

## **SUPPLEMENTARY DATA**

### **Ultimately Simple One-pot Single-step Synthesis of Rare Earth Doped Spherical Mesoporous Metal Oxide Nanospheres with Upconversion Emission Ability in Supercritical Methanol**

Pengyu Wang<sup>a,\*</sup> Kazuya Yokoyama<sup>a</sup>, Tomoya Konishi<sup>b</sup>, Nagatoshi Nishiwaki<sup>a</sup>, Kazuya

Kobiro<sup>a,\*</sup>

<sup>a</sup> *School of Environmental Science and Engineering, Kochi University of Technology,*

*185 Miyanokuchi, Tosayamada, Kami, Kochi 782-8502, Japan*

<sup>b</sup> *Anan National College of Technology, 265 Aoki, Minobayashi-cho, Anan, Tokushima*

*774-0017, Japan*

## Table of Contents

1. Sample name and reaction conditions	S3
2. Rare earth doped MARIMO CeO <sub>2</sub> NPs	S4
3. ZrO <sub>2</sub> :Er MARIMO NPs	S10
4. TiO <sub>2</sub> :Er MARIMO NPs	S12
5. Metal or nitrogen doped TiO <sub>2</sub> MARIMO NPs	S15

## 1. Sample name and reaction conditions.

Table 1. Sample name and reaction conditions.<sup>[a]</sup>

Sample name	Metal salt or nitrogen containing compound			Carboxylic acid	Temperature [°C]
	<b>1</b>	<b>2</b>	<b>3</b>		
CeO <sub>2</sub> :Er (10:1)300	Ce(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Er(OCOCH <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	-	HCOOH	300
CeO <sub>2</sub> :Er (100:1)300	Ce(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Er(OCOCH <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	-	HCOOH	300
CeO <sub>2</sub> :Er :Yb (10:1:1)300	Ce(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Er(OCOCH <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	-	HCOOH	300
CeO <sub>2</sub> :Er:Yb (100:1:1)300	Ce(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Er(OCOCH <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	Yb(OCOCH <sub>3</sub> ) <sub>3</sub> ·nH <sub>2</sub> O <sup>[b]</sup>	HCOOH	300
ZrO <sub>2</sub> :Er (200:1)400	ZrO(NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	Er(OCOCH <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	-	CH <sub>3</sub> COOH	400
TiO <sub>2</sub> :Er (200:1)400	Ti(O <sup><i>i</i></sup> Pr) <sub>4</sub>	Er(OCOCH <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	-	CH <sub>3</sub> COOH	400
TiO <sub>2</sub> :Eu (10:1)400	Ti(O <sup><i>i</i></sup> Pr) <sub>4</sub>	Eu(OCOCH <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	-	CH <sub>3</sub> COOH	400
TiO <sub>2</sub> :Ce (10:1)400	Ti(O <sup><i>i</i></sup> Pr) <sub>4</sub>	Ce(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	-	CH <sub>3</sub> COOH	400
TiO <sub>2</sub> :Yb (10:1)400	Ti(O <sup><i>i</i></sup> Pr) <sub>4</sub>	Yb(OCOCH <sub>3</sub> ) <sub>3</sub> ·nH <sub>2</sub> O <sup>[b]</sup>	-	CH <sub>3</sub> COOH	400
TiO <sub>2</sub> :Fe (10:1)300	Ti(O <sup><i>i</i></sup> Pr) <sub>4</sub>	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	-	<i>o</i> -C <sub>6</sub> H <sub>4</sub> (COOH) <sub>2</sub>	300
TiO <sub>2</sub> :N (1:20)400	Ti(O <sup><i>i</i></sup> Pr) <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub> <sup>[c]</sup>	-	C <sub>6</sub> H <sub>5</sub> COOH	400

