

Electronic Supplementary Information

Designed Synthesis of Well-defined Titania/Iron(III) acetylacetonate Nanohybrids with Magnetic/Luminescent Properties

Kota Shiba,^{*ab} Takuya Kataoka,^c Mitsuhiro Okuda,^{de}
Santiago Blanco-Canosa,^{de} and Motohiro Tagaya^{**cf}

*a International Center for Young Scientists (ICYS), National Institute for Materials Science (NIMS),
1-1 Namiki, Tsukuba 305-0044, Japan.*

*b World Premier International Research Center Initiative (WPI), International Center for Materials
Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba,
Ibaraki 305-0044, Japan.*

*c Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1
Kamitomioka, Nagaoka, Niigata 940-2188, Japan.*

d CIC nanoGUNE, Tolosa Hiribidea 76, E-20018 Donostia-San Sebastian, Basque Country, Spain.

*e Ikerbasque, Basque Foundation for Science, Alameda Urquijo 36-5, Plaza Bizkaia, E-48011,
Bilbao, Basque Country, Spain.*

*f Top Runner Incubation Center for Academia-Industry Fusion, Nagaoka University of Technology,
1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan.*

* Corresponding author; e-mail: SHIBA.Kota@nims.go.jp

** Corresponding author; e-mail: tagaya@mst.nagaokaut.ac.jp

Detailed Experimental Method

1. Chemicals

Titanium tetraisopropoxide (TTIP: Tokyo Chemical Industry Co., Ltd., Fig. S1), Fe(III) acetylacetonate ($\text{Fe}(\text{acac})_3$: Tokyo Chemical Industry Co., Ltd., Fig. S1), isopropyl alcohol (IPA: Wako Pure Chemical Industries, Ltd.), octadecylamine (ODA: Aldrich, Inc., Fig. S1) were utilized in the present study. All the chemicals were used as received.

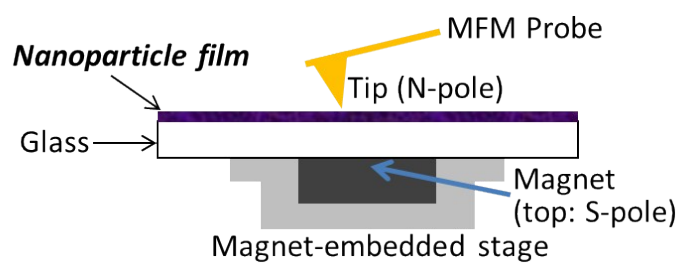
2. Experimental Procedures

For the titania/ODA/ $\text{Fe}(\text{acac})_3$ hybrid synthesis, three starting solutions (solutions A, B and C) were prepared. Detailed composition of each solution is summarized in Fig. S1. The solutions A and B were individually flowed in perfluoroalkoxyalkane (PFA: 1.0 mm inner diameter, 1/16 inch outer diameter, product of YMC Co., Ltd.) tubes with a syringe pump (CXN1070, product of ISIS, Co., Ltd.) at 30 mL/min. Then, two solutions were mixed in a polytetrafluoroethylene (PTFE) fluidic channel with a Y shape junction (the channel cross section of ca. 1 mm², KeyChem mixer, product of YMC Co., Ltd.). The mixture was flowed through a PFA tube with 70 cm in length and was added into the solution C under magnetic stirring at 1500 rpm. After the addition, the final reaction solution was aged at room temperature for 24 h.

