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Visualization of Spin Polarized States in Biologically-Produced Ensembles of Ferromagnetic Palladium Nanoparticles

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We report visualization of spin polarized states in macroscopic ensembles of biologically-produced ferromagnetic palladium nanoparticles using the Faraday effect-based technique of magneto-optical imaging. The ferromagnetic palladium only exists in the form of nanoparticles. Large quantities of palladium nanoparticles may be synthesized via biomineralization from a Pd^{2+} solution. The ferromagnetic Pd nanoparticles are formed in the periplasmic space of bacteria during the hydrogen-assisted reduction of Pd^{2+} ions by hydrogenases. The ferromagnetism in Pd comes from itinerant electrons. A high Curie temperature of ferromagnetic palladium, about 200 degrees centigrade above room temperature, would allow for a range of room-temperature magnetic applications. The processes of the isolation of electron spins in separate nanoparticles, spin hopping, spin transport and spin correlations may even form a basis of quantum computing. So far, measurements of the magnetic properties of Pd nanoparticles (PdNP) have been limited by integral techniques such as SQUID magnetometry, magnetic circular dihroism and muon spin rotation spectroscopy (μSR). In the present study, ferromagnetic Pd nanoparticles are characterized using the technique of magneto-optical imaging. This allows visualization of the spin polarization by the variations in the intensity of polarized light. To perform measurements at relatively low magnetic fields, a spin injection from a colossal magnetoresistive material has been used.

Keywords: Nanoparticles, Palladium, Ferromagnetic, Bacteria, Magneto-Optical Imaging, Spin Injection.

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1. INTRODUCTION

Future quantum computing will strongly depend on spin transfer between clusters of spin-polarized electrons. Before a quantum computer is even designed, there is an opportunity to investigate spin-polarized transport between isolated sites using arrays of spin-polarized nanoparticles. Such an array could be based on palladium nanoparticles. Palladium is a metal on the verge of ferromagnetism. It can be driven into the ferromagnetic state when produced in the form of nanoparticles [1]. It is believed that several factors contribute to ferromagnetism of Pd nanoparticles (PdNP), including strain [2] and the influence of surface states [3]. Pd nanoparticles lose ferromagnetism when grown larger than ~7 nm, when the influence of surface states becomes small and the crystal lattice parameters relax to their equilibrium bulk values.

X-ray magnetic circular dichroism revealed that ferromagnetism in Pd nanoparticles is mainly of spin origin with a small orbital component [4]. Since it comes from itinerant electrons, one could expect spin polarization of nanoparticles and thereby a range of spin-transport phenomena. One such phenomenon, magneto-resistance of a two-dimensional Pd nanoparticle superlattice, has already been observed revealing conduction-electron polarization in Pd of about 4 % [5].

In addition to chemical methods, ferromagnetic Pd nanoparticles may be produced biologically [6]. It was found that they are formed enzymatically in the periplasmic space of bacteria suggestive of spin-polarization assisted reduction of the metal ion. This process involves hydrogenases [7-9] that may allow spin transport during formation of the nanoparticles. The spin-polarized properties of biological Pd nanoparticles could be different from those produced by other methods. In addition to this, the biological route offers a possibility to produce a large amount of nanoparticles in a reasonably short period of time.

Another important advantage of a biological route is that each nanoparticle is surrounded by organic matter that protects it from coalescing with other nanoparticles. An excess of organic matter, however, complicates spin exchange between the nanoparticles. Several methods are already developed to partially remove the biomass material. To improve the contact between nanoparticles, one can press them into a pellet, or disperse them in a solvent and deposit them onto a suitable substrate. To monitor the PdNP spin polarization, a visualization technique would be ideal. In this work we report the application of such a technique together with an exploration of spin-injection from a colossal magnetoresistive material.

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2. EXPERIMENTAL

2.1 Samples preparation

Several batches of Pd nanoparticles grown in bacterial cells of *Desulfovibrio desulfuricans* ATCC 29577 and *Escherichia coli* MC4100 on the different stages of removing organic material around nanoparticles have been investigated. Pre-grown bacteria were transferred under N_2 atmosphere into a Pd^{2+} solution. The suspension was allowed to stand for about one hour at 30 °C for biosorption in order to form the Pd nucleation sites in the biomass. The electron donor was then introduced by letting H_2 bubble through the suspension. The preparations of biologically reduced Pd (Bio-Pd) were centrifuged and washed with distilled water and acetone, and finally dried in the air.