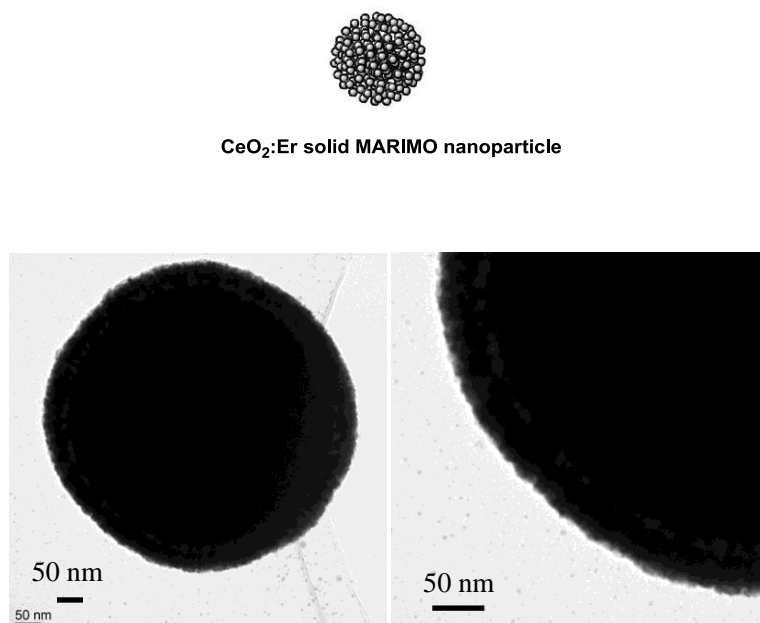
[a] Reaction conditions: 0.35 mmol of metal salt **1**, 0.035 or 0.0035 mmol of metal salt **2** or **3**, 1.75 mmol of carboxylic acid, under 0.28 g mL<sup>-1</sup> methanol density.

[b] Number of hydrate water is not clear. Mole number is supposed as a monohydrate form.

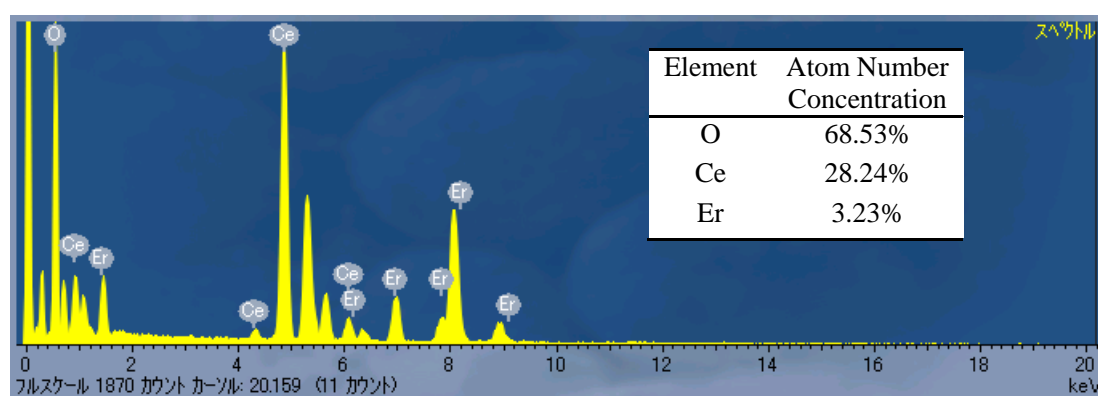
[c] 7 mmol.