3. Characterization

The samples were characterized by X-ray fluorescence analysis (XRF: ZSX Primus II, Rigaku, Japan). XRF analysis was performed using a sample pellet which was made by pressurizing sample powder without diluting it. The fundamental parameter method by the software (EZ scan program, Rigaku) was carried out for the semi-quantitative analysis. All the measurements and data analysis were conducted with an optional software (EZ scan program, Rigaku, Japan). Fourier transform infrared (FT-IR) spectra were obtained using a Fourier transform infrared spectrometer (FT/IR-4100, JASCO, Japan). FT-IR spectra were measured with a KBr pellet containing a small amount of sample powder. The weight ratio between sample powder and KBr was 1:10. All the spectra were recorded after subtracting a background spectrum of pristine KBr. The measurement range, sampling time and resolution were 4000-500 cm⁻¹, 100 and 2.0 cm⁻¹, respectively. X-ray diffraction (XRD) patterns were recorded with a powder X-ray diffractometer (Smart Lab, Rigaku, Japan). XRD patterns were measured under the following conditions: X-ray source of $\text{CuK}\alpha$ line (λ : 0.15418 nm), voltage/current of 40 kV/30 mA, scan speed of 5.0 °/min and sampling width of 0.01 °. All the samples were observed using a field emission scanning electron microscope (FE-SEM: SU8000, Hitachi High-Technologies, Japan). FE-SEM observation was performed at an accelerating voltage of 5 kV and current of 10 μA . Prior to the observation, suspension was drop-casted onto a silicon substrate and the substrate was stored in an oven until it was dried. Then, samples were coated with a

few nanometers of platinum. In addition to the FE-SEM observations, a scanning electron microscope equipped with energy dispersive X-ray spectroscopy (SEM-EDX: ESEM Quanta 250FEG, product from FEI Company for SEM observation and EDAX Apollo X SDD detector, product from EDAX Co., Ltd., for EDS analysis) was also utilized to estimate elemental ratio. SEM-EDX observation was performed at an accelerating voltage of 10 kV and current of 10 μ A. Prior to the observation, sample powder was mounted onto a carbon tape. Ultraviolet-visible (UV-Vis) spectra were obtained using an ultraviolet-visible-near infrared spectrometer (V-770, JASCO, Japan). UV-Vis spectra were measured under the following conditions: wavelength range of 200-870 nm, data acquisition interval of 0.5 nm, UV-Vis band width of 5 nm, near infrared band width of 20 nm and scan speed of 1000 nm/min. For the fluorescence measurements, a fluorescence spectrometer (FP-8500, JASCO, Japan) was utilized. Excitation and fluorescence spectra were measured under the following conditions: band width of 10 nm (excitation/fluorescence), scan speed of 200 nm/min, data acquisition interval of 0.1 nm, response time of 1 sec and PMT voltage of 350 V. In the case of titania, excitation and fluorescence wavelength were set at 426 nm and 460 nm, respectively. In the case of Fe(acac)₃, excitation and fluorescence wavelength were set at 518 nm and 610 nm, respectively. Powder sample was measured using a sample holder with a quartz window. A fluorescence microscope (CKX41, OLYMPUS, Japan) was also used for observing the samples. All the fluorescence microscope images were recorded under the following conditions: exposure time of 100 msec and sensitivity of ISO 400. Prior to the measurement, sample powder was homogeneously mounted on a carbon tape. U-RFLT50 (OLYMPUS, Japan) was used as a light source. The magnetic property of the samples were characterizing with the following apparatuses: magnetic force microscope (MFM: AFM5100N and AFM5000, Hitachi High-Tech Science, Japan) and vibrating sample magnetometer (VSM: Physical property measurement system-vibrating sample magnetometer, Quantum Design Co., Ltd.). MFM images were recorded under the following conditions: scanner of XY 150 mm and Z 5 mm, mode of MFM (controlled Q value) and cantilever of SI-MF40. Prior to the measurement, powder sample was dispersed in a solvent. The suspension was drop-casted onto a glass substrate, and the resultant film after drying was observed. Details of the present observation is schematically shown in Scheme S1. VFM measurements were conducted at room temperature. Powder samples were used for the measurements.



Scheme S1. Illustration of the experimental set-up for the MFM observation.

