Supporting Information for

Synthesis of Au-Based Porous Magnetic Spheres by Selective Laser Heating in Liquid

Zaneta Swiatkowska-Warkocka, Kenji Kawaguchi, Yoshiki Shimizu, Alexander Pyatenko, Hongqiang Wang and Naoto Koshizaki

Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, 305-8565 Ibaraki, (Japan)

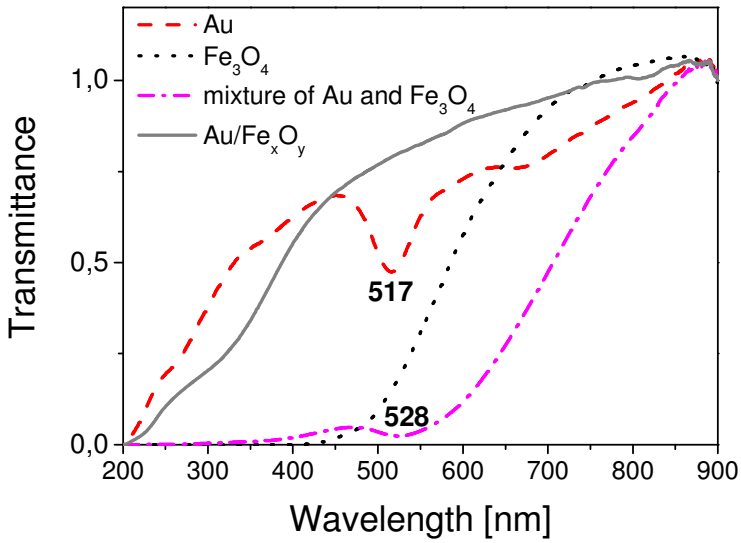

Figure S1. Normalized UV-vis spectra of Au nanoparticles (red, dashed line), Fe_3O_4 nanoparticles (black, dotted line), mixture of Au + Fe_3O_4 before laser irradiation (pink, dash-dotted line) and after laser irradiation (gray, solid line).

Detailed analysis on UV-vis spectra. Figure S1 shows the room-temperature UV-vis spectra of Au nanoparticles, Fe_3O_4 nanoparticles, mixture of Au+Fe_3O_4 nanoparticles before and after laser irradiation dispersed in ethanol. It is known that Au nanoparticles with size ranging from 5 nm to 20 nm in diameter have plasmon absorption bands at about 520 nm.[1] As expected the characteristic absorption band of Au nanoparticles occurred at 517 nm, while Fe nanoparticles did not exhibit any characteristic absorption bands because of the absence of surface plasmon resonance (SPR). Herein, compared to pure Au nanoparticles, the mixture of Au+Fe_3O_4 before laser irradiation shows that the SPR peak is broader and red shifted (528 nm), what could indicate the agglomeration of particles. The exact absorption varies with particles morphology and particle surface coating. For Au/Fe_xO_y particles after laser irradiation no absorbance is observed. This implies that particles after laser irradiation have low surface Au content.

