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Abstract
We have investigated the magnetic properties of trioctylphosphine (TOP)-stabilized
monodisperse palladium nanoparticles of 2, 3, 5 and 10 nm in size, in order to study the possible
effects of surface Pd atoms. These nanoparticles display clear signatures of ferromagnetism
such as hysteresis and saturation magnetization over the entire temperature range studied here
from 2 to 380 K. The magnetization of the nanoparticles increases with decreasing particle size,
indicating a possibly important role played by Pd atoms on the surface of the nanoparticles.
More importantly, we also found that the magnetization of our TOP-stabilized Pd nanoparticles
is one order of magnitude smaller than those of other Pd nanoparticles reported so far, which is
most likely to be due to the weak nature of interface interaction between TOP ligands and Pd
nanoparticles compared to other ligands. This observation is consistent with the view that the
magnetism of Pd nanoparticles is strongly influenced by the interaction of surface atoms with
the ligands. We discuss our experimental findings in terms of a charge transfer mechanism due
to a covalent bond of Pd atoms with the protective TOP ligand, which would increase the
4d density of states of Pd atoms due to localization by the bonded P atoms.

S Supplementary data are available from stacks.iop.org/JPhysCM/20/295209

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Over the past few years, there has been a surge of interest
in nanoparticles of all kinds of materials. Probably one
of the big surprises from these latest studies is that the
magnetic properties of nanoparticles are often remarkably
different from those of their bulk counterparts, in particular
in the case of materials that are known to have nonmagnetic
or antiferromagnetic ground states in bulk form. For
example, the characteristic features of a ferromagnetic material
such as saturated magnetization and $M-H$ hysteresis curve
are nowadays observed in numerous nanoparticles, which
are made of supposedly nonmagnetic or antiferromagnetic
bulk materials. Therefore, it has become very important
for one to examine systematically the magnetic properties

of nanoparticles of various metals and oxide materials,
whose bulk forms exhibit otherwise less interesting magnetic
properties [1, 2].

Reduced coordination number (in clusters of metal atoms),
local symmetry changes (vacancies and surface states) and
electron localization induced by lattice expansion are the
possible key factors that might well induce ferromagnetism in
nanoparticles of otherwise nonmagnetic metals [3]. Recently
it was shown that even nanoparticles of Au can have
ferromagnetism stabilized by different ligands or capping
molecules attached to the surface atoms [4, 5]. For example,
x-ray magnetic circular dichroism (XMCD) studies of thiol-
capped Au nanoparticles were found to have intrinsic spin
polarization arising from interaction between the surface Au
atoms and the ligands attached [4]. More surprisingly, room

temperature ferromagnetism has been reported in nanoparticles of many nonmagnetic or antiferromagnetic oxides, nitrides and chalcogenides, which was taken to be arising from defects or oxygen vacancies [2, 6]. In spite of these observations, the exact mechanism behind the ferromagnetism of these supposedly nonmagnetic nanoparticles still remains largely unknown.

