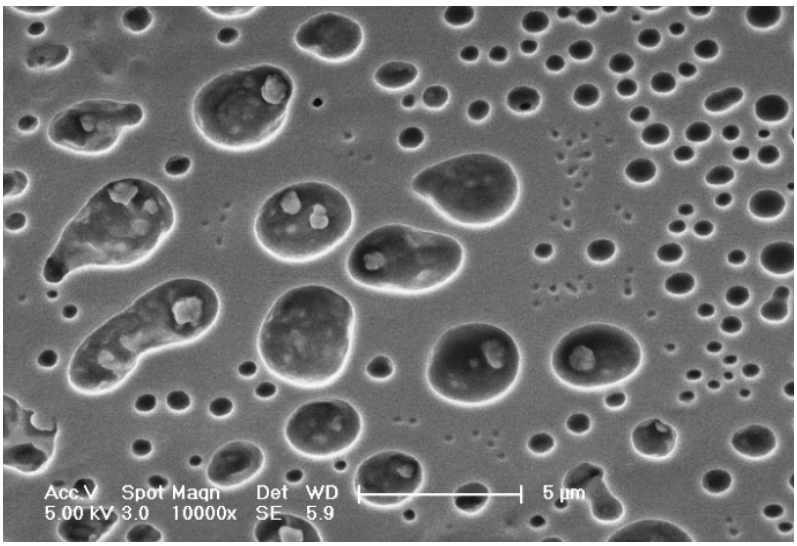

Figure 5.21. The structures formed after drying of MNPs suspended in decane on the assembly of beads underneath the PDMS in the absence of magnetic field

On the other hand, results obtained from the trials of MNPs suspended in decane in the presence of magnetic field and MBs assembly were novel. Most importantly, the formed structures of MNPs were reproducible and repetitive. The experiments were done many times and the repeated patterns have been obtained as seen in Figure 5.22 below.

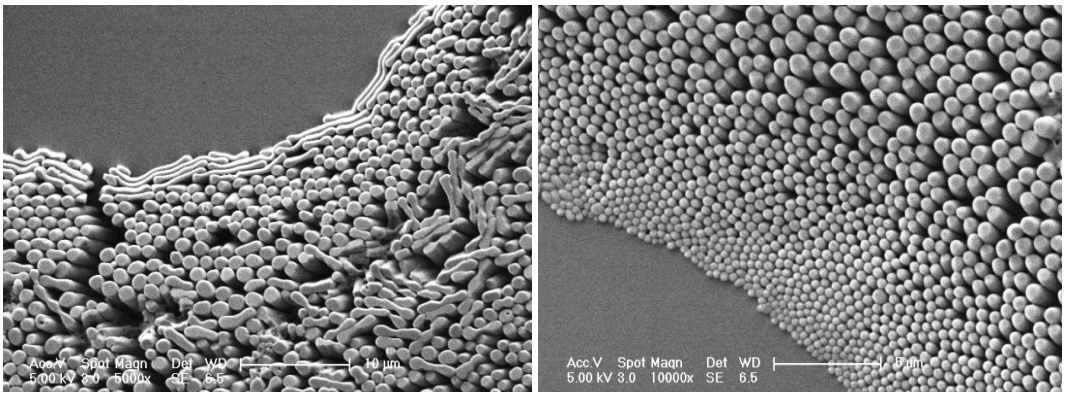

Figure 5.22. The structures formed after drying of MNPs suspended in decane on the assembled beads underneath the PDMS in the presence of magnetic field

