Supplementary Material (ESI) for *PCCP*

Supporting Information

Magneto-Optical $FeGa_2O_4$ Nanoparticles as Dual-modality High Contrast Efficacy T_2 Imaging and Cathodoluminescent Agents

Chih-Chia Huang,[a] *Chia- Hao Su,*[a,b] *Mei-Yi Liao*[c] *and Chen-Sheng Yeh**[a]

[a]Department of Chemistry, National Cheng Kung University, Tainan 701, Taiwan

[b]National Taiwan University Research Center for Medical Excellence, College of Medicine, National Taiwan University, Taipei 100, Taiwan

[c]National Nano Device Laboratories, Chi-Mei building, National Cheng Kung University, Tainan, 701, Taiwan.

*Corresponding author: csyeh@mail.ncku.edu.tw

Experimental Section

Preparing $FeGa_2O_4$ nanoparticles. To prepare an amorphous GaOOH particles solution as a Ga source, laser ablation of gallium metal was performed for 20 min.[1] We used an unfocused Nd:YAG laser (Quantel Brilliant), operated at 10 Hz (5-ns pulse width) with a wavelength of 1064 nm. A gallium plate (> 99.9%, 1.5 cm × 1 cm) was placed on the bottom of a Pyrex vial filled with 5 mL of solution from a 4-mL aqueous solution containing 2.2 mM of CTAB (99+%) (cetyltrimethylammonium bromide, Acros Organics) mixed with 1 mL of 2-propanol (J. T. Backer) containing 1 mM of PVA (88 % hydrolyzed, *M*w = 22000) (polyvinyl alcohol, Acros Organics). Commercial PVA (88 %) is available in partial hydrolysis of poly (vinyl acetate) to PVA and remains acetate groups of poly (vinyl acetate).[2] Urea ($(NH_2)_2CO$) (99%) (Showa Chemical) was a source of hydroxide ion for co-precipitation of amorphous GaOOH particles and $FeCl_2{\cdot}4H_2O$, (J. T. Backer).

$FeGa_2O_4$ nanoparticles were prepared via a reaction of $FeCl_2$, urea, and amorphous GaOOH particles in a reflux system at 120 °C for 2.5 h: 5 mL of amorphous GaOOH (1.13 ± 0.09 mM), 0.002 g of $FeCl_2{\cdot}4H_2O$, and 0.1 g of urea were mixed with constant magnetic stirring until the solution turned clear yellow. The solution was then transferred to a flask with a reflux condenser, which was maintained at 120 °C for 2.5 h. The solution gradually changed from light yellow to black as reflux occurred. The resulting precipitates were collected using centrifugation and were washed several times with distilled water.

In vitro MRI. The experiments were done using a spectroscope (3T MRI Biospec; Bruker Optik GmbH, Ettlingen, Germany). A gradient system mounted on the table of a 3T magnet (inner diameter: 6 cm; maximal gradient strength: 1000 mT m^{-1}) was used to yield high-resolution images. A quadrature coil (inner diameter: 3.5 cm) was used for RF transmission and reception. For T_1 and T_2 measurements, $FeGa_2O_4$ nanoparticles with various concentrations of iron (0-0.2 mM) were dispersed in 0.5% agarose gel. The acquired MRIs (matrix size: 256 × 192; field of view: 60 × 60 mm^2; slice thickness: 3 mm) had an in-plane resolution of 234 μm after image smoothing. Both T_1- and T_2-weighted images were acquired using a multi-slice multi-echo (T_1-weighted) and fast-spin echo (T_2-weighted) sequence with a repetition-time/echo-time (TR/TE) of 427/9.4 ms and a NEX (number of averages) of 10 (T_1), and with a TR/TE of 4500/62.7 ms and a NEX of 5 (T_2). T_1 value measurements were taken using a multi-slice multi-echo sequence with a TR of 6000 ms, a TE of 8.7 ms, and 45 inversion recovery points (TI: 13.3-6000 ms; field of view: 60 × 60 mm^2; slice thickness: 6 mm; image matrix: 128 × 128). This allowed for simultaneous imaging of 26 vials with 0.3 mL of contrast agent per vial. An average signal of 50 voxels was evaluated for all TI values. T_2 value measurements were taken with a spin-echo sequence of TR/TE of 4000/10.1 ms, 60 echo points with 60 different echo times, and a NEX of 5 (field of view: 60 × 60 mm^2; slice thickness: 6 mm; imaging plane: 256 × 192).