With the renewed interest in the induced magnetic ground states for otherwise nonmagnetic materials, Pd is a natural choice for systematic investigations, since it is well known to be very close to a magnetic instability in bulk form. For example, even a small amount (2.3%) of Ni doping is enough to stabilize bulk ferromagnetism in Pd [7]. Giant spin fluctuations, known as a *paramagnon*, present in bulk Pd is certainly much more favourable for ferromagnetism or, to put it more correctly, a blocked state in Pd nanoparticles, than any other nonmagnetic materials [8]. In fact, there have been several reports showing the ferromagnetic nature of Pd nanoparticles. First, it was found that Pd nanoparticles with average radius smaller than 7 nm possess magnetic moments even at room temperature, and was argued that atoms on the surface of the nanoparticles are responsible for the observed ferromagnetism [9]. Based on their subsequent studies of the size dependence of the saturation magnetization, they claimed that the ferromagnetic ordering occurs only on the (100) facets of their nanoparticles and, furthermore, it is mainly two to five layers from the surface that contribute to the observed ferromagnetism with an estimated magnetic moment of about 0.75 μ_B/Pd-atom [10]. Recently, Pd nanoparticles with an average size of 2.4 nm prepared by using $R_4N^+X^-$ were also reported to retain permanent magnetism even above 300 K due to local symmetry changes at twin boundaries as well as surface anisotropy induced by a reduction in the coordination number [3]. On the other hand, capping agents like alkane–thiol molecules having covalent bonding to Pd nanoparticles with smaller sizes (1.2–2.4 nm) is found to stabilize ferromagnetic behaviour by increasing the density of states near the Fermi level, leading to permanent magnetism in these nanoparticles [11]. Another noticeable example of the induced ferromagnetism in nanometre-scale Pd is a Pd/$La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ composite [12], in which moments are induced at the Pd sites through an exchange interaction by the strongly magnetic $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ in close proximity with Pd dots. Thus, despite being extensively used as catalysts for many organic reactions such as olefin hydrogenation and carbon–carbon coupling reactions [13], magnetic properties of Pd nanoparticles seem to be yet unexplored and open up a new door to Pd research of both basic and technological importance.

In this work, we report our systematic studies of the magnetic properties of monodisperse Pd nanoparticles with special attention to achieving a narrow size distribution of the nanoparticles and using a new capping material of trioctylphosphine (TOP) ligand. With these two focuses of our researches, we intended to eliminate any possible inconsistency in the observed results and also tried to observe effects of new capping materials on the magnetism of Pd nanoparticles.

2. Experiments and discussion

Pd nanoparticles were prepared by a synthetic procedure, slightly modified from a method originally developed by some of us for the synthesis of monodisperse nanocrystals of metal oxides, which involves formation of a metal–ligand complex followed by ageing at high temperatures [14]. The key modification in our method is the one-step thermal decomposition of the metal complex without intermediate addition of any further reductant or processing. The aforementioned synthesis procedure was adopted to prepare monodisperse Pd nanoparticles with particle sizes of 2, 3, 5, and 10 nm by thermal decomposition of Pd–TOP complex, controlled by varying the concentration of stabilizing ligand [15].

Pd–TOP complex, which was prepared by the reaction of 0.1 g of Pd(acac)$_2$ (0.33 mmol) and 1 ml of TOP under argon atmosphere, was injected into 9 ml of TOP at room temperature. Subsequently, the solution was slowly heated to 300 °C and further aged at the same temperature for 30 min, generating a black colloidal nanoparticle solution. A black precipitate obtained by adding 50 ml of EtOH into the colloidal solution could easily be redispersed using nonpolar organic solvents like hexane or tetrahydrofuran (THF) to yield a visibly homogeneous solution. We stress that all our syntheses were carried out under controlled pure Ar gas atmosphere in order to prevent any possible contaminations [16]. But we must comment that our samples were inevitably exposed, although for a very short time, to air during the whole process of our investigations. Furthermore, it is to be noted that although our synthesis method is good at producing monodisperse Pd nanoparticles as demonstrated by our characterization, it is not easy to adopt for the production of nanoparticles with size greater than 10 nm.

Transmission electron microscope (TEM) images of Pd nanoparticles shown in figure 1 attest the uniform size distribution of the particles obtained from this synthesis procedure, whose average sizes are found to be 2 ± 0.4, 3 ± 0.5, 5 ± 0.5 and 10 ± 1 nm, respectively. More importantly, the high-resolution TEM (HRTEM) images shown in the insets of figure 1 reveal the atomic lattice fringes, demonstrating the good crystalline nature of our nanoparticles. We also note that the x-ray powder diffraction patterns confirm the face centred cubic structure of the metallic Pd. By profile matching the XRD data using the Fullprof Rietveld refinement program, we found that lattice constant decreases with decreasing size of nanoparticles. Interestingly enough, molecular dynamics studies using many-body potential derived from first-principles calculations of small Pd cluster also showed that the lattice parameter of Pd nanoparticles is reduced with decreasing cluster size from 3.0 to 1.4 nm [17].