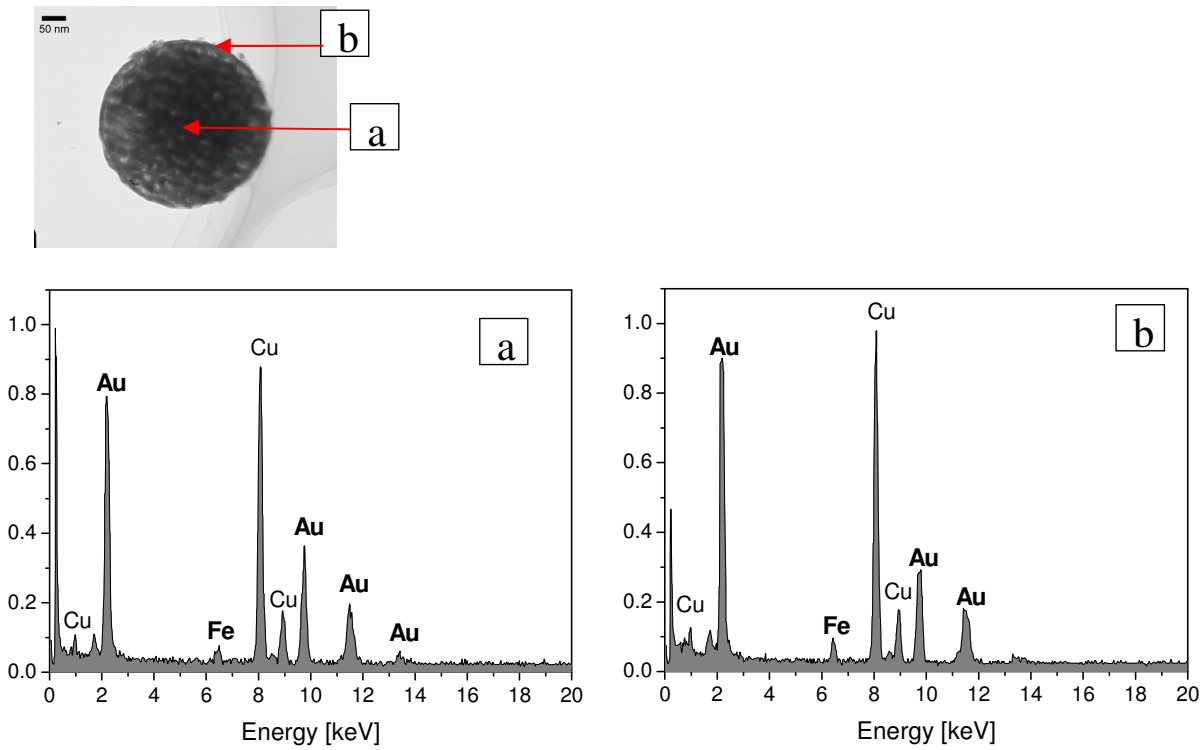

Figure S2. TEM image of Au/Fe_xO_y particle after acid treatment and EDS spectra obtained at (a) the center and (b) the edge of the particle.

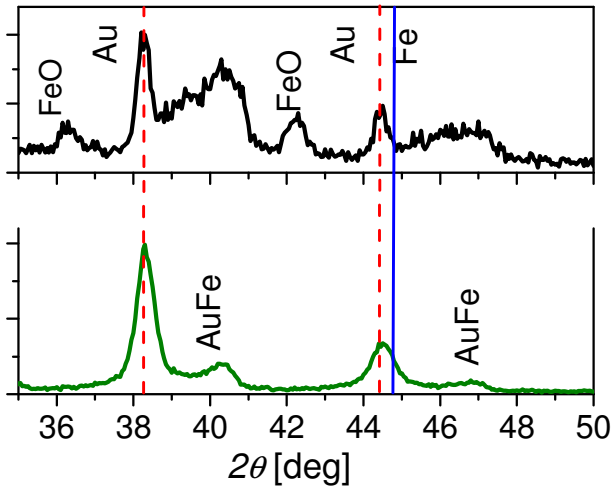

Figure S3. XRD pattern for Au/Fe_xO_y particles before (top, black line) and after acid treatment (bottom, green line). (Au, dashed vertical line; Fe solid vertical line).

