

Correction to "Synthesis of Magnetic Noble Metal (Nano)Particles"

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Langmuir 2011, 27 (12), 7783–7787. DOI: 10.1021/la105051v

■ INTRODUCTION

Recently, some of us reported on the production of magnetic noble metal nanoparticles.^{1,2} It was claimed, that when noble metal nanoparticles were synthesized in a sufficiently strong magnetic field, they would acquire (ferro)magnetism. The obtained magnetism was reported to be equivalent to that of iron if present at about 2% of the total mass. This amount of iron was orders of magnitude larger than what was actually detected with the techniques used.

We here report on new experimental results that were obtained while trying to enhance the yield of magnetic material.

■ MATERIALS AND METHODS

Noble metal precursors chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$, $\geq 99.9\%$), silver nitrate (AgNO_3 , $\geq 99.8\%$), and reducing agent sodium borohydride granules (NaBH_4 , $\geq 99.9\%$ metal basics) were used. Reagent-grade Millipore water produced by an AFSTM 3D Millipore water purification system was used in all sample formulations. All materials were used as received without further purification.

Reactions for nanoparticle clusters as detailed below were carried out on an IKA Labortechnik RCT magnetic stirrer plate set at rotational speeds from 600 to 1000 rpm. These stirrers were ordered from IKA-Werke GmbH & Co. KG. No magnetic stir bars or beans were introduced during the preparation procedure. The stirrer plate, which produces 20 mT at the point of contact, was the only source of magnetic induction. Magnetic clusters were identified and separated by looking at those that spin with the rotation of the stirrer's magnetic field. The magnetic clusters were then separated by fishing them out with a glass pipet and suspending them in water.

Aqueous solutions were prepared by mixing the noble metal precursor or the reducing agent with water in the required concentrations. Clusters were prepared by mixing equal volumes of aqueous solutions of the metal precursors with the reducing agents in a 1:10 molar ratio and keeping the precursor solution concentration constant (1 mmol). This method predominantly produces diamagnetic particles and just a fraction of ferromagnetic particles.

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were conducted using a JEOL JSM-6010LA scanning electron microscope (SEM) operating at 20 kV, at 1000 \times magnification. The samples were deposited on a silicon wafer by placing the (nano)particle cluster (suspended in water) and evaporating the water in a Heraeus heater operated at 70 °C. EDS was performed using microprobe (low-resolution) modes.

X-ray photoelectron spectroscopy was performed in a Kratos Axis Ultra DLD with an Al K α (mono) X-ray source operated at 10 mA 15 kV and 150 W. The lens mode is set to hybrid and iris (Aper) mode. The survey is performed from 1200 to -5 eV with a step size of 0.25 eV and a dwell time of 500 ms. Samples for this measurement ((nano)particle clusters in water) are placed on a silicon wafer and dried before placing on the instrument.

Inductively coupled plasma–optical emission spectroscopy (ICP–OES) was executed on the Optima 5300dv instrument from PerkinElmer Incorporated. Samples were not acidified with hydrochloric acid.

■ RESULTS

The produced noble metal clusters were shown to be magnetic, with specific magnetizations as reported in the previous papers.^{1,2} The bulk synthesis route as presented in the original paper² was used here only because the first method did not result in sufficient amounts of magnetic material. Attempts to increase the yield of these ferromagnetic (nano)particle clusters were not successful. The surface composition of the Pt clusters was examined by means of X-ray photoelectron spectroscopy (XPS) (Figure 1).

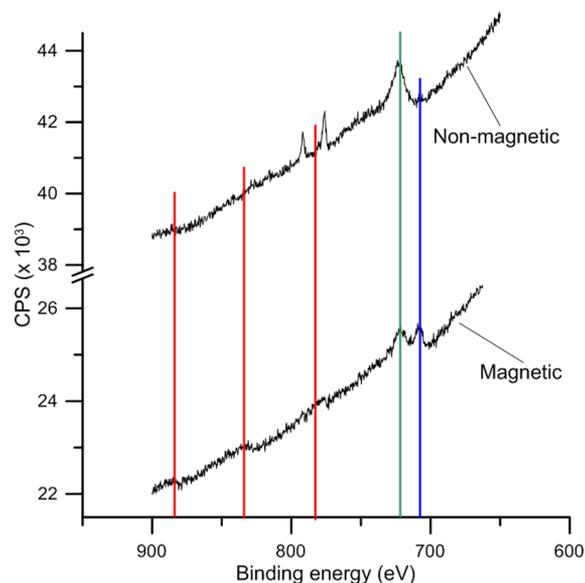


Figure 1. XPS spectrum of magnetic and nonmagnetic Pt (nano)particle clusters. Blue lines correspond to Fe 2p peaks, and red lines are Fe Auger peaks corresponding to peaks of oxides of iron; the green line represents the Pt 4s peak.

