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Two- and Three-Dimensional Network of Nanoparticles via Polymer-Mediated Self-Assembly

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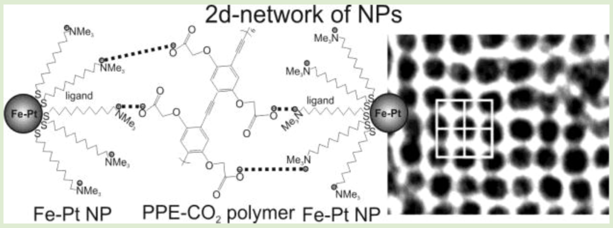
Supporting Information

ABSTRACT: We show a route to produce a two- and three-dimensional network of nanoparticles via polymer-mediated self-assembly. A negatively charged polymer, CO_2-functionalized poly (*para*-phenyleneethylene) (PPE-CO_2), is used to build this network of iron−platinum (Fe−Pt) nanoparticles. The nanoparticles arrange locally in hexagonal and cubic lattice type network structures. The size and form of the networks are characterized with atomic force microscopy (AFM), transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and grazing incidence small-angle X-ray scattering (GISAXS). In thin film the network is perturbed due to the force field acting during spin coating.



Arrays of nanoparticles (NPs) as well as magnetic materials are of potential interest because of their application in the field of DNA motifs,[1] biosensors,[2] photovoltaics,[3] optics,[4] catalysts,[5] plasmonics,[6] and high density data storage devices.[7] Using polymers[8] and biopolymers[9] as ligands, particle-cooperated self-assembly,[10] the Langmuir−Blodgett technique,[11] block copolymer templates,[12] supramolecular interactions,[13] surface segregation,[14] multipoint hydrogen bonding,[15] and DNA-base-pairing[16] are reported strategies to produce assemblies of NPs. For direct application as sensors[17] or in microelectronics[18] or in photovoltaics,[19] a planar array of NPs on solid substrate is important. Spin-coating and dip-coating techniques can produce a monolayer of NPs on a solid substrate from a dispersion of NPs, but the NPs are not chemically bound there. Conjugate polymers[20] with multiple functional groups offer the possibility to bind to two or more NPs at the same time. Electrostatic interaction in between the functional groups present in the water-soluble conjugate polymers and functional groups present in the ligands attached to the NPs can bind the NPs with each other to form a network. The spin coating of such a network of NPs on top of a solid substrate can produce a network of NPs.

In this Letter, we show a new route to produce a two- and three-dimensional network of magnetic NPs using conjugate polymers on a solid substrate.

The synthesis procedure is illustrated schematically in the Scheme 1. Fe−Pt NPs with oleic acid and oleylamine were synthesized according to the reported procedure.[21] The ligands were exchanged via place exchange reaction with SH-C_{11}-trimethylammonium bromide. Fe−Pt NPs with these trimethylammonium cationic ligands react with CO_2-functionalized poly (*para*-phenyleneethylene) (PPE-CO_2) polymer in water at pH = 7. The polymers and the cationic ligands of the NPs ionize in water at pH = 7. As a result, they bind to each other via ionic interaction. Because of the presence of 24 carboxylic acid groups in one single polymer chain, more than one NP was bound via their ligands. After 24 h, the network of NPs was obtained as dark precipitate at the bottom of the reaction container. This precipitate was stored for the structural characterization by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS).

A dispersion of the network of NPs in water was spin-coated on top of silicon cleaned by acid solution[22] to prepare a thin film of the network of NPs. The residual water was removed by heating the sample up to 100 °C in a vacuum oven for 24 h. These samples are investigated with grazing incidence small-angle X-ray scattering (GISAXS)[23] and atomic force microscopy (AFM).

Details of SAXS and AFM analysis are given in the Supporting Information.