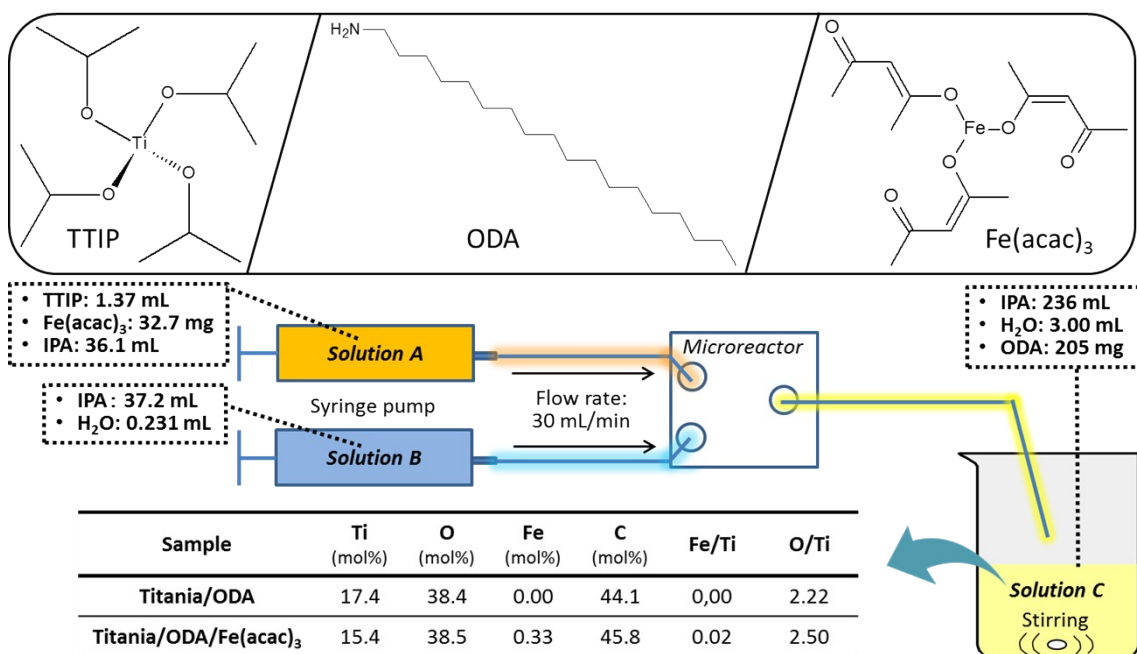


Fig. S1 Chemical structures of the reagents used in this study, an illustration of the experimental setup for the present microfluidic synthesis, and the resultant chemical compositions of the nanohybrids measured by XRF shown in a table.