### 3. Rare earth doped MARIMO CeO<sub>2</sub> NPs

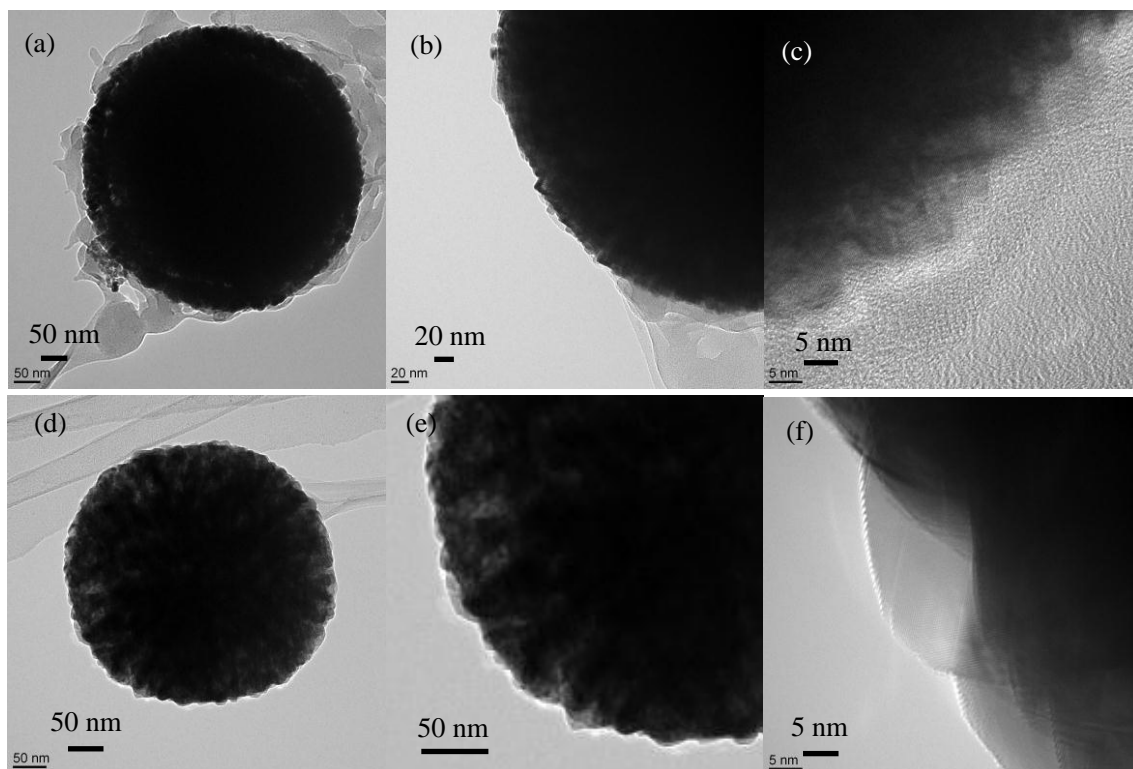
#### 3.1 CeO<sub>2</sub>:Er MARIMO NPs



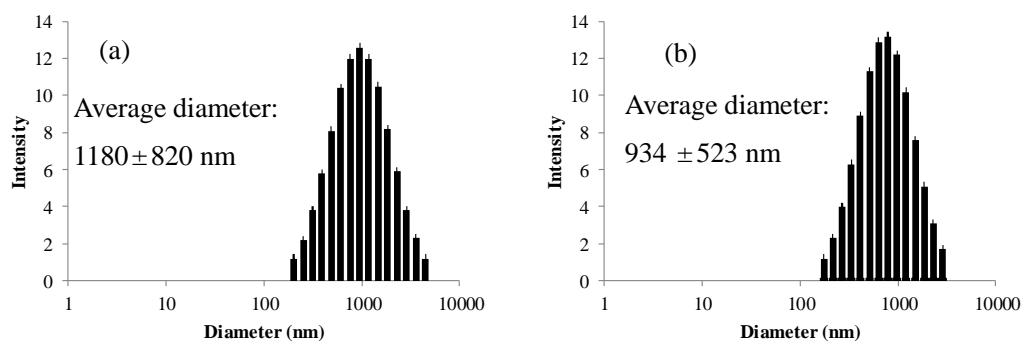
**Fig. S1.** TEM images of CeO<sub>2</sub>:Er (10:1)300 MARIMO NPs.



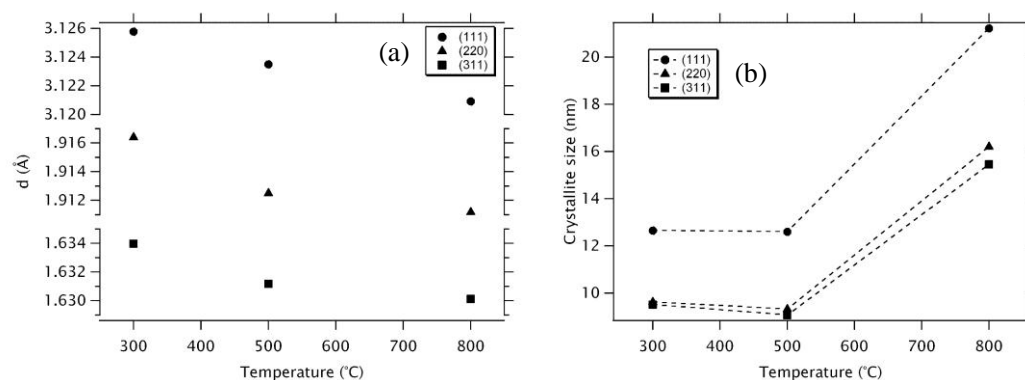
**Fig. S2.** EDX spectrum and atom number concentration of CeO<sub>2</sub>:Er (10:1)300 MARIMO NPs.