The biocompatibility of $FeGa_2O_4$ nanoparticles. To evaluate the biocompatibility of the $FeGa_2O_4$ nanoparticles, we used an MTT assay. A Vero (monkey kidney) cell line (4×10^3

cells/well) was cultured in a 96-well microplate containing α-modified minimal essential medium (MEM) (containing 20% FBS+ 1% PSN+ 4 μg/mL basic FGF) at 37 °C supplied with 5% CO_2/95% air. After 24 h, serial diluents of loaded nanoshells samples (at concentrations of 100, 10, 1, 0.1, 0.01, and 0.001 μg/mL) were added to the culture wells to replace the original culture medium. Subsequently, the cells were incubated with the $FeGa_2O_4$ nanoparticles for 24 h. The culture medium was then removed and replaced with 100 μL of fresh culture medium (α-modified MEM) containing 10% MTT reagent. The resulting cells were incubated at 37 °C for 4 h to allow the formation of formazan dye. The cultural medium in each well was centrifuged and collected, and then transferred to an ELISA plate. The quantification of cell viability was done using an ELISA plate reader at an optical absorbance of 540/650 nm.

Characterization. Electron micrographs using transmission electron microscopes (at 200 KV) (Philips CM-200) accompanied by an energy dispersive spectrometer (EDS) analysis were taken after a drop of the sample had been placed on a copper mesh coated with an amorphous carbon film and the solvent had been evaporated in a vacuum desiccator. Field emission scanning electron microscope (FE-SEM) images of the $FeGa_2O_4$ nanoparticles on the Si substrates were taken using an FE-SEM at 10 kV (Philips XL-40 FEG). Samples were excited by a 10 kV electron beam for CL measurements on a FE-SEM (Jeol 6330) at room temperature. X-ray diffraction (XRD) results were collected on a diffractometer (Rigaku D-Max IIIV) using Cu Kα radiation (λ = 1.54056 Å) at 30 kV and 30 mA. IR spectra were measured using a KBr plate in a

Fourier transformation infrared (FTIR) spectrometer (200E; Jasco International Co., Ltd., Tokyo, Japan). X-ray photoelectron spectra (XPS) (VG Scienti¯c 210) were recorded using an Mg Kα source (12 kV and 10 mA). The binding energy scale was calibrated to 284.6 eV for the main (C ls) peak. A thermogravimetric analysis (TGA) was done using ~10 mg of sample on a thermogravimetric analyzer (Netzsch TG209; Trendtop Scientific Corp., Chung-Ho City, Taipei Hsien, Taiwan) at a heating rate of 30 °C/min under dried air. The Ga and Fe ions were quantified using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Jobin Yvon JY138 Spectroanalyzer). The $FeGa_2O_4$ nanoparticles were magnetized (*M-H* loops) at 300 K with applied fields of up to 10 kOe using a Quantum Design MPMS-7 SQUID magnetometer. The ZFC and FC magnetization curves in a temperature range between 5 and 300 K at a 500 Oe applied field were measured for $FeGa_2O_4$ nanoparticles. The zeta-potential of the $FeGa_2O_4$ nanoparticles dispersing in an aqueous solution (pH = 6) was measured using a Zetasizer analyzer (Malvern, UK).

References

1. C. C. Huang, C. S. Yeh and C. J. Ho *J. Phys. Chem. B* 2004 **108***,* 4940-5.
2. H. S. Mansur, C. M. Sadahira, A. N. Souza and A. A. P. Mansur *Mater. Sci. Eng. C* 2008 **28** 539-48.