The removal of organic matter and particle cleaning included phenol-chloroform Bio-Pd treatment which allowed separation of cell wall bound PdNPs and extraction of protein-bound PdNPs (I. Mikheenko, unpublished). Alternatively an organic layer was removed by suspending the Bio-Pd powder in 6 M NaOH [10] increasing the amount of Pd in the sample up to 70 %. The prepared powdered samples were pressed into pellets; liquid samples were deposited onto the substrates in the form of a suspension, and then dried in the air.

2.2 Experimental technique

Magneto-optical imaging (MOI) is used to visualize spin polarization in ferromagnetic Pd nanoparticles. The method is based on the ability of certain materials to change the polarization of light in the presence of a local magnetic field known as the Faraday effect. Specially prepared in-plane magnetized bismuth-substituted ferrite garnet films [11] were used as sensors. The indicator film was placed directly on a flat surface of the pellet or the substrate with a deposited layer of PdNPs. The whole assembly was positioned on the cold finger of a continuous He-flow cryostat [12]. An optical window on the cryostat allowed for sample observation using a polarized light microscope. A DC magnetic field was applied to magnetize the colossal magneto-resistive material ($La_{0.67}Ca_{0.33}MnO_3$) together with the PdNPs. The brightness of the images obtained with crossed polarizers gives the magnitude of spin polarization in the samples.

Magnetic properties of the samples were measured using a SQUID-based Quantum Design MPMS XL system.

3. RESULTS AND DISCUSSIONS

An electron microscopy image of a typical Bio-Pd preparation is shown in Fig. 1. The Pd nanoparticles are seen as black dots and these are localized in the periplasm (insert). The magnetic moment as a function of magnetic field of a bacterial powder containing Pd nanoparticles at a temperature of 200 K is shown in Fig. 2. To fully magnetize an ensemble of separated Pd nanoparticles, a magnetic field of a few Tesla is necessary.

Twelve different samples were examined by MOI at different temperatures down to 3.7 K using magnetic fields up to 85 mT. This field is close to the saturation field of the used garnet indicator films. None of the samples showed variation in the intensity that would be linked to spin-polarization of Pd. Thus the applied magnetic field was not sufficient to create a detectable change in the magnetic moment in the Pd nanoparticles.

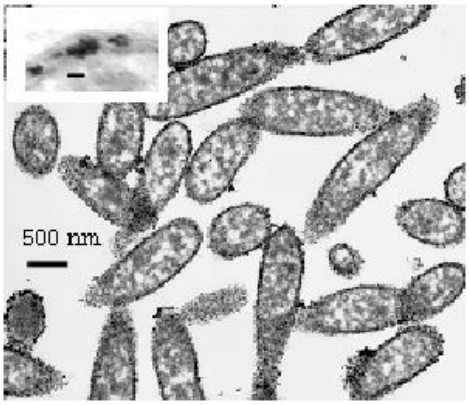

Fig. 1 – An electron microscopy image of bacteria loaded with Pd nanoparticles (black dots). Insert shows localization of Pd NPs in the periplasm, bar size is 50 nm

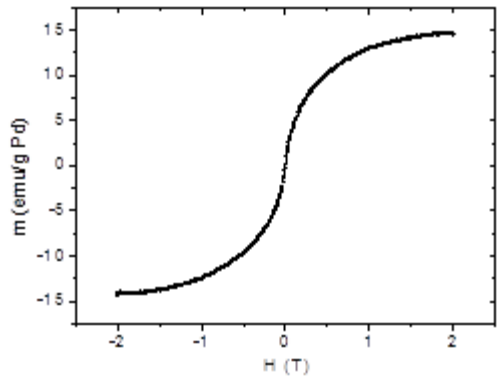

Fig. 2 – Magnetic moment as function of magnetic field of a batch of non-treated Bio-Pd nanoparticles produced by bacteria at 200 K