In contrast to what was reported by Kowlgi et al.,² peaks of ferromagnetic impurities, in particular, of Fe, were served in the XPS spectra (Figure 1), whereas these are absent in the spectra of nonmagnetic material. Peaks were observed at binding energies of 707 and 720 eV, which are characteristic Fe 2p values, for the magnetic nanoparticle clusters. Another interesting observation was the small and relatively insignificant peaks at binding energies corresponding to Auger peaks of iron or its oxides, whereas Fe 2p peaks were insignificant in nonmagnetic (nano) particle clusters. The origin of the two peaks close to the Auger lines in the spectrum of the nonmagnetic material is unknown; the positions are

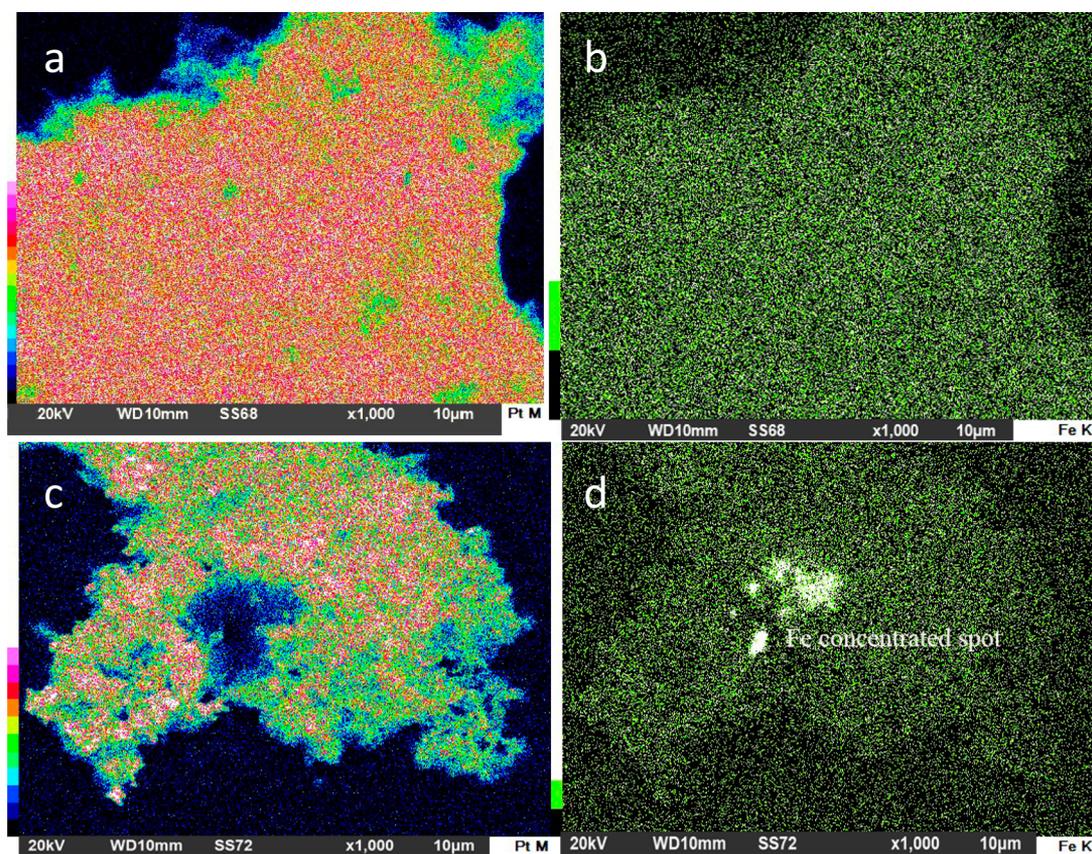


Figure 2. EDS mapping of a nonmagnetic Pt nanoparticle cluster (a, b) and a magnetic nanoparticle cluster (c, d) with the mapping of Pt (a, c) and Fe (b, d). The color differences are due to prolonged exposure.

those for barium. These results suggest that the origin of ferromagnetism in magnetic nanoparticle clusters is due to traces of Fe, presumably present on the surface of nanoparticle clusters.

Also, energy-dispersive X-ray scattering on the clusters revealed the presence of iron, although it requires some expert searching (Figures 2 and 3): the iron is present in an extremely localized form as small atomic clusters on the surface of the noble metal clusters. Point analysis gave 4 wt % iron for clustered Pt nanoparticles and 34 wt % for clustered silver nanoparticles. It is important to stress that the total amount of iron present in the clusters is below the detection limit as can be seen from Table 1.

Table 1. Comparison in Composition of Nonmagnetic and Magnetic Pt (Nano)Particle Clusters from XPS and EDS Results^a

element	atomic percentages from XPS		mass percentages from EDS		
	nonmagnetic (%)	magnetic (%)	nonmagnetic (%)	magnetic	
				Pt spot (%)	Fe spot (%)
Pt	28	12	85	70	43
Fe	nd	2	n.d.	1	4

^aThe contribution of the Si background has been subtracted, but elements such as Na, C, and O constitute the remaining share of mass and atomic percentages. The sensitivity of the EDS instrument is $\pm 1\%$; n.d. = not detected.