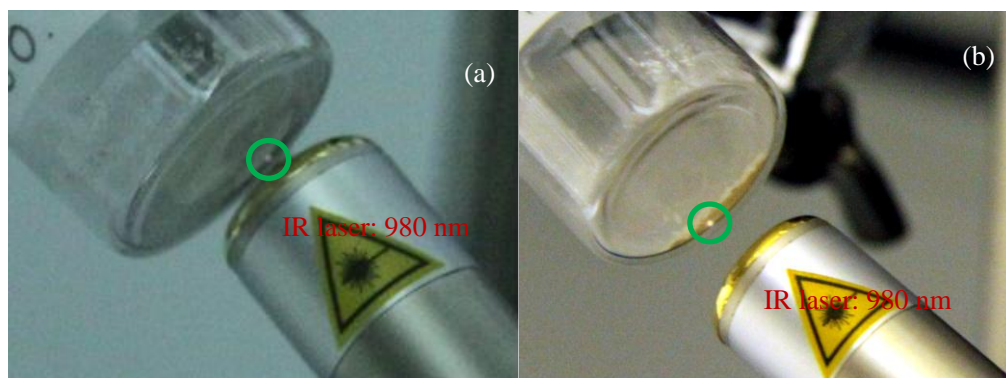
**Fig. S3.** TEM images of CeO<sub>2</sub>:Er (100:1)300 MARIMO NPs (a, b, and c) before and (d, e, and f) after calcination at 800 °C for 60 min in air.



**Fig. S4.** DLS plot of CeO<sub>2</sub>:Er (100:1)300 MARIMO NPs (a) before and (b) after calcination at 800 °C for 60 min in air.



**Fig. S5.** (a) Calcination temperature dependence of lattice constant and (b) calcination temperature dependence of primary crystallite sizes of the CeO<sub>2</sub>:Er (100:1)300 MARIMO NPs.

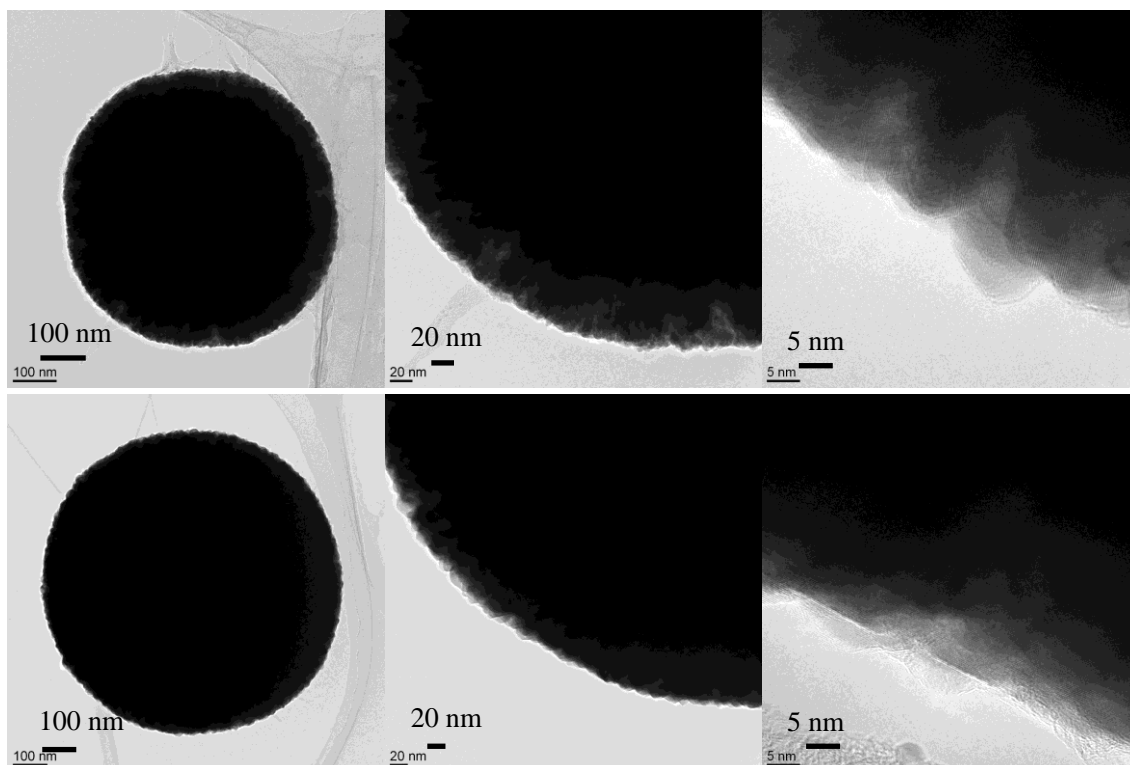


**Fig. S6.** Green light emission of CeO<sub>2</sub>:Er (100:1)300 MARIMO NPs (a) before and (b) after calcination at 800 °C for 60 min in air.