Figure 1a,b shows the TEM images of the networks of Fe−Pt NPs. The Fe−Pt NPs are visible as spherical dark objects. Two local types of mesoscopic crystalline arrangement of NPs can

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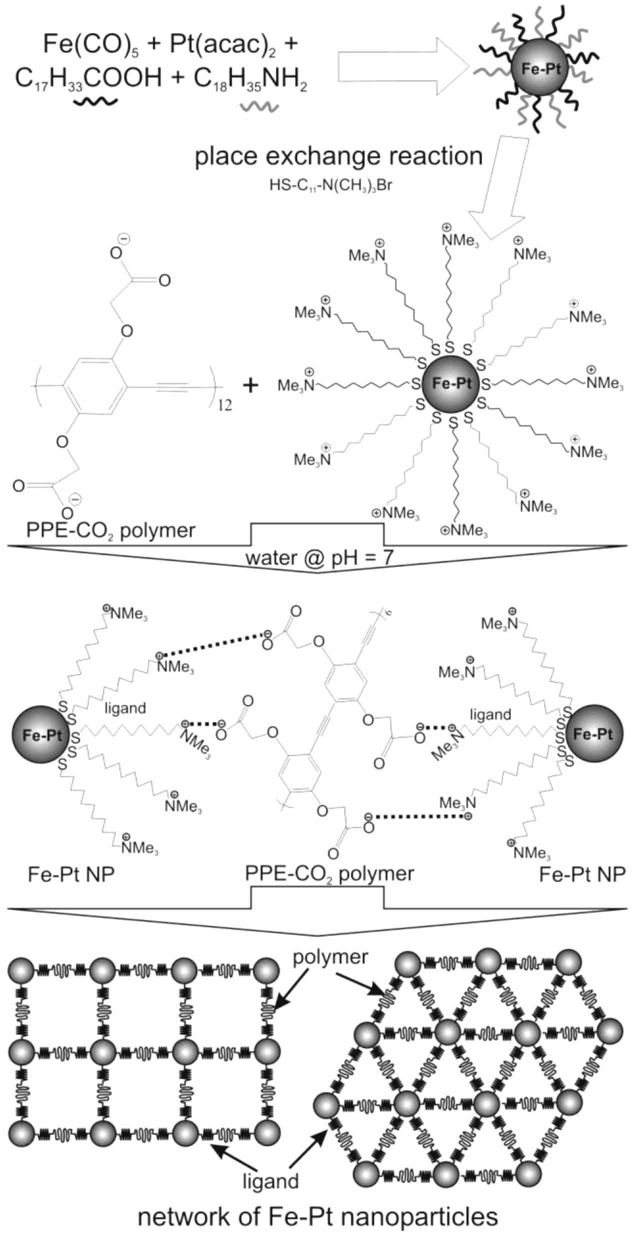
Scheme 1. Formation of the Network of Fe−Pt NPs and Two Possible Arrangements, Cubic and Hexagonal