DISCUSSION

The above-presented results from XPS and EDS measurements clearly indicate that the magnetism in noble metal nanoparticles as claimed to develop according to previous published papers^{1,2} is not present. This was ultimately verified by acid washing of the magnetic nanoparticle clusters: this removed not only the iron surface impurities but also the magnetism. This final experiment also explains how it is possible that the careful experiments carried out by Kowlgi et al. could lead to such erroneous results. The ultimate test for this paper was the inductively coupled plasma–atomic emission spectroscopy (ICP–AES). The quantities of the most probable ferromagnetic impurities (cobalt, iron, neodymium, and nickel) were found to be 3 orders of magnitude lower than the yields of ferromagnetic noble metals produced during synthesis. The reason for this apparent contradiction is the fact that before this analysis, samples were acidified with 0.6 M hydrochloric acid. Another reason for not finding the impurities is that most used techniques typically produce overall results. Here only the local EDS that was used could eventually demonstrate small localized atomic clusters of iron. The source of the iron has not been traced unambiguously but is most likely due to the glassware that was used.

CONCLUSIONS

The development of magnetization in noble metal nanoparticles as previously reported by some of us^{1,2} is due to localized iron impurities on the surface of the nanoparticle clusters.

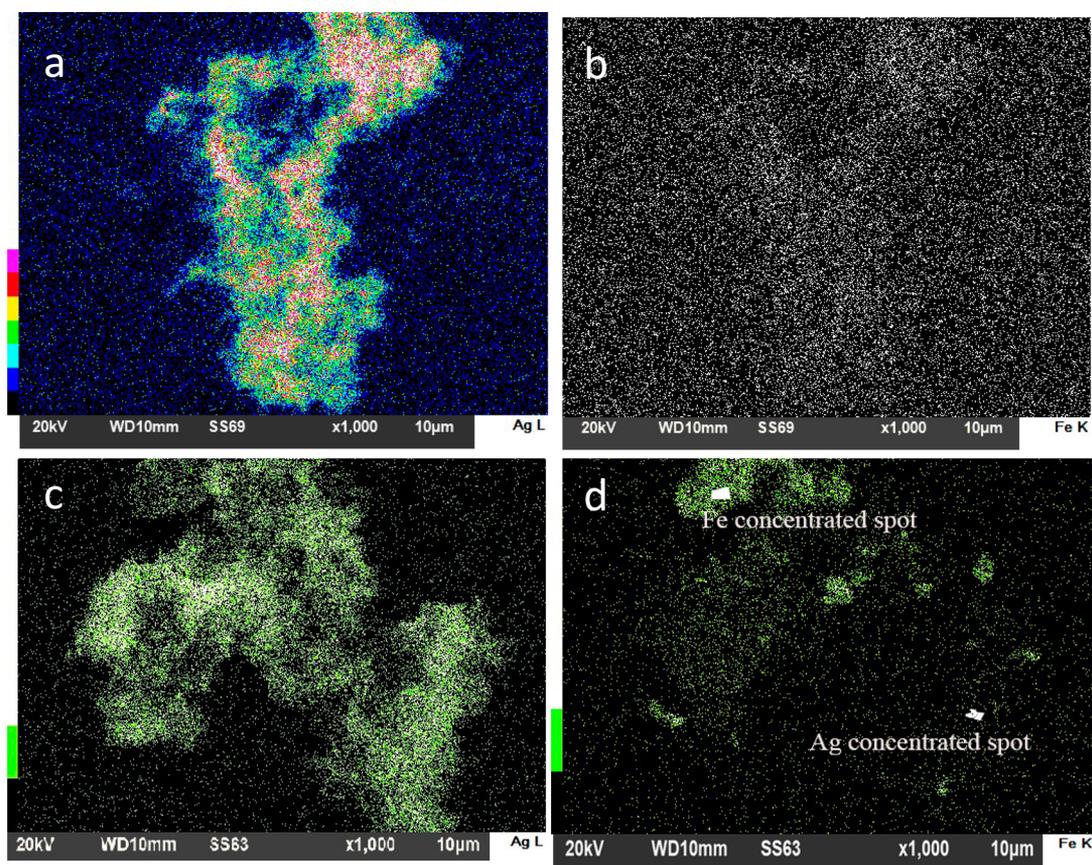


Figure 3. EDS mapping of a nonmagnetic Ag nanoparticle cluster (a, b) and a magnetic Ag nanoparticle cluster (c, d) with the mapping of Ag (a, c) and the mapping of Fe (b, d). Fe is insignificant in the nonmagnetic cluster, and in the magnetic sample it is concentrated in spots along the periphery of the NP cluster; the spots taken for point analysis are also indicated.

The erroneous result of the previous papers could be traced to an acid washing step before the conclusive ICP–AES experiment.

■ ACKNOWLEDGMENTS

We acknowledge financial support from the Ministry of Economic Affairs in The Netherlands in the framework of the IOP-Self Healing Materials (SHM) Program.

■ REFERENCES

- (1) Kowlgi, K.; Zhang, L.; Picken, S.; Koper, G. Anomalous magnetism in noble metal (nano)particles. *Colloids Surf, A* **2012**, *413*, 248–251.
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