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Anomalous magnetism in noble metal (nano)particles

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ABSTRACT

In a previous article published in Langmuir 27 (2011) 7783–7787, we reported on a novel synthesis route to make magnetic noble metal nanoparticles and nanoparticle clusters. In this article we demonstrate an enhanced method of recovering the magnetic particles after synthesis and give an insight into the temperature dependence of their magnetization. Based on our findings, we conclude that the magnetism induced by our method has a dominant contribution from the surface instead of the bulk as is common for classical magnetism.

1. Introduction

Nobel metal nanoparticles are nowadays finding their way in many applications such as biomedicine, catalysis, etc.; see [1] for a very recent review. The main route to making magnetic noble metal nanoparticles involves capping agents [2], which have the disadvantage of bringing about a surface modification that then has to be compatible with later applications such as in biomedicine [1]. The capping agent is essential for the magnetic properties albeit that a small magnetic effect may remain after their removal [3]. Recently, we have demonstrated that it is possible to make magnetic noble metal nanoparticles in relatively large quantities by a bulk technique [4]. The only modification to standard synthesis routes for metallic nanoparticles is the application of a sufficiently strong magnetic field. The method produces both ferromagnetic and diamagnetic nanoparticles, but it is relatively easy to harvest the ferromagnetic ones. When prepared without protective agent, the ferromagnetic nanoparticles will subsequently cluster into larger aggregates that can attain the macroscopic size of 1 mm and beyond!

For many applications, such as photo-thermal cancer treatment [5] and in catalysis engineering, the temperature dependence of the magnetism is important and so far we could only report on temperatures up to room temperature. In the present paper, we report on some new data regarding the temperature dependence of the magnetism. The important result is that we determined the temperatures beyond which we do not observe ferromagnetic behavior. These temperatures are 833 K and 850 K for platinum and gold respectively.

2. Experimental

The materials, methods and instrumentation techniques employed in this work, unless specified, are based on our previous report [4]. To obtain ferromagnetic samples of higher purity, metal clusters were washed several times in water under constant action of the magnetic stirrer. Magnetometry for temperature dependence was carried out on a Versalab vibrating sample magnetometer (VSM) from Quantum Design (QD). Magnetic (nano)particle clusters were washed at least twice with ethanol and water before drying and loading them into sample holder made of ceramic. Zircar® cement was applied to secure the sample to the holder. The ramping rate for temperature scans was 50 K/min.

3. Results and discussion

Let us briefly illustrate the behavior of the magnetic noble metal nanoparticles that we recently obtained with our slightly improved synthesis procedure. In Fig. 1 TEM-micrographs of typical nanoparticle clusters of the various noble metals are displayed. The primary size of the nanoparticles of platinum, gold, silver and copper

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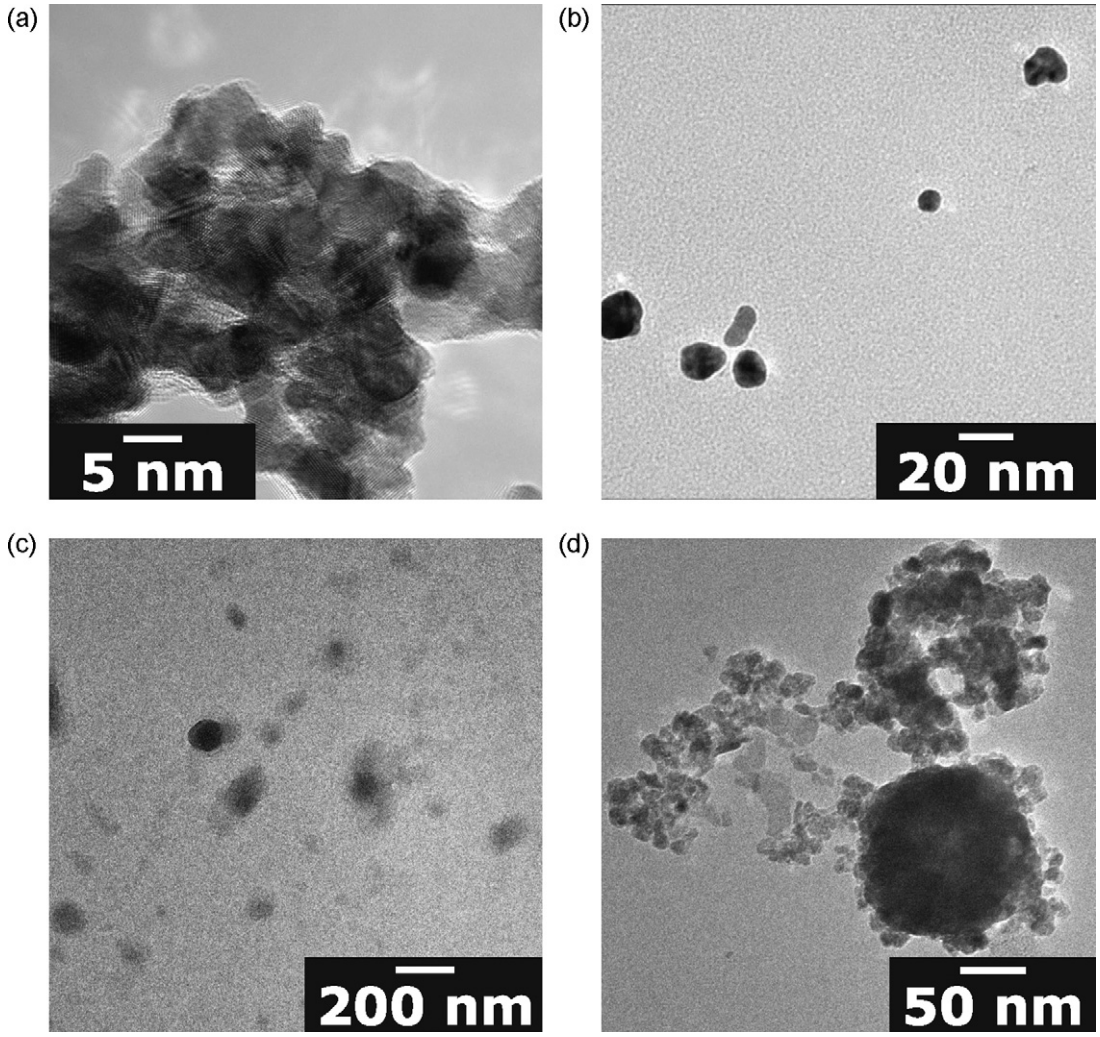