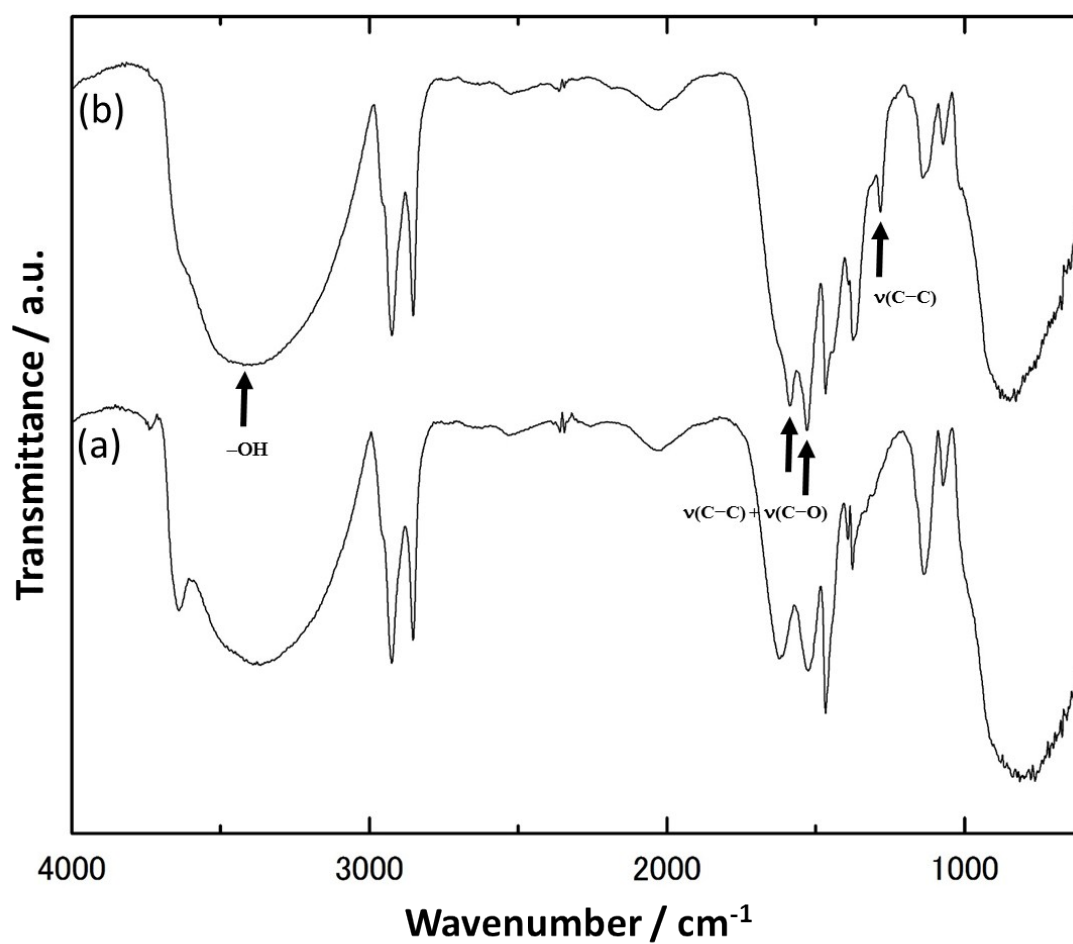


Fig. S2 FT-IR spectra of the (a) titania/ODA and (b) titania/ODA/Fe(acac)₃ nanohybrids. The arrows indicate the characteristic absorption bands.

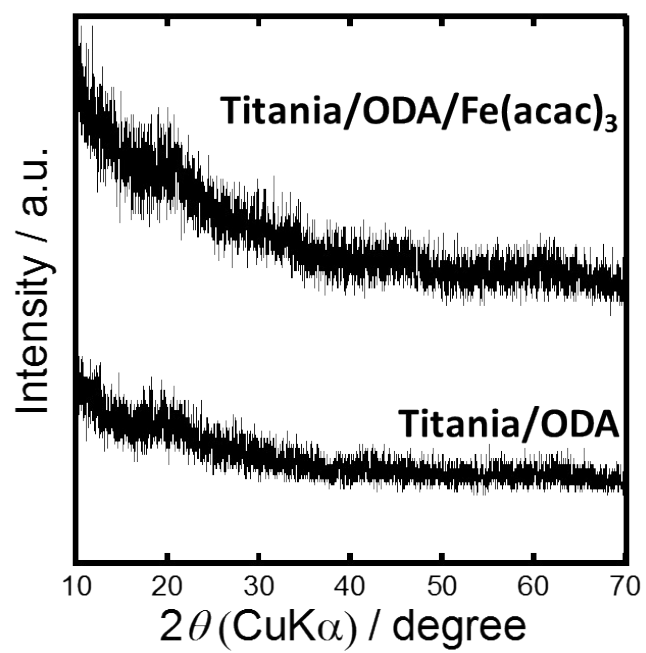


Fig. S3 XRD patterns of the titania and titania/ODA/Fe(acac)₃ nanohybrids.