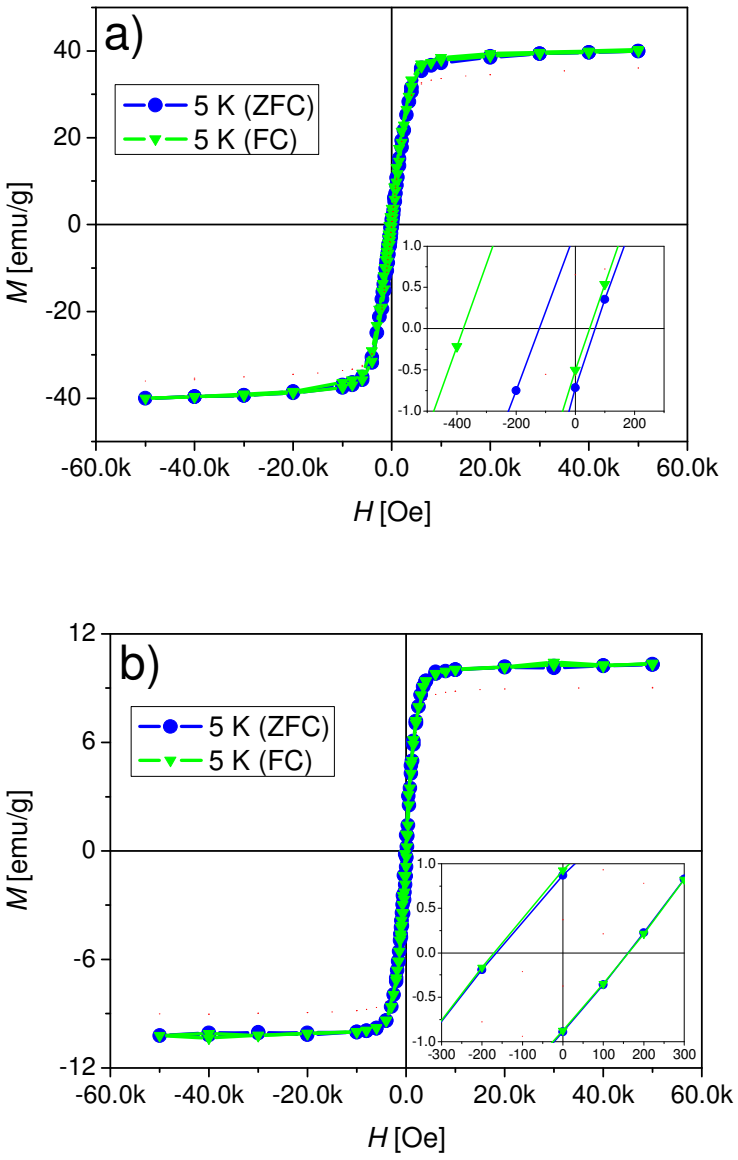

Figure S4. Magnetic hysteresis loop pattern of Au/Fe_xO_y particles before (a) and after acid treatment (b) at 5 K. Field cool (FC) means that the sample is cooled from 300 K to 5 K in the 50 kOe field, Inserts demonstrate the magnification around origin of hysteresis loops of the obtained particles.

Detailed analysis on magnetic properties at 5 K. Figures S4a and S4b illustrate the FC (H_{FC}=50 kOe) and ZFC hysteresis loops at 5 K for a cycling field ±50 kOe of samples before and after acid treatment, respectively. According to Figure S4a, particles before acid treatment exhibit the properties of exchange bias system, with a horizontal shift along the field axis of the FC hysteresis loop with respect to the ZFC hysteresis loop. The loop shift is defined as an exchange bias field $H_{exch} = |(H^+ + H^-)/2|$, where H^+ and H^- are positive and negative coercive fields. The FC hysteresis loop is shifted with an exchange bias field of 166 Oe. The coersive field given by $H_c = (H^+ - H^-)/2$ is 95 Oe for ZFC and 214 Oe for FC, respectively. The exchange bias and coercive field enhancement indicates a magnetic interaction through the interface between ferromagnetic and antiferromagnetic phase.[2] From XRD results we can suppose that in this case antiferromagnetic phase is presented by FeO component and ferromagnetic phase by Fe. In contrast, there are

no differences between ZFC and FC hysteresis loops for particles after acid treatment (coercive field H_c is 163 Oe for ZFC and FC). It means that the significant FeO-Fe interface connection exists before acid treatment and it disappears after acid treatment. This result is confirmed by XRD results which show that FeO component is removed by acid treatment.