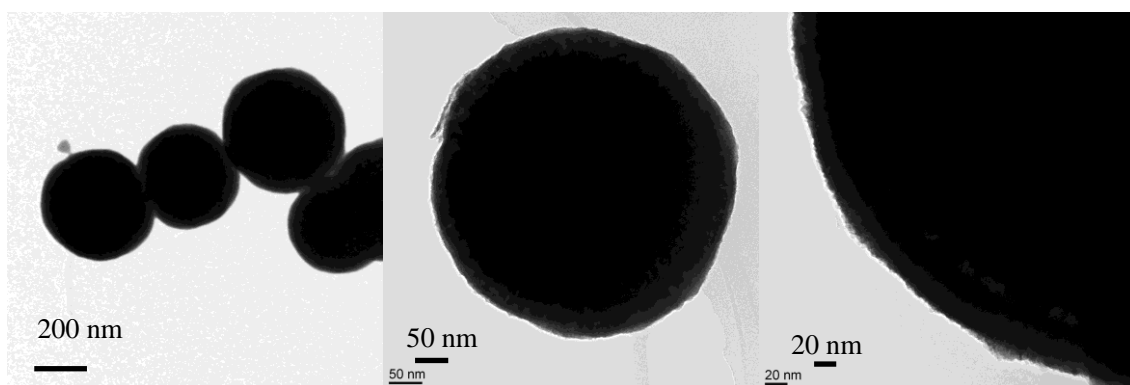
### 3.2 $\text{CeO}_2\text{:Er, Yb}$ co-doped MARIMO NPs



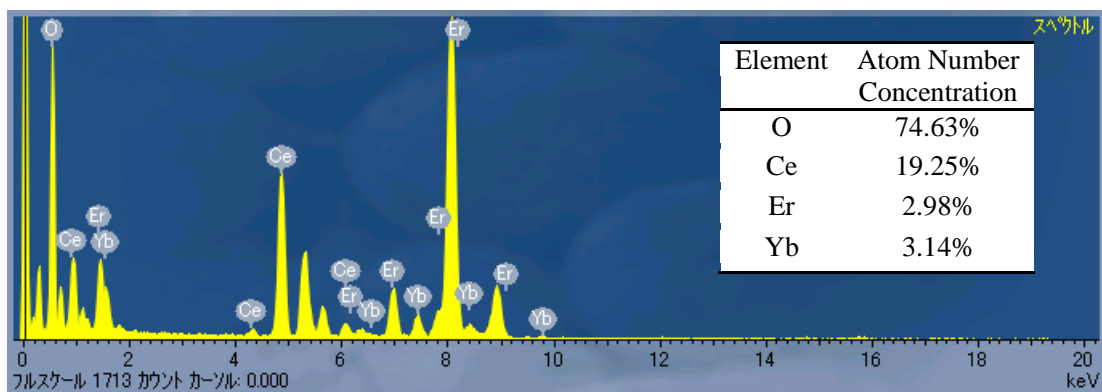
$\text{CeO}_2\text{:Er, Yb}$  co-doped solid MARIMO nanoparticles



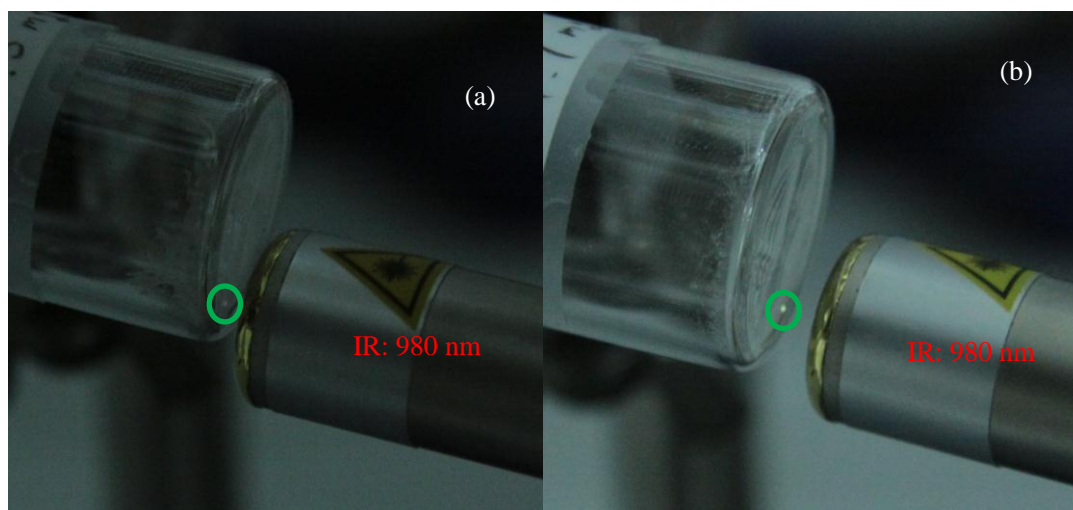
**Fig. S7.** TEM images of  $\text{CeO}_2\text{:Er, Yb}$  (100:1:1)300 MARIMO NPs (a, b, and c) before and (d, e, and f) after calcination at 800 °C for 60 min in air.