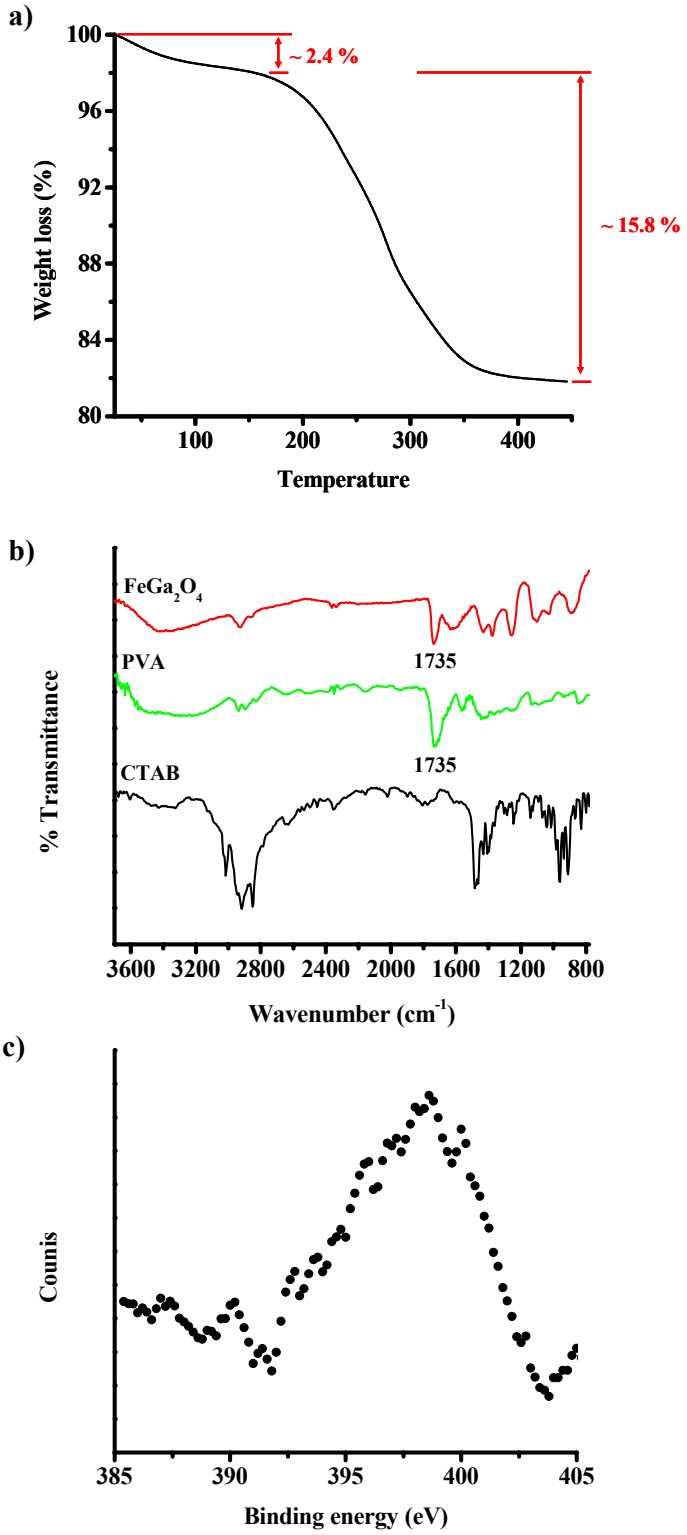

Figure S1. a) TGA profile for as-prepared $FeGa_2O_4$ nanoparticles. b) FTIR spectra of $FeGa_2O_4$, pure PVA, and pure CTAB. The absorption bands at 3550-3200 cm^{-1} and 1735 cm^{-1} in curve b is related to the stretching O-H and stretching C=O from the hydroxyl and acetate groups of PVA.[1] c) XPS spectrum of $FeGa_2O_4$ nanoparticles for N(*1s*) signal.