To overcome this obstacle we used the effect of spin injection. A well-known class of easily magnetized 100 % spin-polarized colossal magneto-resistive materials (CMR) was already proved to be effective for injecting spins into conductive materials [13, 14]. In the case of the PdNPs-containing pellets, we used a CMR thin film in tight contact with the pellet. The magnetic field available in the MOI set-up was used to magnetize the CMR film. The spin-polarized electrons were driven from CMR to Pd by the eddy currents of a magnetic field parallel to the surface of the film. At low temperatures, this parallel field was created by a superconducting film placed below the CMR film.

The result of the experiment at different temperatures for a segment of a pellet composed of PdNPs associated with bacterial cell walls is shown in Fig. 3. The organic matter was only partially removed in this preparation. The average distance between Pd nanoparticles in the sample is relatively large and their spin correlations are weak. That is why the effect is seen at low temperatures only and vanishes at about 60 K.

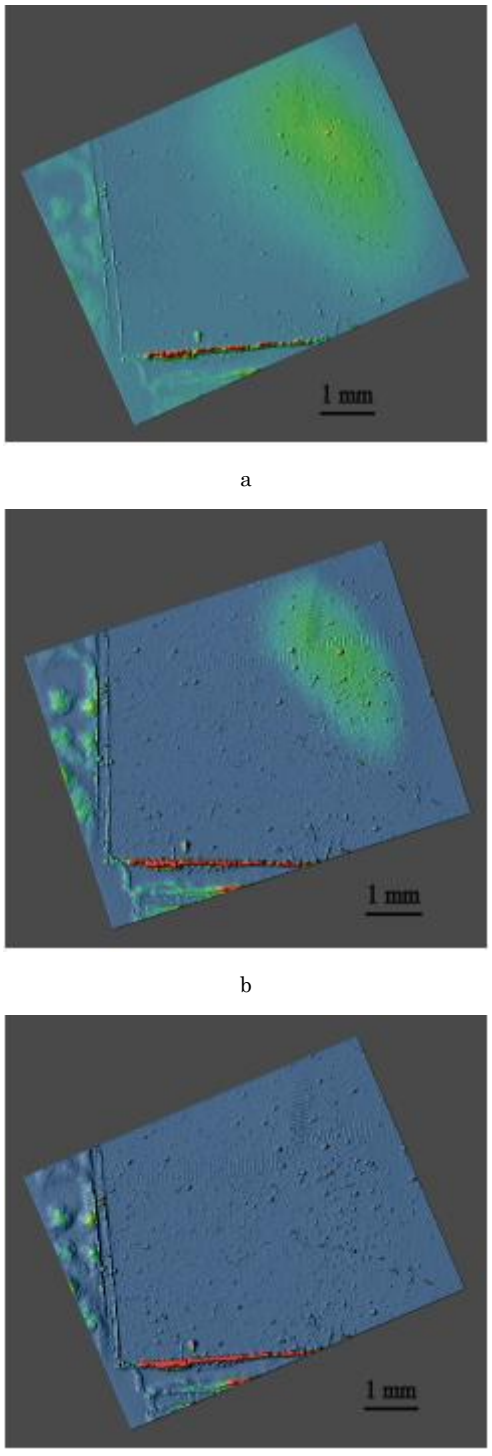

Fig. 3 – Color-coded representations of MOI images of a section of pellet containing Pd nanoparticles at three different temperatures: 20 K (a), 45 K (b) and 60 K (c). The images were obtained using spin injection from the underlying CMR film

The images produced by the MOI technique are most sensitive to the layer of material positioned directly below the indicator film. We were not able to see the effect from the superconducting or CMR film that are situated several millimeters below the indicator film neither at increasing nor decreasing external magnetic field. It is worth noting that at higher temperatures the outline of the segment becomes sharper. The pictures in Fig. 3 are produced by intensity-light color coding of monochrome MOI images. The blue to red colors correspond to an increase in the intensity of polarized light.

One could expect that well-rectified samples with small distances between Pd nanoparticles would be more susceptible to spin injection from CMR than the sample in Fig. 3. To check this, we attempted MOI imaging in the best rectified sample at room temperature.

