Direct Evidence for Ferromagnetism of Nanometer-Scale Palladium by Contact with Perovskite Manganite

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Theoretical predictions of possible ferromagnetism in Pd have stimulated much interest in experimental studies of thin Pd films with heterostructures as well as nanometer-scale Pd materials. The free Pd atom with an electronic configuration of $[Kr]4d^{10}$ is not magnetic on the basis of Hund's rule. According to recent theoretical calculations,[1,2] however, a slight enhancement of 4d electron localization induced by reduced dimensionality, local symmetry changes, and lattice expansion would give rise to ferromagnetism in Pd. In fact, the 4d band in the Pd metal is not completely filled, so the condition for ferromagnetism based on the Stoner criterion lies close to the threshold of ferromagnetic (FM) instability.[3] Spontaneous FM order in bulk Pd, however, has not yet been observed experimentally. On the other hand, in free-standing Pd nanoclusters with an average diameter of 2.4 nm, the presence of possible ferromagnetism was reported.[4] However, the observed Pd moment was so small (about 10^{-3} μ_B per atom) that only a small fraction of surface atoms held a permanent magnetic moment. The magnetic moment of Pd was also identified in ultrathin Pd/Fe and Pd/Ni films epitaxially grown by the sputtering method, where the Pd film consisted of a few atomic layers and was magnetized by contact with the FM substrates.[5,6] These studies demonstrated that the magnetic properties of Pd are strongly affected by the material with which it is in contact as well as by reduced dimensionality. Although these early works have provided grounds for the possible ferromagnetism of nanoscale Pd materials, there has been little success in determining the genuine FM order in Pd. This is largely due to the difficulty of reproducibly making nanometer-sized Pd materials and also of measuring their magnetic moments precisely.

Recently, using a colloidal template method, a macroporous perovskite manganite $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ (LCSMO),[7] which is known to exhibit FM as well as colossal magneto resistance,[8] was made. The pores of LCSMO are three-dimensionally ordered and can thus be filled with another material. This template approach affords a controlled growth of nanodots or ultrathin films on the walls of the LCSMO framework, yielding bifunctional hybrid materials.[9] This technique, with slight modifications, was used for the synthesis of Pd/LCSMO hybrid materials. One important advantage of this method was that various shapes of materials such as thin films and dots can be fabricated simply by varying the concentration of the precursor solution and the dipping time. This enabled fabrication of nanometer-scale Pd materials adhered to the LCSMO skeleton.

This communication provides direct evidence for ferromagnetism of Pd magnetized by LCSMO and serves as the first example showing the Pd moment being induced by the rough magnetic oxide surface. Thus far, the induced Pd moment has been found in hybrid
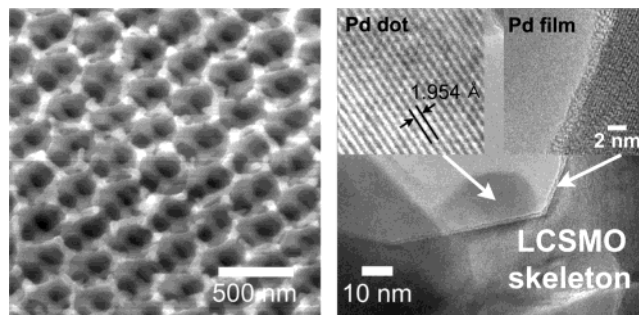

Figure 1. Left panel: SEM image of the same Pd/LCSMO sample showing the Pd phase adhered to the LCSMO skeleton. Right panel: TEM image of a pore wall at higher magnification confirming the presence of Pd nanodots and ultrathin Pd film coated on the wall. (Insets) Enlarged images of the Pd nanodot and Pd/LCSMO interface.

metal films grown epitaxially. In Pd/Ni or Pd/Fe films, however, it was not possible to directly distinguish the induced Pd moment from the hybrid film because the overall magnetic property was always measured. It is worth mentioning that the Pd moment of our Pd/LCSMO sample was quantitatively analyzed since the Pd content can be precisely determined by inductively coupled plasma/mass spectroscopy (ICP/MS). More importantly, the induced maximum Pd moment was about 0.6 μ_B per atom, which is comparable with the theoretical value of 0.5 μ_B per Pd atom calculated from the Pd/Fe film.[10]

Since all the LCSMO samples with different cation ratios yielded virtually identical nanohybrid materials, the data presented below concern the $x = 0.1$ composition of $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ unless stated otherwise. The general procedure used to fabricate the Pd/LCSMO hybrid material is described in Supporting Information. In a similar manner, Pd adhered to carbon (Pd/C) was also prepared using a macroporous carbon replica, to examine whether nonmagnetic carbon can also induce a magnetic moment in nanosized Pd materials. Evidence for the Pd content was provided by elemental analysis using ICP/MS. The wt % of Pd gradually increased with increasing dipping time. A dilute Pd precursor solution was used to prepare nanodots or ultrathin films, which were expected to be very susceptible to the magnetic field induced by LCSMO. An SEM image of the hybrid Pd/LCSMO material prepared by dipping the precursor solution once shows that approximately uniform nanopores formed a well-ordered, close-packed array. Due to the very low Pd content, however, the presence of the Pd phase was not easily distinguished by SEM alone. Nevertheless, the SEM image of Pd/LCSMO exhibits a very slight dilation of the LCSMO skeleton compared with the pristine LCSMO structure. TEM was thus used to image the Pd phase in the LCSMO framework. As illustrated in Figure 1, Pd nanodots are seen along with the LCSMO

