Controlling the anisotropic magnetic dipolar interactions of PbSe self-assembled nanoparticles on GaAs†

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We report on the observation of an anisotropic magnetic dipolar interaction that results from binding PbSe nanoparticles (NPs) to GaAs surfaces by an organic linker. The observed dependence of the blocking temperature on the alignment of the linking molecule relative to the surface normal indicates that the anisotropy is caused by the attachment of the organic linker to the NPs. The presented results may serve as a strategy for fine-tuning the magnetic interactions and anisotropy on surfaces.

The study of magnetic nanoparticles (NPs) has attracted a lot of attention both because of the basic physics involved and the great technological importance of ferromagnetic NPs in memory devices, inductors, and other applications related to nanotechnologies.[1–4] It has been found that magnetic materials exhibit enhanced magnetism when forming NPs.[5,6] This property further enhances the interest in magnetic NPs. As a result, a significant number of studies were performed on magnetic dipolar interactions in two-dimensional (2D) arrays of NPs.[7–10]

Here we report the observation of an anisotropic magnetic dipolar interaction that results from binding PbSe NPs to GaAs surfaces by an organic linker. This system has been chosen because of the ability to bind the NPs to the substrate with different molecules that are organized so that their tilt angle versus the surface normal is different from each other. We found that the magnetic moment is anisotropic and has the same cooperative characteristics found in 2D layers of magnetic nanoparticles.[9,11–14] Whereas usually the anisotropy of magnetism is difficult to control, in the present case the anisotropy was found to depend on the alignment of the long axis of the organic molecule linker relative to the surface normal. By varying the organic molecules that are used to link the NPs to the substrate, it is possible to vary the anisotropy. While in former studies the effect of the organic monolayer on magnetism was found for NPs that are usually not magnetic,[9] here we demonstrate that the ability to control anisotropy is general and can be applied for various type of NPs. By using different experimental observations we find further support for the interesting effect that allows control of magnetic anisotropy.

For the current study we used PbSe nanoparticles synthesized as described in the supplementary material.[15]

A Jasco V-570 UV/Vis/NIR spectrophotometer was used to obtain the absorption spectrum of the PbSe NPs, as shown in Fig. 1. The measurements were carried out at room temperature. The TEM micrograph (Fig. 2) was taken by a Technai T12 transmission electron microscope operating at 120 kV with a magnification of 52 k. The magnetic moment of the PbSe NPs (about 1 Bohr magneton per PbSe molecule at the applied field of 1 T) was measured by a SQUID magnetometer.

The PbSe NPs with diameters of 4.5 nm were attached to a p-type GaAs surface through self-assembled monolayers of 1,8-octanedithiol and 1,4-benzenedimethanethiol (Sigma–Aldrich Co). The process that followed is described in ref. 16. The thickness of the layer was verified using a spectroscopic ellipsometer. In addition to ellipsometry, the quality of the monolayer was also verified by atomic force microscopy and contact potential difference measurements (CPD) using a Kelvin Probe. The AFM measurements indicated that the density of the adsorbed NPs is about 6.0 × 10^{10} cm^{-2}, for both types of organic linkers, and proved that the particles are distributed homogeneously on the surface (Fig. 3).

Zero-field-cooled (ZFC) and field-cooled (FC) measurements were performed with a SQUID (superconducting quantum interference device) magnetometer with an absolute sensitivity of 10^{-7} emu, with the magnetic field applied either parallel or perpendicular to the sample plane. The samples

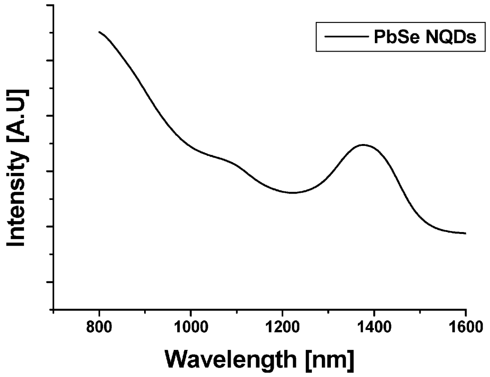

Fig. 1 Absorption spectrum of PbSe NPs capped with OA and TOP. The spectra of these NPs exhibit pronounced excitonic transitions with the lowest energy exciton ($1S_h$–$1S_e$) centered at 1380 nm.

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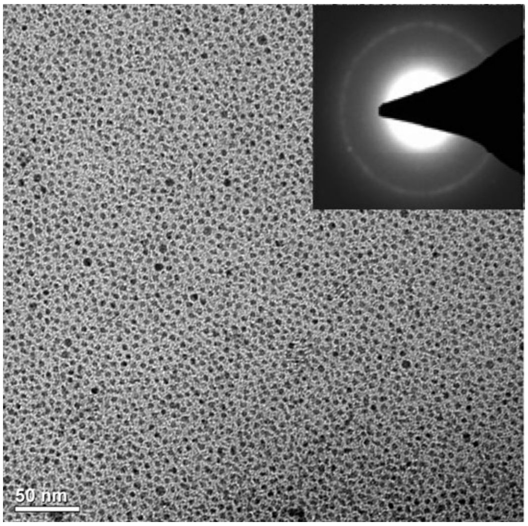

Fig. 2 TEM image of PbSe NPs capped with OA/TOP and suspended in chloroform solution. Inset–Electron diffraction of the PbSe NPs.