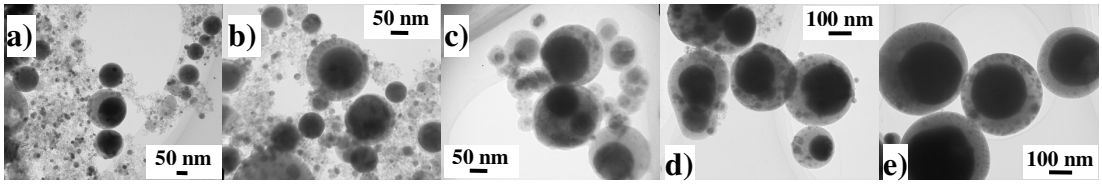

Figure S5. TEM images of Au/Fe_xO_y particles obtained by pulsed laser irradiation with different irradiation time: a) 5 min, b) 10 min, c) 15 min, d) 30 min, and e) 60 min.

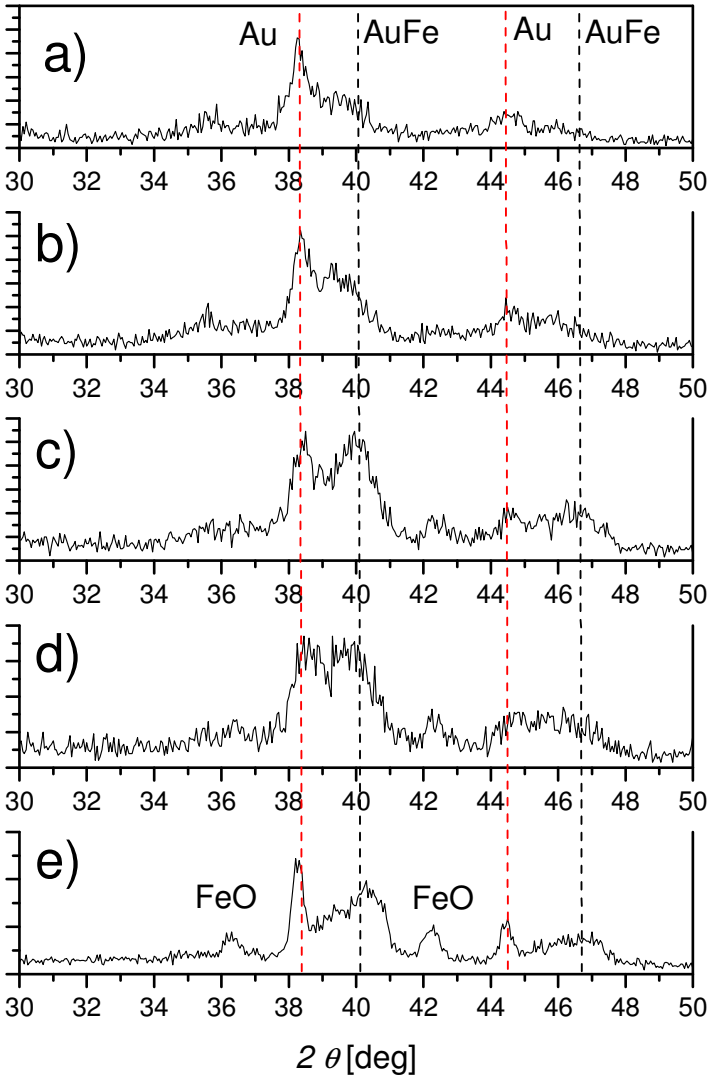

Figure S6. XRD pattern for Au/Fe_xO_y particles prepared by pulsed laser irradiation with different irradiation times: a) 5 min, b) 10 min, c) 15 min, d) 30 min and e) 60 min.

References:

(1) Daniel, M. C.; Astruc, D. Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chem. Rev.* **2004**, *104*, 293.

(2) Nogues, J.; Leighton, C.; Schuller, I. K. Correlation between antiferromagnetic interface coupling and positive exchange bias. *Phys. Rev. B* **2000,** *61*, 1315.