1. H. S. Mansur, C. M. Sadahira, A. N. Souza and A. A. P. Mansur *Mater. Sci. Eng. C* 2008 **28** 539-48.

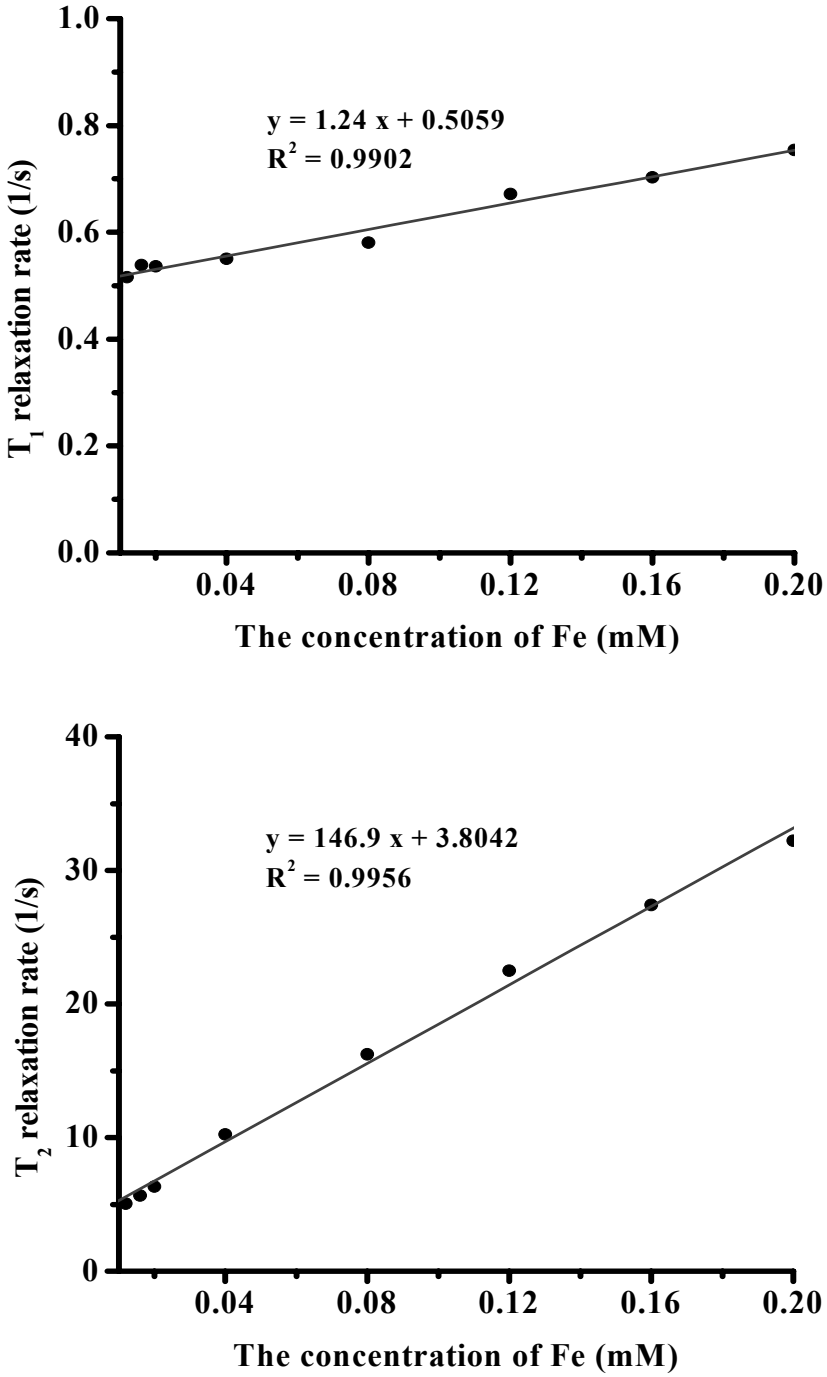

Figure S2. T_1 relaxation ($1/T_1$, s^{-1}) and T_2 relaxation ($1/T_1$, s^{-1}) rates of $FeGa_2O_4$ nanoparticles as a function of iron concentrations (mM).