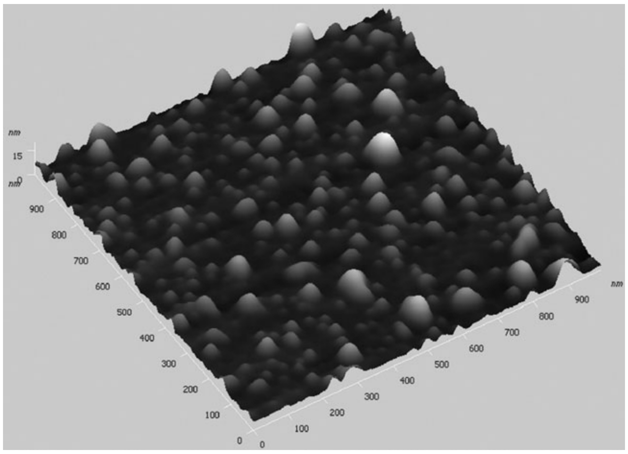

Fig. 3 AFM image (1000 × 1000 nm^2) of PbSe nanoparticles adsorbed via SAM of 1,8-octanedithiol.

were placed in plastic straws, which have a low background contribution to the magnetic moment (about 10^{-6} emu at 1 T).

Fig. 4 shows the field-cooled (FC) and zero-field-cooled (ZFC) magnetization per surface area measured for PbSe NPs attached to the GaAs substrate via organic monolayers of 1,8-octanedithiol (A,B) and 1,4-benzenedimethanethiol (C,D) for a field applied parallel or perpendicular to the surface. The blocking temperatures, T_B, in a magnetic field parallel to the surface of the sample, are larger than those in a perpendicular field, indicating the stronger interaction between nanoparticles. Moreover, with a 1,4-benzenedimethanethiol monolayer, the blocking temperature in the perpendicular field is only about 50 K (Fig. 4D). We propose that the difference between the NPs adsorbed on the 1,8-octanedithiol versus those adsorbed on 1,4-benzenedimethanethiol stems from the different alignment of the two types of molecules relative to the surface normal. Whereas 1,8-octanedithiol molecules are aligned parallel to the surface normal, the benzenedimethanethiol molecules are aligned at a tilt angle of 50 ± 10° relative to the surface normal.[16,17] The observed dependence of the blocking temperature on the alignment of the linking molecule relative to the surface normal indicates that the anisotropy is caused by the attachment of the organic molecule to the NPs. The monotonically increased (at least until 250 K) behavior of FC dependences, shown in Fig. 4B and D, is distinct from the same dependences for the field applied perpendicular to the surface normal (Fig. 4A, C). This also obviously demonstrates that the attached organic molecule breaks the spherical symmetry of the magnetism of the NPs. Hence, the spatial distribution of magnetic moment orientations can be described by an oblate ellipsoid with its shortest axis nearly parallel to the normal of the substrate surface. Indeed, the magnetic moment decreased with increasing temperature when the field was applied parallel to the surface normal (above 50 K) and increased when the field was applied perpendicular to the surface normal. This implies that at low temperatures almost all the spins are aligned parallel to the long axes of the oblate ellipsoid and that only with increasing temperatures can the spins change their direction and be aligned parallel to the short axes of the ellipsoid. We conjecture that the orientation of the axes of the ellipsoid is determined by the orientation of the organic molecules relative to the surface.

The dipolar interactions between NPs in the present study are similar to what has been reported previously in the case of 2D arrays of Fe_3O_4[7,8,18] and $CoFe_2O_4$[9] nanoparticle 2D arrays. The anisotropy, the lack of significant temperature dependence of the signal, and the magnitude of the signal itself are very similar to what has been observed previously for $CoFe_2O_4$,[10] Co,[12,13] PbS, and Fe_3O_4.[9] NPs organized in 2D structures.