We have measured the magnetic properties of nanoparticles using a commercial SQUID magnetometer (MPMS-5XL, Quantum Design, USA). M–H isotherms were taken at 2, 20, 300 and 380 K in the field range of -5 T $\leqslant H \leqslant 5$ T. We have also made M–T measurements under 100 Oe from room temperature down to 2 K, while increasing temperatures after both zero-field cooling (M_{ZFC}) and field cooling under 100 Oe (M_{FC}).
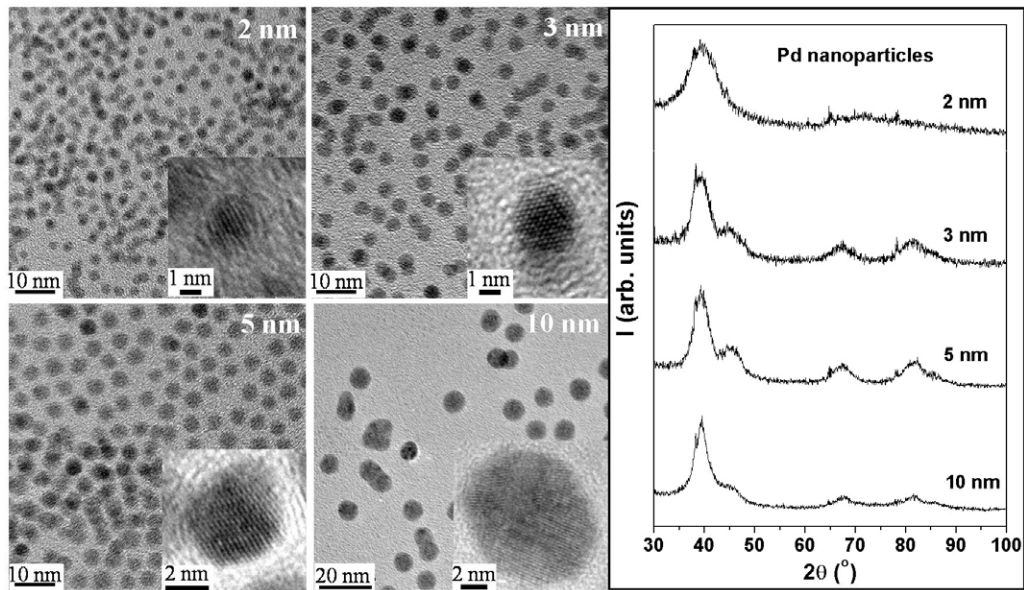
Figure 1. TEM images and XRD data of Pd nanoparticles: 2, 3, 5 and 10 nm. The insets show the HRTEM images of the nanoparticles.
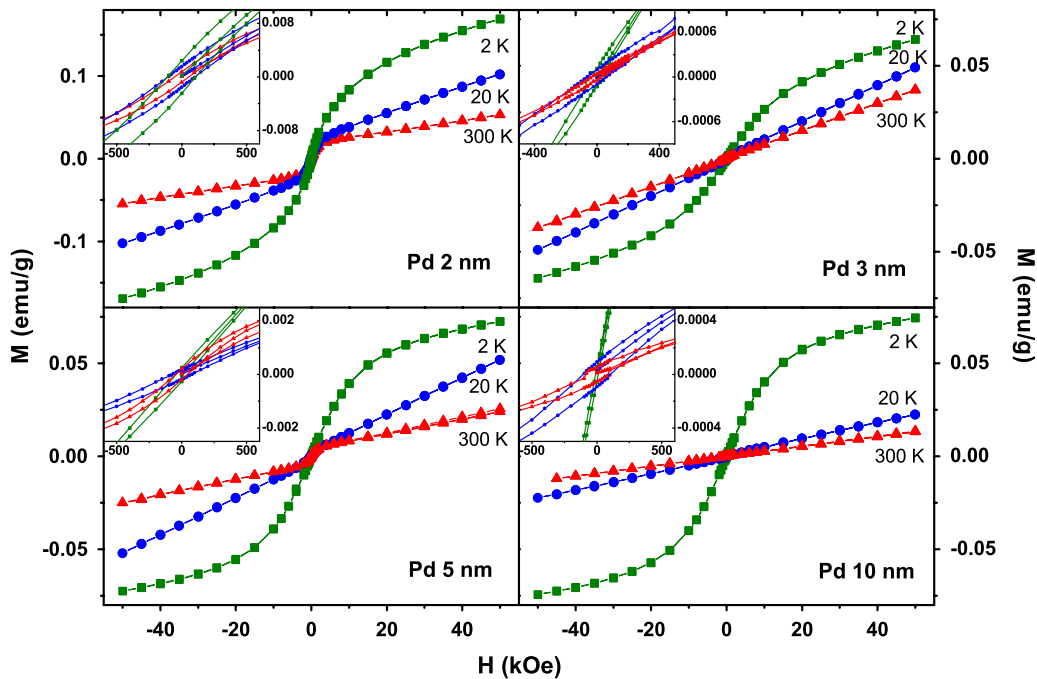