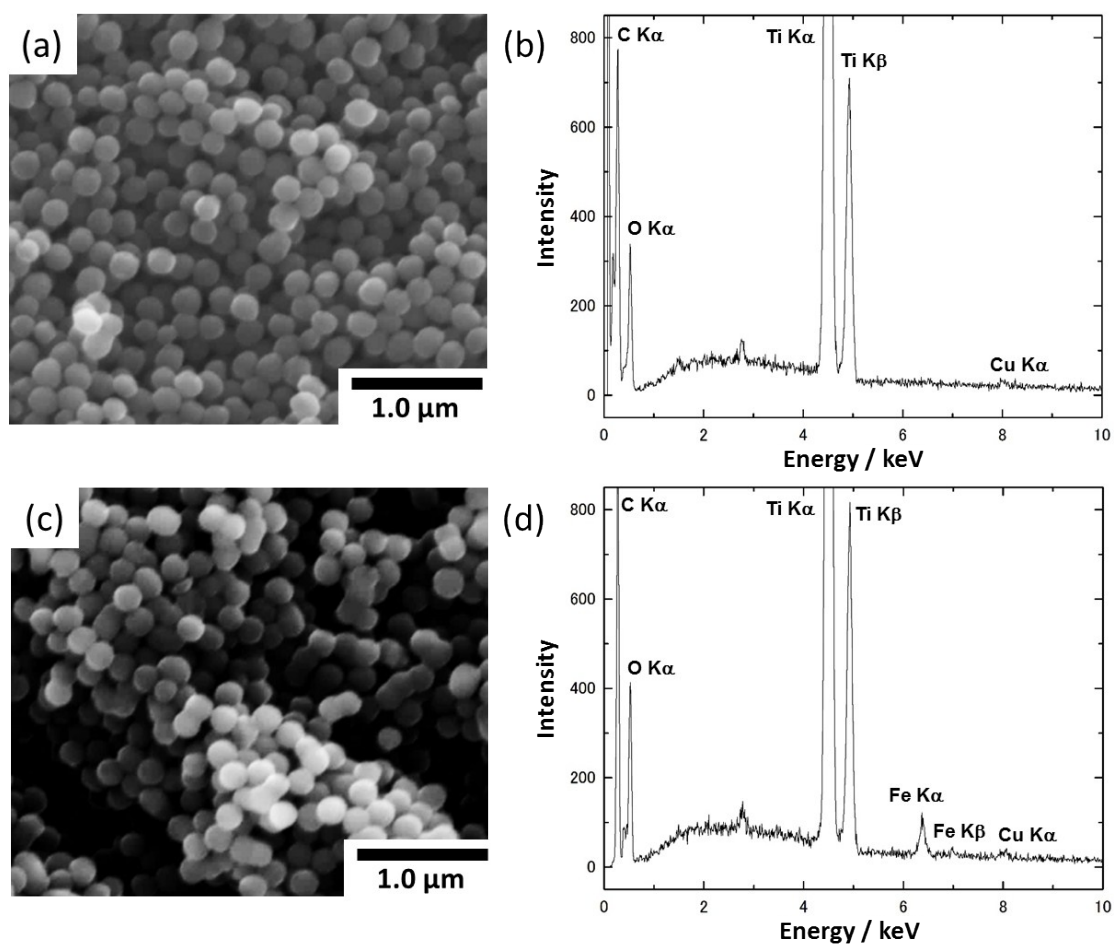


Fig. S4 (a, c) SEM images and (b, d) EDS spectra of (a, b) titania and (c, c) titania/ODA/Fe(acac)₃ nanohybrids.