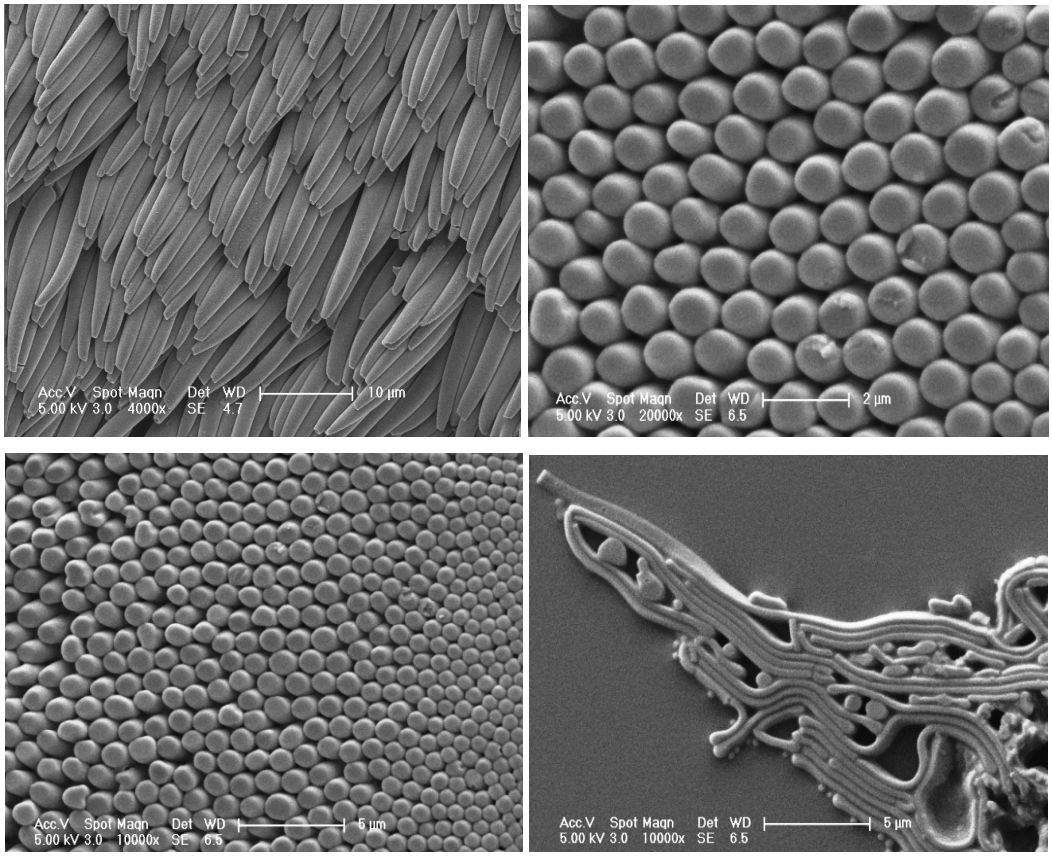

Figure 5.22. The structures formed after drying of MNPs suspended in decane on the assembled beads underneath the PDMS in the presence of magnetic field (cont'd)

In order to investigate the effect of the MBs pattern onto the structures formed by MNPs instead of filling the channels of a CD and obtaining patterns shown in Figures 5.19 and 5.22, a monolayer of MBs were also studied. Due to time constraints, the monolayer formation was not achieved onto a CD surface but we are able to have a monolayer onto a glass surface. In Figure 5.23, although the monolayer was not giving similar results, or any particular MNP structures, it is impossible to make a direct comparison as the difference in glass and CD substrate may be the reason of the observed behavior. Therefore, it is important to perform these experiments with a monolayer on a CD surface.

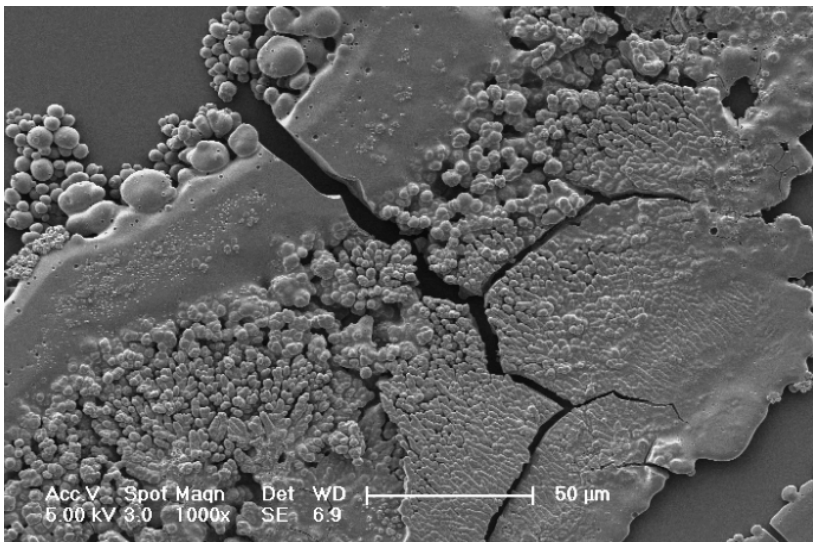

Figure 5.23. The structures formed after drying of MNPs suspended in decane on the drying droplet of beads underneath the PDMS and on glass slide in the presence of magnetic field

In Figure 5.23, there were two parameters that have been changed. One was using the glass slide and the other was the using of MBs monolayer. One of them or both of them has prevented the formation of structures formed by MNPs. To understand which one of two was responsible from this result, a droplet of MBs was let to dry on a CD. The MBs dried in a chaotic pattern (not in monolayer form) onto the CD. After covering the CD with a thin layer of PDMS, the droplet of MNPs was dropped on and let to dry in the presence of magnetic field. Figure 5.24 shows the resulting images.