Fig. 1. Transmission electron microscopy (TEM) micrographs of the magnetic (nano)particle clusters of (a) platinum, (b) gold, (c) silver, and (d) copper respectively.

are 5.8 ± 1 nm, 14.8 ± 3.6 nm, 112.3 ± 10.1 nm and 15.2 ± 2.6 nm, respectively. Since these particles were prepared without protective agent, they cluster into aggregates of various sizes which are also polyhedral like the primary particles.

In Fig. 2 the typical magnetic behavior of the nanoparticles is shown for the various noble metals. The behavior of the ferromagnetic particles is relatively pronounced, albeit much smaller than that of iron which has a saturation value of 222 Am^2kg^{-1} [6]. The highest saturation magnetization, M_{sat} of 13 Am^2kg^{-1} was shown by gold sample, which also had the highest coercivity, B_C of 20 mT along with the silver sample. The remanence, M_R however, was most prominent in the platinum sample. The behavior of the diamagnetic particles is modest and for comparison shown in the same plots. The gold sample was the most susceptible of them all with a mass susceptibility χ of -2.4×10^{-6}. Magnetic properties of all samples are given in Table S1 of the Supporting information. The improved synthesis procedure was most beneficial for the gold nanoparticles where the saturation magnetism is six times larger than what we reported earlier [4].

Fig. 3(a) summarizes our main findings on the temperature dependence of the zero field and field cooled magnetization of the gold particles. Similar graphs have been obtained for platinum (see Supporting information). The high temperature magnetization, in zero and finite magnetic field, clearly demonstrates vanishing ferromagnetism beyond a temperature of about 850 K. This is a surprisingly high temperature, far below the melting point 1337 K of bulk gold and also below the melting point of about 985 K that was reported for 15 nm gold nanoparticles [7].

At low temperatures ferromagnetic order persists leading to remanence at zero magnetic field. At increasing temperatures thermal energy becomes stronger and at some point the ferromagnetic ordering is lost, this is what is commonly known as the Curie temperature [8]. At the Curie temperature, T_C, the magnetization M is known to vary with temperature, T as:

$$M \propto (T - T_C)^{\beta} \quad (1)$$

with the exponent β, which has the typical value of 1/3 [8]. In Fig. 3(b) a plot is made of the spontaneous magnetization as a function of the temperature difference with the Curie temperature. From this graph we obtain a value of 0.78 for the exponent β in Eq. (1). This value is very much larger than the commonly reported value for bulk materials, but it is exactly equal to what has been measured and calculated as the magnetization exponent for surface layers, see [9] and references therein. This supports our hypothesis made in the earlier paper [4] that the magnetism that we induce during synthesis in the noble metal particles is not a bulk effect but a surface effect.

Fig. 4(a) shows the dependence of magnetization on temperature for gold particles. On heating a progressive loss in ferromagnetic order is observed with a clear transition into a