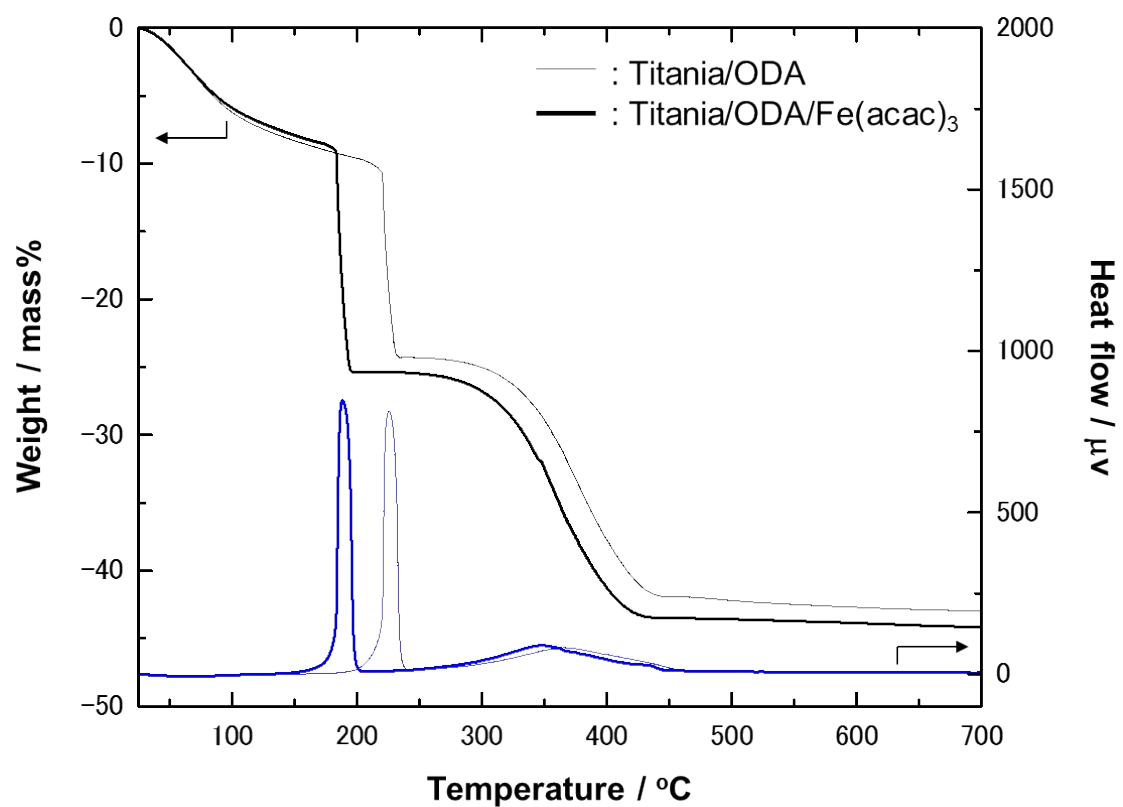


Fig. S5 TG (black)-DTA (blue) curves of (a) titania/ODA (normal line) and (b) titania/ODA/Fe(acac)₃ nano hybrids (bold line).

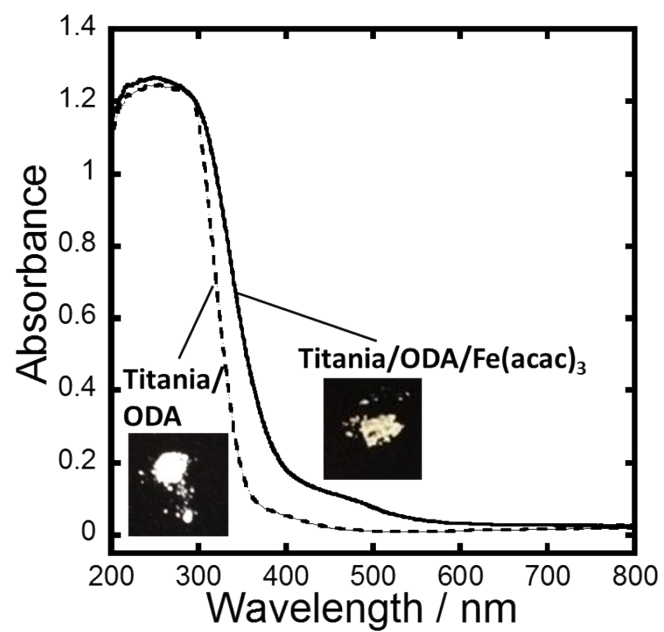


Fig. S6 Diffuse reflectance UV-Visible spectra of (a) titania/ODA and (b) titania/ODA/Fe(acac)₃ nanohybrids (Inset: the photographs of nanohybrids at the powder state).