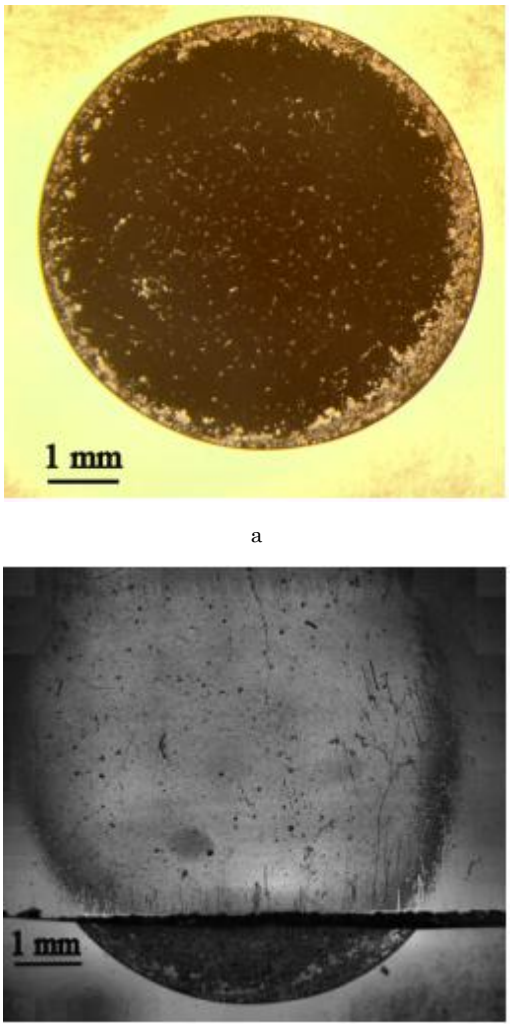

Fig. 4 – a) Optical image of NaOH-cleaned PdMPs deposited to a CMR substrate. The area covered by Pd is a nearly circular disk with white NaOH crystals on the rim. b) MOI image of the sample shown in a)

The Bio-Pd powder in this preparation was cleaned in 6M NaOH and deposited directly on the CMR film as shown in Fig. 4a. The result of MOI imaging is shown in Fig. 4b. In this experiment the indicator film was shifted to partially reveal a nearly circular area covered by Pd NPs. Due to the crystallization of NaOH in the process of drying a range of its crystals appeared on the periphery of the covered area. The Pd content is lowest there. It created the corresponding dark rim in the MOI image in Fig. 4b.

The successful magnetic imaging of the array of Pd

nanoparticles, which are in electrical contact with the CMR, indicates strong spin polarization in biological nano-Pd and demonstrates the possibility to move spins from one material to another enhancing its magnetic moment.

The resolution achieved in Fig. 4a is already sufficient to see the features on the sub-millimeter scale. The experiments shown in Fig. 3 and 4 can be treated as the visualization of the spin-injection from CMR to ferromagnetic Pd. When injected, the electrons in Pd retain direction of their spins in a locked state defined by the spin interactions between the separate nanoparticles.

It is not difficult to extend this experiment to the visualization of the spin transport between Pd nanoparticles. For this, one can make a gap in the CMR film revealing the underlying substrate, and deposit a Pd nanoparticle film across it. By injecting spin-polarized electrons in the Pd layer on one side of the gap and removing them from the other it is possible to achieve spin transport across the gap along the connected Pd nanoparticles that are not in contact with CMR.

The MOI technique can provide resolution down to about one micrometer [11]. The better resolution, which may be needed to monitor processes related to spin-based quantum computing, could be provided by spin-polarized electron microscopy or polarized x-ray microscopy.

4. CONCLUSIONS

Magneto-optical imaging was used to visualize spin polarization in biologically produced ensembles of ferromagnetic Pd nanoparticles. The high level of polarization, sufficient for the detection by the indicator films, was achieved at relatively low applied magnetic fields by the spin injection from a colossal magneto-resistive material. The visual monitoring of spin polarization would help to understand spin transport and may be useful in designing quantum computers.

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