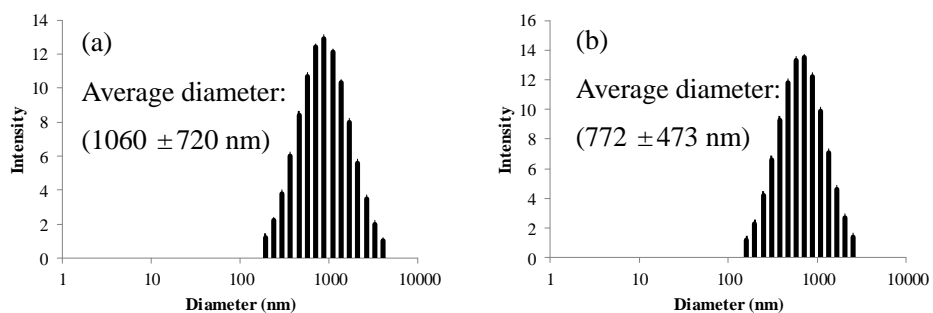
**Fig. S8.** TEM images of  $\text{CeO}_2\text{:Er, Yb}$  (10:1:1)300 MARIMO NPs.



**Fig. S9.** EDX spectrum and atom number concentration of CeO<sub>2</sub>:Er,Yb (10:1:1)300 MARIMO NPs.

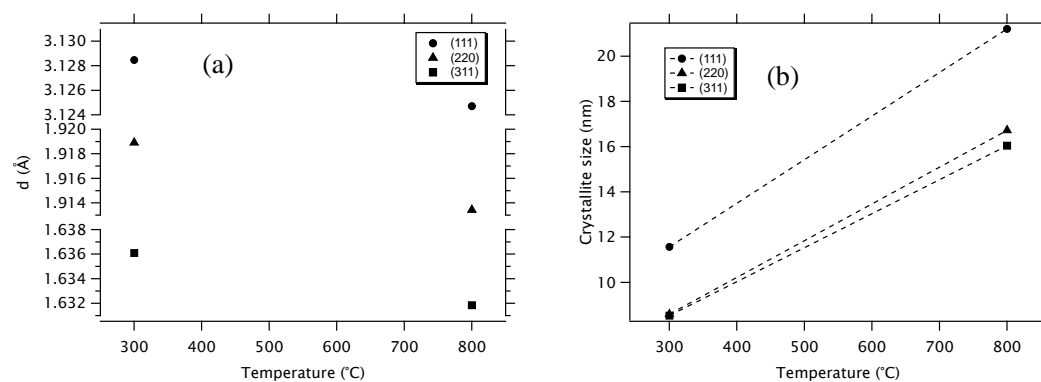


**Fig. S10.** Green light emission of CeO<sub>2</sub>:Er,Yb (100:1:1)300 MARIMO NPs under irradiation of low intensity IR laser (980 nm, 10 mW) (a) before and (b) after calcination at 800 °C for 60 min in air.