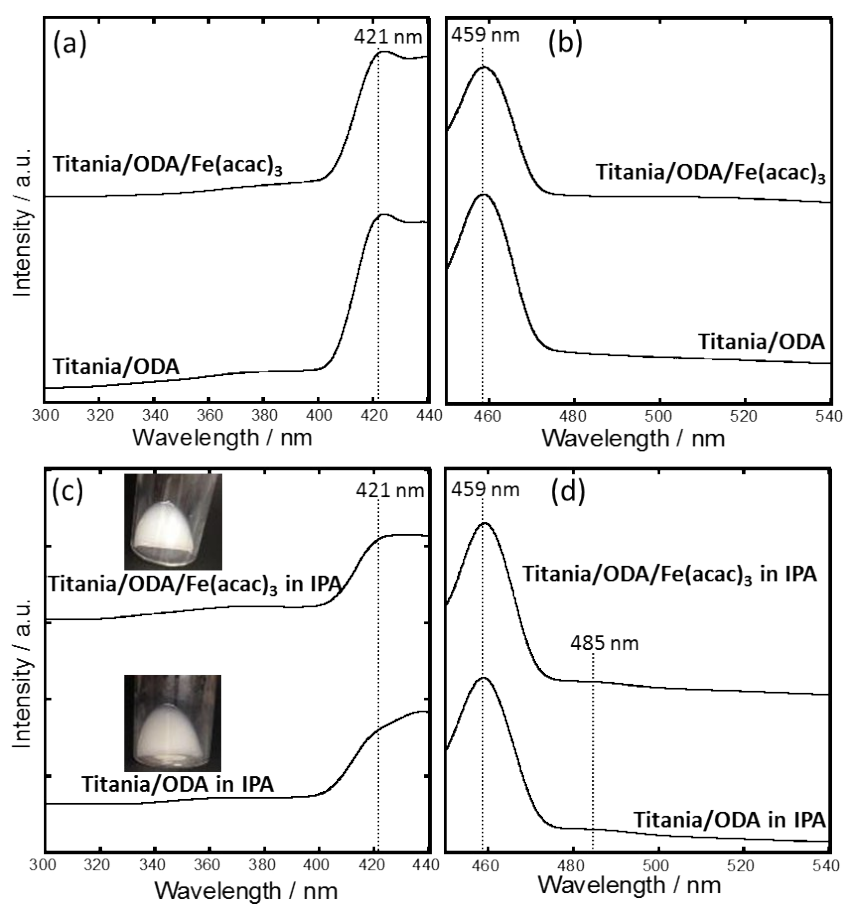


Fig. S7 (a, c) Excitation and (b, d) luminescence spectra of the nanohybrids at (a, b) powder state and (c, d) dispersion state in IPA (Inset in (c): the photographs of the dispersion state). The monitored luminescence and excitation wavelengths for the excitation and luminescence spectral measurements were 421 nm and 459 nm, respectively.

