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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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