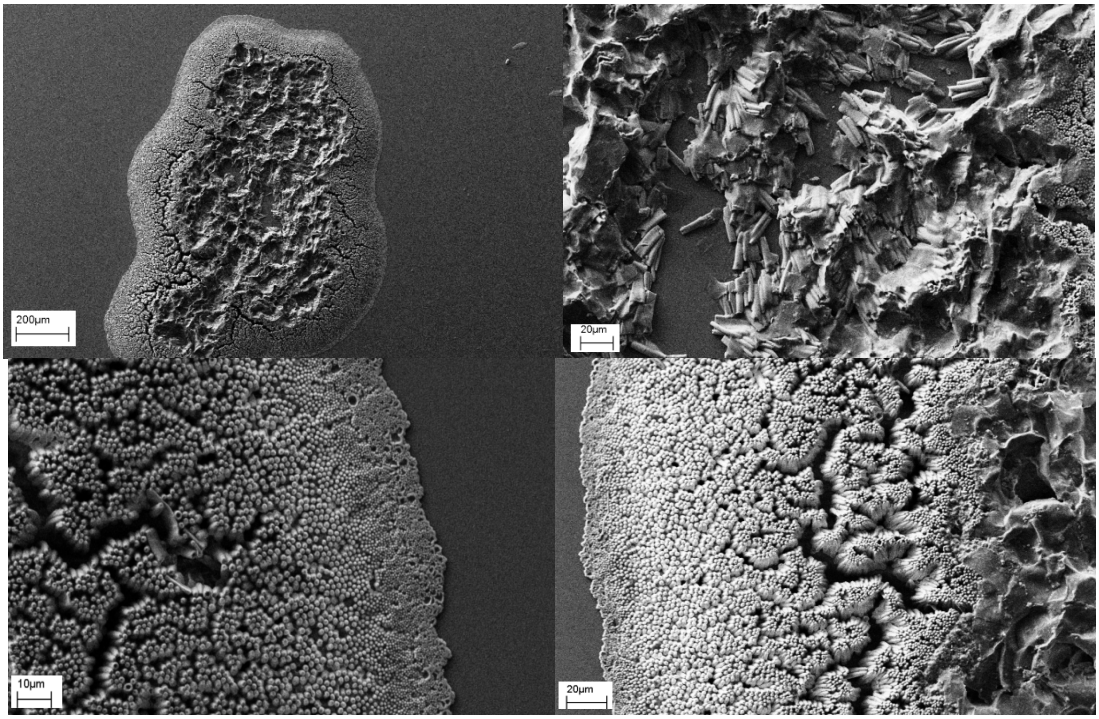

Figure 5.24. The structures formed after drying of MNPs suspended in decane on the drying droplet of beads underneath the PDMS and on CD in the presence of magnetic field

It was concluded that the presence of MBs in assembled form or in drying droplet form play an important role in the formation of MNPs structures on the PDMS. By comparing Figure 5.23 and 5.24, it can be said that assembled MBs are forming better MNP structures than the MBs assembled on surfaces during drying of a MB droplet both in the presence of magnetic field. The presence of magnetic field and MBs under the PDMS have caused formation of MNPs structures. Also, the solvent was another important parameter in the formation of the structures. The volatilities of solvents have caused different structural formations as can be seen in the above figures.

6. CONCLUSION and RECOMMENDATIONS

6.1. CONCLUSION

In this study, the aim is to find a simple way to obtain a renewable pattern by using MNPs. The obtained patterns can be used in sensing, diagnosis, nanomedicine and separation processes. The ease of obtaining the resulting patterns, non-expensive materials used in the experiments and reproducible patterns obtained at the end are the main three prominent properties of the whole work.

The assembly of MBs on both hydrophilic and hydrophobic glass slides was investigated. It was found that the surface of commercially available CD was suitable for the assembly of MB-c. The assembly of the MBs was achieved using the convective-assembly method that allows the packing of particles in well ordered manner as the solvent evaporates from the moving droplets. The optimal conditions for the convective-assembly were 20 μL of MB-c suspension with 0.1 weight per cent, 30º of angle between the glass slide and the CD and 7 μm/s stage velocity. After filling the microchannels of the CD, a thin layer of PDMS is covered onto the surface for further process.

It was demonstrated that the presence of a patterned layer sandwiched between the applied magnetic field and the MNPs assembled on the surfaces had a dramatic effect on the formation of unique higher structures. Furthermore, drying droplet of MNPs in various solvents, onto the PDMS in the presence of magnetic field created repetitive and tubular like structures. The obtained resulting MNP structures were characterized by using SEM.

As a conclusion, the represented work offers a new, renewable, less-time consuming and inexpensive way of having repetitive patterns which can be used in vast areas of nanotechnology and nanobiotechnology applications such as sensing and diagnosis.

6.2. RECOMMENDATIONS

As a future work, MNP structures formed on the PDMS which have either the MBs assembly into the microchannels of the CD or a monolayer of the MBs on the CD surface may be compared. In this thesis, the existence of MBs enhanced the magnetic field gradient. By referring to equation 2.1, other parameters as magnitude of magnetic field may be manipulated on. Although knowing that Fe_3O_4 MNPs have highest magnetic susceptibility value, instead of Fe_3O_4 MNPs, another type of MNPs may be synthesized and used which will change the magnetic susceptibility factor. Therefore, resulting MNP structures may undergo a change.

In this thesis, CD was used as a template for MBs assembly. Instead of using CD, a different template may be used which have a different pattern on its surface.

The MNP structures had been forming tubular like structures in y-axis of a coordinate system. The reason for that direction may be the magnet position during the drying process. When magnet is applied on x-axis, the direction of resulting MNP structures may be tested.

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