Figure 2. *M* versus *H* curves for Pd nanoparticles with sizes of 2, 3, 5 and 10 nm, measured at three different temperatures of 2, 20 and 300 K. Insets show an enlarged picture at low field regions.

Figure 2 shows some of the typical *M*–*H* curves taken for Pd nanoparticles with four different sizes, providing evidence for ferromagnetism at all measured temperatures. Of particular interest is that the hysteresis curve of the Pd 2 nm particles shows a coercivity of 50 Oe at 380 K and 109 Oe at 2 K, larger than in any other Pd nanoparticles we measured. We also note that even with 5 T a full saturation of the magnetization was not obtained for any of our nanoparticles, strongly indicating the coexistence of paramagnetic elements and blocked ferromagnetic entities with presumably superparamagnetic

behaviour inside our nanoparticles. Nevertheless, a tendency towards saturation is observed at 2 K for all our nanoparticles. On the other hand, the larger coercivity and saturated magnetization values are the definitive evidence for the ferromagnetic nature of the Pd nanoparticles. We have ruled out the possible effects of extrinsic impurities by measuring the magnetization of Pd 3 nm particles, whose magnetization curves remained almost unchanged even with intentional mixing of Fe_3O_4 nanoparticles up to 2000 ppm (see figure 1 in the supporting information (available at
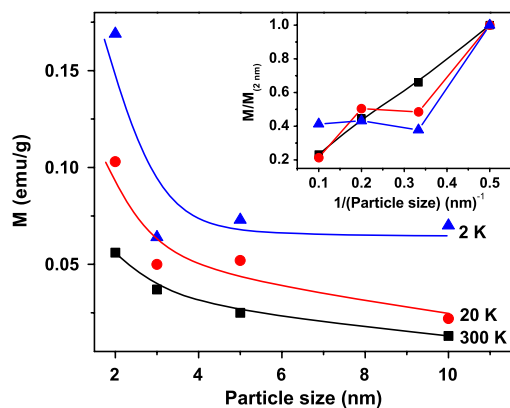
Figure 3. Particle size dependence of the magnetization of Pd nanoparticles measured at 2, 20 and 300 K under 5 T. Inset shows the approximate inverse size dependence of magnetization normalized to the values of 2 nm particles. The solid lines are guide to the eyes.