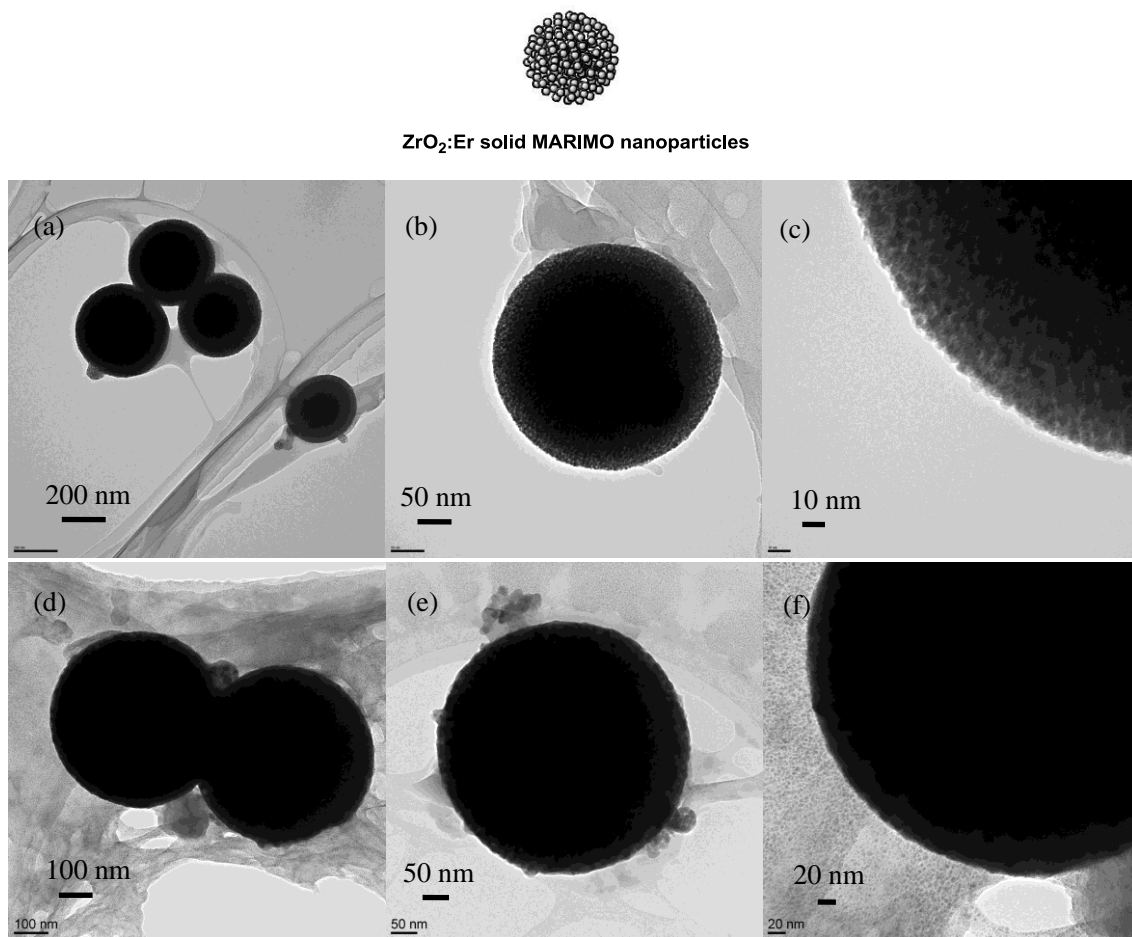
**Fig. S11.** DLS spectra of CeO<sub>2</sub>:Er,Yb (100:1:1)300 MARIMO NPs (a) before and (b) after calcination at 800 °C for 60 min in air.



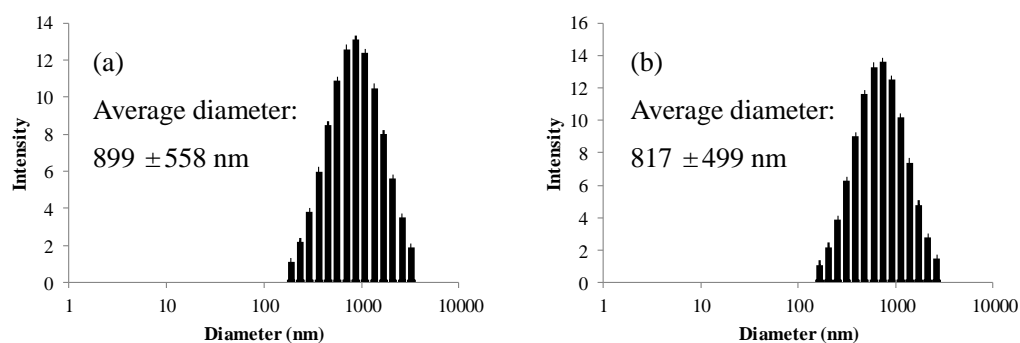


**Fig. S12.** (a) Calcination temperature dependence of lattice constant and (b) calcination temperature dependence of primary crystallite sizes of the CeO<sub>2</sub>:Er,Yb (100:1:1)300 MARIMO NPs.