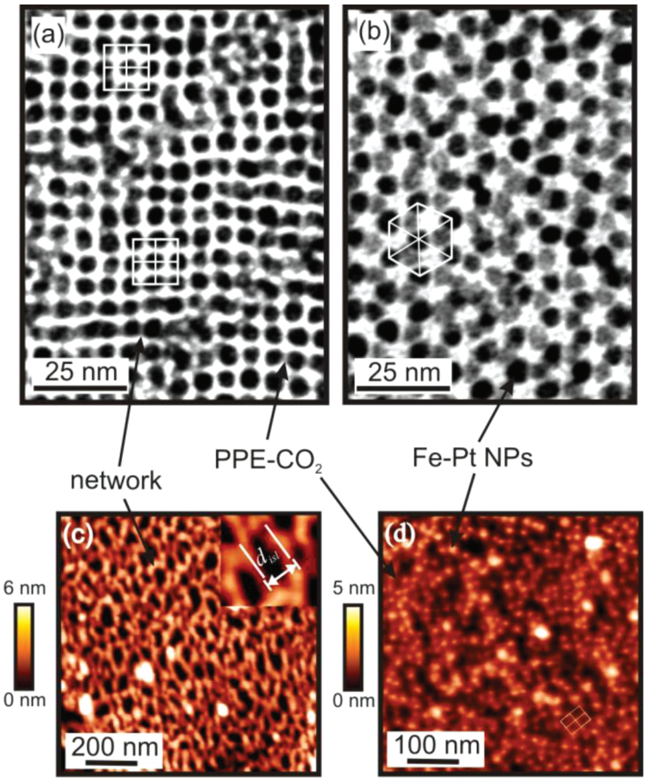


Figure 1. (a, b) TEM images of the networks of Fe−Pt NPs. The circular features in the TEM images are the NPs. Cubic (a) and hexagonal close packing (hcp) (b) arrangements of the NPs are observed. (c, d) AFM topography images showing the network and individual nanoparticles. D_{isl} is the distance between two neighbor islands present in the network. The local cubic lattice structure present in the network is shown by drawing a unit cell.

easily be identified. The first one is cubic (a), and the other one is hexagonal close packing, hcp (b). The 4-fold symmetry for cubic packing and 6-fold symmetry for hcp are illustrated by drawing the unit cells. The PPE-CO$_2$ polymers binding the neighboring NPs are also visible in the TEM images as the gray bridges marked by the arrows in Figure 1a. The two types of lattice structures resulted from the growth of individual domains which prevents installation of large ordered areas. The numerous defects in the obtained structures could arise from an oligomerization process which would likewise generate this sort of assembly. Most of the formed networks have an hcp arrangement. Only a few of the formed networks have a cubic arrangement. The shape of the NPs itself is found to be spherical. The diameter of the Fe−Pt NPs is measured from the TEM images by using ImageJ software and found to be (5.5 ± 0.5) nm with oleic acid and olylamine ligands. The interparticle distances in the network are measured by SAXS (see Supporting Information, Figure S1) and found to be (6.2 ± 0.5) nm.

Figure 1c,d shows AFM images of the monolayer of a network of NPs formed on top of silicon substrate via spin coating with different magnifications. The network structure is very clearly visible and results in different heights (Figure 1c). However, the regular lattice structures present in the bulk are not present in the thin film because of the very strong lateral shear force acting during spin-coating. The magnified topography image (Figure 1d) shows how NPs are connected with each other via the polymers forming the network. Only few domains having the deformed cubic and the hcp lattice structures can still be seen in the thin film (shown in Figure 1c).

For improved statistics the thin film network of NPs was further characterized with GISAXS.[23] The two-dimensional (2D) GISAXS pattern and the out-of-plane cut are presented in Figure 2. Two most prominent lateral lengths were extracted. The first one (denoted by q^* in Figure 2b) corresponds to a lateral length of (85 ± 15) nm, which is the inter-island distance (d_{isl}) present in the network. The second most prominent lateral length (denoted as q_d in Figure 2b) is (9 ± 1) nm, which corresponds to the interparticle distance between the NPs present in the network. The strong shear force acting on the network during the spin coating process stretches the network itself. As a result, the interparticle distance in the monolayer is larger than that in the bulk and less regular which

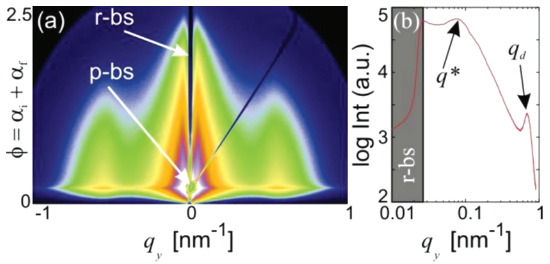


Figure 2. GISAXS investigation of the network of Fe−Pt NPs. (a) 2D GISAXS pattern; (b) out-of-plane cut at exit angle of α_f = 0.16°.

results in the absence of higher order maxima in the GISAXS data.