stacks.iop.org/JPhysCM/20/295209)). The M_S and H_C calculated after subtracting the strong paramagnetic signal are shown in table 1. As further supporting data, the subtracted M versus H curves are shown in figure 2 of the supporting information (available at stacks.iop.org/JPhysCM/20/295209). As summarized in table 1, the saturation magnetization is found to be 0.1 emu g^{-1} for the Pd 2 nm particle and decreases to about 0.05 emu g^{-1} for the larger size particles. The coercive field H_C exhibits more systematic changes with the particle size. We note too that the saturation magnetization of our Pd nanoparticles is about one order of magnitude smaller than those of other Pd nanoparticles reported so far [3–6]. The origin of this difference will be discussed later.

In order to study the size dependence of the magnetic properties of our Pd nanoparticles, we have plotted in figure 3 the magnetization values taken at 5 T at several temperatures. As one can see, the magnetization decreases progressively with increasing particle size. The inset of figure 3 shows that the magnetization is approximately inversely proportional to the size of the nanoparticles. Such a size dependence would naturally indicate that a larger contribution to the magnetism comes primarily from atoms on the surface of the nanoparticles. As an explanation for our observations, we

propose a core/shell structure for our nanoparticles, where the ferromagnetism is associated with the surface atoms while the core still remains paramagnetic. A similar mechanism for the magnetization of Pd nanoparticles was recently proposed for thiol-capped Pd nanoparticles [18]. According to [18], the observed permanent magnetism of their Pd nanoparticles has been explained by considering an increase in the density of states due to the thiol bonds at the 4d residual band of the Pd cluster. This increase in the density of states would naturally give rise proportionally to an increase of the magnetic moment for the surface Pd atoms as the Stoner enhancement factor would suggest in the standard theory of metallic magnetism [19]. A similar mechanism has also been proposed for the seeming ferromagnetism of thiol-capped gold nanoparticles [5].

A further interesting point is that the effect of surface states is diminished in the larger sized particles. As we cannot extend our synthesis method easily to make monodisperse nanoparticles larger than 10 nm, we instead obtained aggregates of Pd particles of about 100 nm size in our attempts to produce larger size particles. These aggregates consist of nanoparticles of about 5–15 nm in size (see the TEM image in figure 4). The measured $M–H$ of this sample displays unsaturated magnetization and negligible coercivity values. This observation, we think, is consistent with our explanation of surface-induced ferromagnetism in our Pd nanoparticles with smaller size. How can ferromagnetism then be stabilized on the surface of Pd nanoparticles? In order to answer this question, we should point out that bulk Pd is so close to a magnetic instability with an already large density of states (DOS) at the Fermi level ($N(E_F)$) that even small perturbations can produce a significant change in the DOS of Pd nanoparticles. One particular source of perturbation that is relevant to nanoparticles like ours is the localization effect of Pd d electrons due to hybridization between ligand and surface atoms. Such increase in $N(E_F)$ at the surface states could explain the ferromagnetism of our Pd nanoparticles very well.

In order to further study the magnetic properties of our samples, we have measured $M–T$ curves after both zero-field cooling (ZFC) and field cooling (FC) with 100 Oe. As shown in figure 5, the $M–T$ data display the conventional blocking behaviour of typical magnetic nanoparticles from 380 down
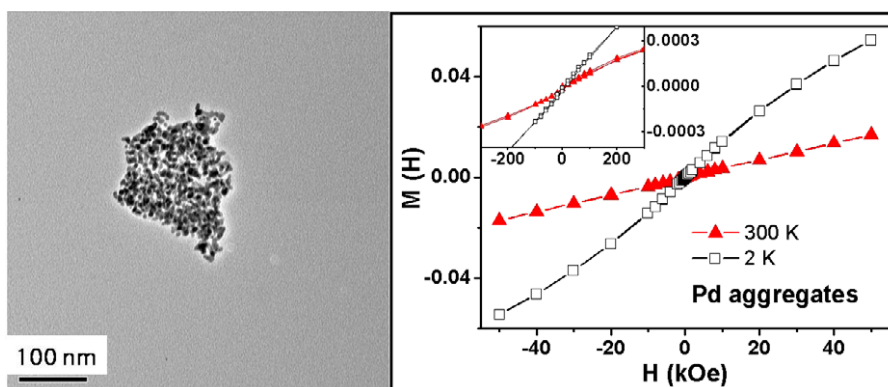
Figure 4. TEM image (left) showing the Pd aggregates containing 5–15 nm size particles and (right) its $M–H$ characteristics at 300 and 2 K. Inset shows an enlarged picture of the low field region.