The anisotropy in 2D layers of magnetic NPs is attributed to a collective effect due to a strong dipolar interaction between the nanoparticles.[13] It arises because groups of particles have their dipole moment aligned parallel to each other and rotate in unison towards the direction of an applied magnetic field. This cooperative behavior is clearly observed by the abrupt growth with increasing temperature of the magnetic moment signal (Fig. 4C) and the saturation in the magnetic field parallel to the surface.[13] The dependence of the magnetic moments on temperature, M(T), as shown in Fig. 4, follows neither the Bloch $T^{3/2}$ law nor the more general equation accounting for the NPs effects:[19]

$$M_S(T) = M_S(0)(1-BT^{\alpha}), \tag{1}$$

where $M_S(T)$ is the saturation magnetization at the temperature T, B is dependent on the NPs structure parameter, and α is the NPs size-dependent and structure-independent parameter. This model works only in the whole temperature range where the magnetic energy is larger than the anisotropy energy and the thermal energy.[20] Since in our case the magnetization is almost independent of the temperature and the anisotropy is relatively small, this formula can be used. The best fit to the data was obtained after adding to eqn (1) the surface term, $A_{surf}(T)$,[20] arising from the NPs surface spin glass behavior:

$$M_S(T) = M_S(0)(1-BT^{\alpha}) + A_{surf}(T) \tag{2}$$

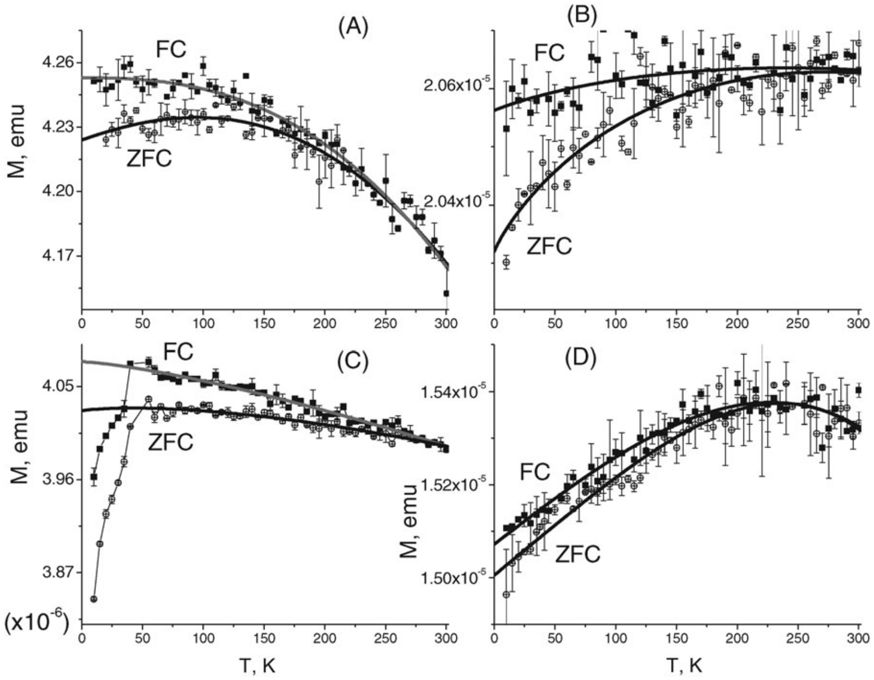

Fig. 4 Field-cooled (FC) and zero-field-cooled (ZFC) magnetization (H = 500 Oe) for PbSe nanoparticles, adsorbed *via* SAM of 1,8-octanedithiol (A, B) and via SAM of 1,4-benzenedimethanethiol (C, D) for a magnetic field applied perpendicular (A, C) and parallel (B, D) to the normal of substrate surface. The solid lines are used for guiding the eyes. The bold lines indicate the best fit of the FC magnetization curves on the A and C graphs to eqn (2).

In the case of solutions of manganese and copper ferrite nanoparticles and cobalt ferrite nanoparticles, the magnetization is strongly dependent on temperature and A_{surf} depends exponentially on T.[20,21] However, in the present case, since the magnetization of the samples is only weakly dependent on temperature, the best fit of FC curves, presented in Fig. 4A and C, was obtained when A(T) was assumed to depend linearly on temperature. The parameters of eqn (2) that were obtained, based on the fitting of the results in Fig. 4A and C, are $M_s(0) \approx 4*10^{-5}$ emu, $A_{surf}/T \approx 2*10^{-9}$ emu/K, and $\alpha \approx 2.0$ and 1.7, $B \approx 0.7*10^{-6}$, and $1.1*10^{-6}$ $K^{-\alpha}$ for the data in Fig. 4A and C, respectively. The results are similar to those obtained in ref. 20. According to the fit, the temperature behavior of magnetization is largely determined by the A_{surf} term, indicating that attaching the nanoparticles to the surface via the organic linkers plays a major role in changing the anisotropy and the blocking temperatures. Although most of the data can be fitted to eqn (2), in the case of the PbSe nanoparticles adsorbed via 1,4 benzenedimethanethiol, the curve of M(T), in a field parallel to the sample surface, could not successfully be fitted at low temperatures (Fig. 4C). This may result from very strong coupling between the spins on the NPs and the substrate.

In conclusion, the observed dependence of the blocking temperature on the alignment of the linking molecule relative to the surface normal indicates that the anisotropy is caused by the attachment of the organic molecules to the NPs. The presented results provide an indication of how magnetic interactions on surfaces can be controlled.

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