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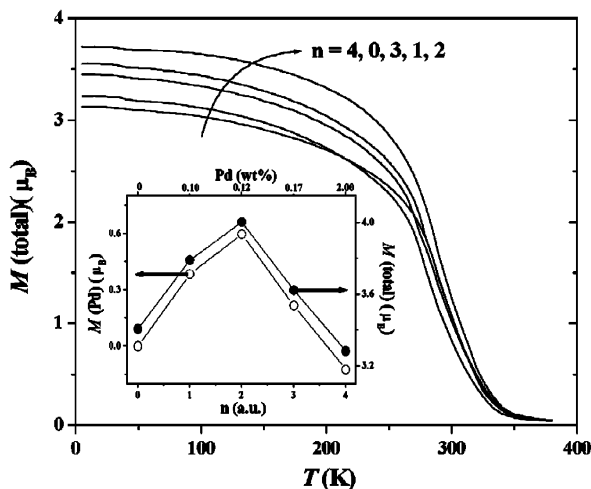[‡] Division of Electromagnetic Metrology.

Figure 2. Temperature-dependent magnetization curves of hybrid Pd/LCSMO samples with different Pd contents measured at 0.5 T. Numbers (*n*) represent dipping times. The inset shows the composition dependence of the magnetic moment calculated per Pd atom. Solid lines are guides to the eye.

framework. In addition, ultrathin films coated on the oxide replica are also visible in the TEM image. This indicated that Pd materials showed a tendency to adhere strongly to the LCSMO framework.

Pd in the hybrid Pd/C sample formed spherical nanodots on the interior void surface of the carbon skeleton. The spherical shape is clearly identified in the TEM image (Supporting Information). The difference between the LCSMO and carbon replicas as templates to support Pd is striking in terms of the shape of the Pd phase, which appears to depend heavily on the oxophobic and oxophilic natures of carbon and LCSMO, respectively.[11] The PdO material that forms at the initial stage of annealing was not strongly adhered to the surfaces of the oxophobic carbon, which eventually led to the creation of spherical Pd nanodots with small contact areas. It is worth noting that the Pd nanodots and thin films of Pd/LCSMO were not uniformly distributed through the whole LCSMO network. Accordingly, neither the thickness of the films nor the average radius of the dots could be accurately determined. Close examination of the TEM images of the first dipped sample, however, showed that the Pd clusters were less than approximately 14 nm in diameter. As anticipated, the thickness of the LCSMO skeleton gradually increased with dipping time.

As shown in Figure 2, magnetic moments of the Pd/LCSMO samples were noticeably enhanced in comparison with that of the pristine LCSMO sample. Apparently, the nanosized Pd materials were magnetized by contact with the LCSMO oxide. There were no other sources of enhanced ferromagnetism. Namely, possible impurities such as PdO and Pd-doped manganite are not ferromagnets, and they were not even identified as present by XRD. Thus, this ferromagnetism must have originated from the pure Pd metal. To elucidate the nature of the induced FM moment further, the magnetization properties of the Pd/C samples were measured, showing the absence of an FM moment. This result ruled out the possibility of surface ferromagnetism of spherical Pd nanodots and instead supported the hypothesis that the LCSMO oxide magnetized Pd in the interfacial area.

This inset shows the Pd moment deduced in the Pd/LCSMO data as a function of Pd content. A remarkable feature is that the Pd moment was maximized when the Pd content was 0.12 wt %. Further increase of Pd gradually reduced the Pd moment, and the induced Pd moment suddenly disappeared in a Pd/LCSMO sample containing 2 wt % Pd. This indicated that the magnetic moment was induced only in very small Pd nanodots or ultrathin Pd layers

that were in direct contact with the LCSMO surfaces. It is desirable to compare this result with the Pd moment (0.4 μ_B) in Pd/Fe multilayers epitaxially grown in the (001) direction.[5] The maximum number of Pd layers in which an FM moment is sustained throughout the whole layer is four atomic layers, which is about 1.08 nm of thickness. One additional Pd layer destroyed the ferromagnetism of the whole Pd layer, indicating that thick Pd layers do not possess magnetic moments. In view of the magnetization of Pd in contact with the FM material, this agrees qualitatively with the result presented in this communication. However, the thickness dependency of the Pd magnetization appears to be dependent on the magnetic moment of the contact material. The magnetic coupling caused by an exchange interaction mechanism in the Pd/LCSMO interface might be stronger than in the Pd/Ni film.[6] Another point to note is that lattice effects might play a significant role in determining the induced moment of the Pd/Ni film but be negligible in the Pd/LCSMO sample due to the rough oxide surface of LCSMO.

In conclusion, Pd/LCSMO hybrid materials with very low Pd content were fabricated through a template method. It was found that the Pd moment was even induced by the rough LCSMO oxide interface, this being the first time that such a phenomenon has been reported. These experiments demonstrate that nanosized Pd dots can also be magnetized by a FM oxide. Accordingly, the general view that the induced Pd moment can be observed only in ultrathin multilayer films containing an FM layer is not extendable to other material systems. Alternative theoretical investigations should instead be considered, in which the induced moment is primarily a result of exchange interactions between the 3d bands of the FM material and the 4d electrons of Pd although lattice expansion that induces a narrowing of the 4d band also plays a role in the creation of the magnetic moment.

Supporting Information Available: Detailed description of experimental procedure, SEM micrographs, XRD data, TEM images, and magnetic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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