Table 1. Lattice parameter (a), saturation magnetization (M_S) and coercivity (H_C) of Pd nanoparticles.

Pd	2 nm	3 nm	5 nm	10 nm
a (Å)	3.311 ± 0.003	3.895 ± 0.001	3.906 ± 0.001	3.904 ± 0.001
M_S (emu g^{-1})	0.1	0.04	0.05	0.05
H_C (Oe) at 2 K	117	86	45	11
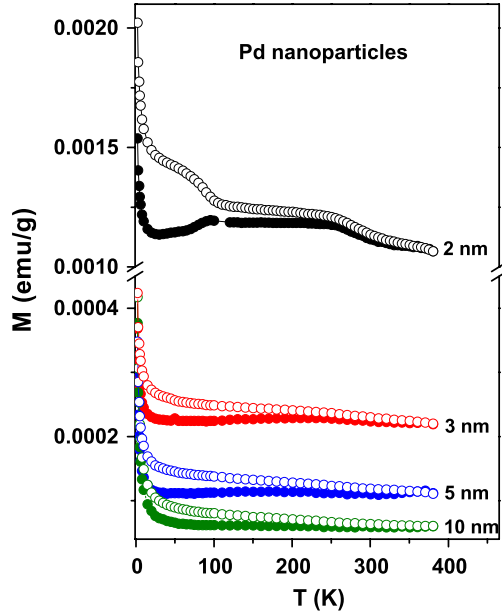
Figure 5. Magnetization versus temperature for Pd nanoparticles measured after zero-field cooling, M_{ZFC} (solid symbols) and field cooling, M_{FC} (open symbols) under an applied field of 100 Oe.

to 2 K, except for an unusual sharp increase observed in the magnetization below 20 K for all the samples. The zero-field cooled magnetization of nanoparticles shows a peak at the blocking temperature, where the superparamagnetic relaxation time is equal to the timescale of the experimental technique. The low-temperature upturn might as well be due to some Pd moments that are not frozen even at the low temperatures, exhibiting a Curie-like tail. A similar Curie-like upturn is generally observed in graphite compounds, whose origin is ascribed to oxygen which is physisorbed in the interstitial voids in the lattice of carbon structures and acts as a paramagnetic impurity [20, 21]. Above 20 K, the M_{ZFC} and M_{FC} curves are nearly flat and merge at about 380 K for 3, 5 and 10 nm particles, whereas the 2 nm particles show a broader peak spreading over a wide temperature range from 100 to 260 K. Upon close inspection, the magnetization of 3 and 5 nm also show some evidence of the broad peak, although much weaker. We acknowledge that the origin of this anomalously broad peak is unclear, but a most plausible explanation would be that it is due to broad blocking behaviour.