In summary, we have shown a route to synthesize two- and three-dimensional networks of NPs, using ionic interaction in between the conjugate polymers having anionic carboxylic acid groups in the repeating units and the cationic ligands attached to the NPs. The network has predominantly a hexagonal lattice structure with some domains having a cubic lattice structure. A thin film of the network of NPs has been successfully produced by spin coating. Thus, polymer-mediated self-assembly via ionic interaction of NPs followed by spin coating can be a pathway to produce a thin film network of NPs.

EXPERIMENTAL METHODS

Iron pentacarbonyl, $Fe(CO)_5$, and platinum(II) acetylacetonate, $Pt(acac)_2$, were purchased from Acros Chemical Co. All other used solvents were purchased from Sigma-Aldrich Chemical Co. Milli-Q water and the solvents were used without further purification. A Digi-Sense temperature controller R/S (model 68900-11) was used to control the temperature during synthesis of NPs.

CO_2-functionalized poly(*para*-phenyleneethylene) ($PPE-CO_2$) polymer with a molecular weight of 6.6 kg/mol and polydispersity of 1.88 was used for synthesis of the network. The iron−platinum (Fe−Pt) NPs were synthesized through thermal decomposition of $Fe(CO)_5$ and $Pt(acac)_2$ in hot organic solvents following a procedure described elsewhere.[21] Oleic acid and oleylamine were used as ligands to avoid agglomeration of NPs. Ethanol was added to the NPs in hexane to obtain the precipitate of NPs. This precipitate was centrifuged and mixed with thiol ligands $SH-C_{11}$-trimethylammonium bromide with 1:3 ratios. The thiol ligands replaced the preliminary stabilizing ligands attached to the NPs through a place exchange reaction. The dark precipitate of the NPs was obtained by adding ethanol to the reaction mixture after a place exchange reaction. The excess oleic acids and oleyl amine ligands were removed away by repeated washing with dichloromethane. The NPs with the thiol ligands were then dispersed and stabilized in methanol at the final stage.

The precipitate of the formed networks of NPs was placed on a 300-mesh carbon-coated Cu-grid from dispersion in water and dried at room temperature. The dried networks of NPs on the Cu-grid have been investigated by JEOL 2000 *fx* TEM operating at 200 keV.

The thin film of the networks of NPs on top of silicon was investigated by using an NTEGRA-Aura atomic force microscope (AFM). The AFM was operated in semicontact mode using an ultrasharp cantilever having a tip with a high aspect ratio and an asymptotic conical shape. The background due to the scanner-tube movement was fully subtracted from the raw data. Statistical analysis of the AFM data via calculation of the power spectral density function is shown in the Supporting Information.

Samples for the SAXS measurement were prepared by casting a drop of dispersion of networks of NPs in water on Kapton foils followed by drying at room temperature in a closed chamber. The SAXS measurement was carried out using an in-house set up from Molecular Metrology Inc. (presently sold as Rigaku S-Max3000) at a wavelength of λ = 0.154 nm. The distance between the sample and the detector was 1.5 m.

GISAXS experiments were carried out at the beamline BW4 of the DORIS III storage ring at HASYLAB (DESY, Hamburg, Germany). At the selected wavelength, λ = 0.138 nm, the beam was focused to the size smaller than 25 μm × 40 μm ($V \times H$). The sample was placed horizontally on a goniometer. A beamstop was used to block the direct beam in front of the detector. Besides, a rod-like moveable beamstop (r-bs) and a point-like beamstop (p-bs) were also used to block the very high reflected intensity on the detector. To achieve high surface sensitivity, the incident angle α_i = 0.15° was used. The scattered intensities were recorded by a 2D detector (MARCCD 165; 2048 × 2048 pixel; pixel size 79.1 μm) positioned at a distance of D_{SD} = 1.993 m behind the sample.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Small-angle X-ray scattering investigation and AFM analysis of the networks of NPs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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