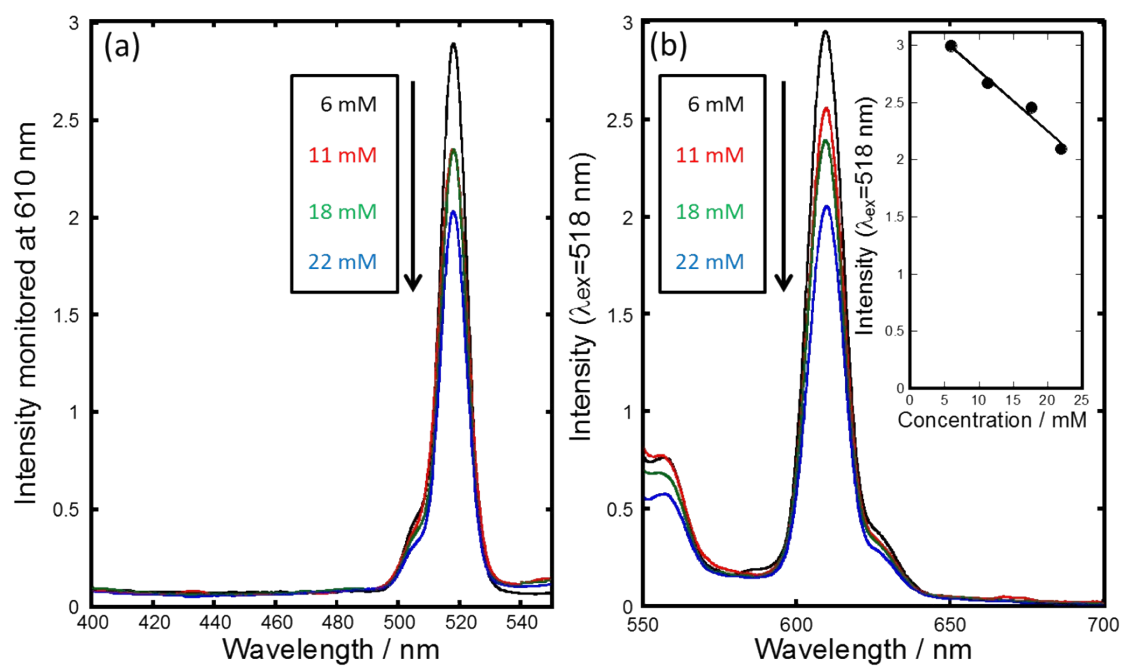
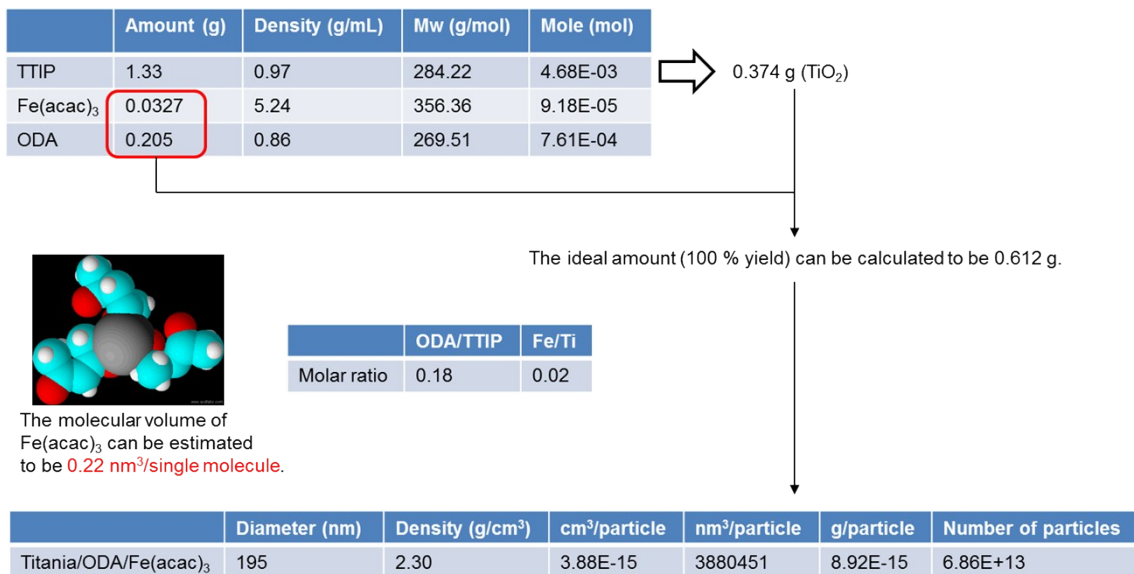


Fig. S8 (a) Excitation and (b) luminescence spectra of Fe(acac)₃ in IPA at the different concentrations (Inset in (b): the relationship between the concentration and luminescence intensity). The monitored luminescence and excitation wavelengths for the excitation and luminescence spectral measurements were (a) 610 nm and (b) 518 nm, respectively.



In the present case, a single particle should contain 8.03E+05 Fe(acac)₃ molecules inside.

Then, the occupied volume by a single Fe(acac)₃ molecule in the present hybrid particle is estimated to be 4.83 nm³, enabling to derive 1.61 nm if an Fe(acac)₃ molecule is geometrically isotropic.

The Fe(acac)₃ molecule has a one dimensional length of 0.59 nm if it is geometrically isotropic.

Consequently, the molecular distance between Fe(acac)₃ can be calculated to be 1.02 nm.

Fig. S9 Estimation of Fe(acac)₃ molecular distance in the titania/ODA/Fe(acac)₃ nanohybrids based on a geometrical calculation.