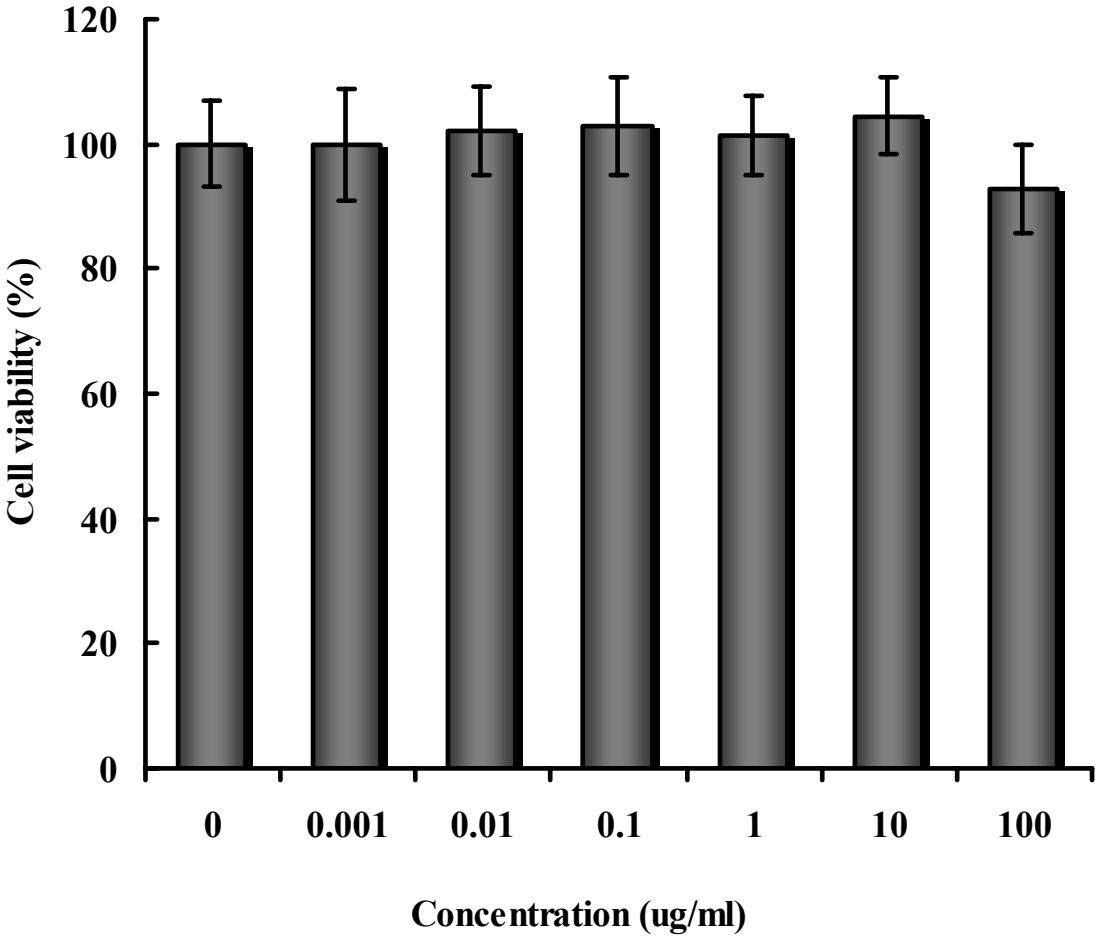

Figure S3. MTT assay of $FeGa_2O_4$ nanoparticles cultured with Vero cells for 24 h.