We note that M_{ZFC} and M_{FC} of 3, 5 and 10 nm particles merge at about 380 K. M–H curves show coercivity right up to 380 K, which decrease roughly linearly with temperatures before flattening off above 300 K. From the coercivity values obtained at different temperatures between 2 and 300 K and the blocking behaviour observed up to 380 K, it can

be inferred that our nanoparticles of 3, 5 and 10 nm have blocking temperatures well above room temperature. Using this observation, we can then estimate the magnetic anisotropy energy for our nanoparticles using the following formula [22]: $KV = 25k_B T_B$, where K is the magnetic anisotropy energy of a single particle, V, the total volume of the particle, k_B, the Boltzmann constant, and T_B, the blocking temperature taken to be 380 K. This simple calculation puts the estimate of the magnetic anisotropy energy at $K \simeq 10^7$ J m^{-3} for the 3 nm sample. As we pointed out, we think that our Pd nanoparticles have magnetism mainly due to the surface states; which would then put this number at much higher values. We note that this estimated magnetic anisotropy energy is even larger than that of magnetites of a similar size that we studied with $K \simeq 10^5$ J m^{-3} [23, 24]. If we take the magnetic data reported for Pd nanoparticles in the literature, for example [3, 9–11], most of the Pd nanoparticles seem to have similarly large blocking temperatures and so a large magnetic anisotropy, indicating that these unusual features are an intrinsic property of the Pd nanoparticles. Therefore, not only do Pd nanoparticles become magnetic due to the surface states, but they may also exhibit an extremely large magnetic anisotropy energy.

Here we can think of two main sources of the unexpectedly large magnetic anisotropy energy for Pd nanoparticles. The first one is obviously the small size of the Pd samples. It is well known that upon reducing the particle size most of magnetic nanoparticles show their magnetic anisotropy energies increasing simultaneously [25]. Second, we can also reckon that the proposed core–shell structure for Pd nanoparticles would have some significant effects on the increased magnetic anisotropy energy. Although it is not theoretically well understood, it is experimentally shown that magnetic anisotropy of nanoparticles can be significantly enhanced by forming a core–shell structure [26]. One such example is the nanoparticles of Au-capped Co clusters [27], whose blocking temperature is reported to be three times larger than that of Co clusters without Au capping. Therefore, the bonding between the ferromagnetic Co and the paramagnetic Au shell is found to increase the magnetic anisotropy energy of Co particles. A similar mechanism could prevail in our Pd nanoparticles, which possess a large magnetic anisotropy possibly driven by the hybridization of paramagnetic core and ferromagnetic surface atoms. Having said that, we acknowledge that it is still a puzzle to us how Pd nanoparticles can have such a large magnetic anisotropy value.

Finally in our TOP-protected Pd nanoparticles, we think that a charge transfer mechanism increases the density of states for the 4d band of Pd atoms at the surface layers, which would lead to a permanent magnetism for Pd nanoparticles. A similar mechanism has been proposed for ferromagnetism observed in thiol-capped Pd and Au nanoparticles [5, 18]. It is also

worth noting that the magnetization of our Pd nanoparticles is about one order of magnitude smaller than those of any other Pd nanoparticles reported so far, indicating a smaller increase in the density of states of the surface atoms. Compared with the thiol-capped Pd nanoparticles, this mechanism seems to be less efficient for our TOP-protected Pd nanoparticles probably due to the weak interaction of TOP ligands with Pd nanoparticles [28]. This weak interaction gives rise to smaller magnetization in our TOP-stabilized Pd nanoparticles compared to other Pd nanoparticles. Therefore, our findings together with others [18] suggest an interesting route to explore the magnetism of nanoparticles, i.e. controlling the magnetism via capping ligands: which, we believe, offers much larger opportunities for possible applications.

3. Conclusion

In order to understand the magnetism of Pd nanoparticles, we studied monodisperse Pd particles prepared using one-step thermal decomposition of Pd complex. Unlike other reports on Pd before us, our samples have capping layers of TOP ligand. From the thorough studies, we concluded that all our Pd nanoparticles have ferromagnetism, which grows stronger with reducing particle size. All our observations can be explained in terms of the enhanced density of states of Pd atoms on the surface. Furthermore, we found that there are strong effects on the magnetism due to different capping layers. These unusual observations, we think, open up an interesting possibility of exploring or even tailoring the magnetism of nanoparticles via capping ligands.

Acknowledgments

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