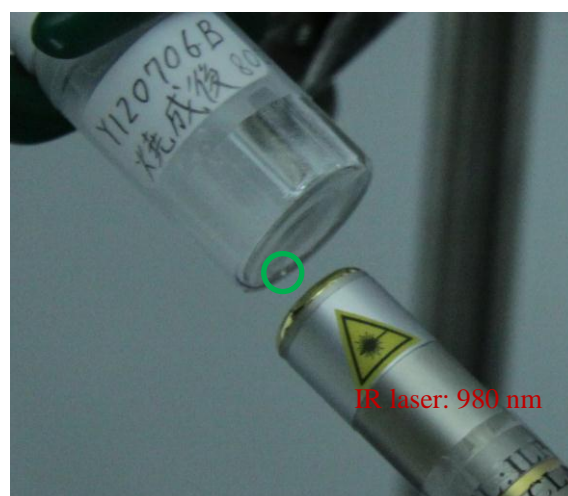
#### 4. ZrO<sub>2</sub>:Er MARIMO NPs



**Fig. S13.** TEM images of ZrO<sub>2</sub>:Er (200:1)400 MARIMO NPs (a, b, and c) before calcination and (d, e, and f) after calcination at 800 °C for 60 min in air.

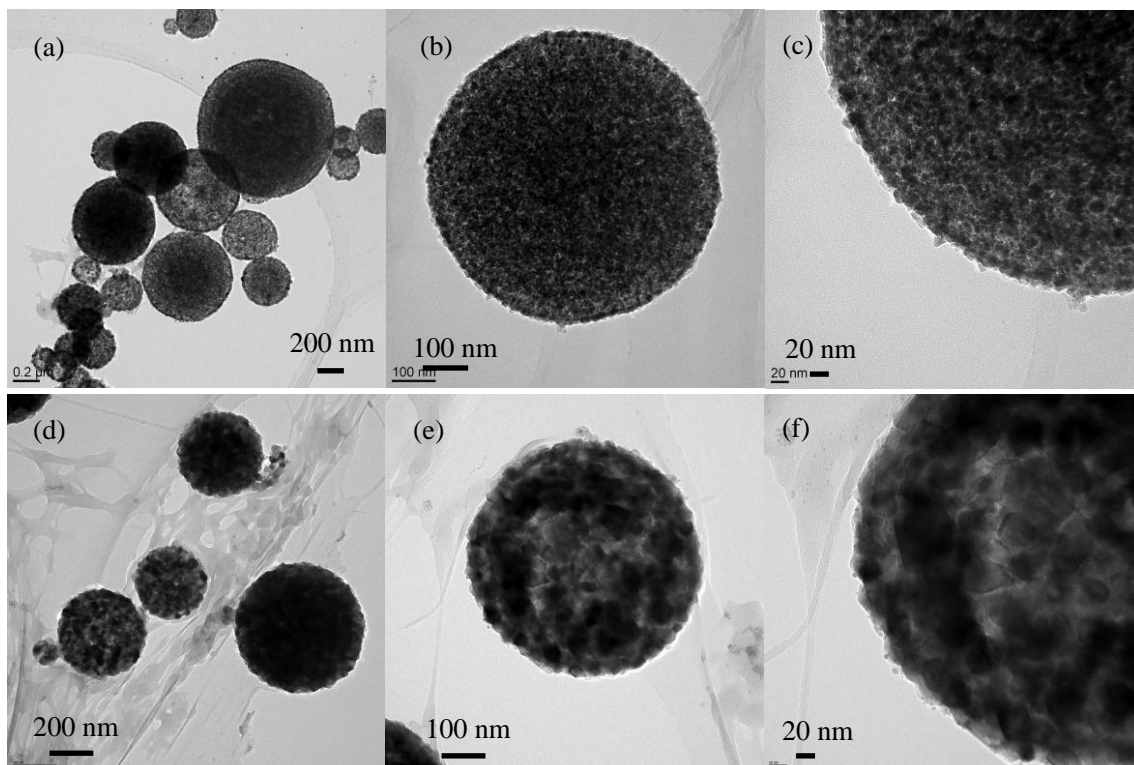
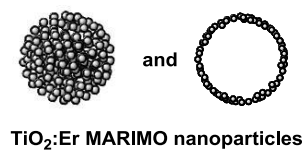


**Fig. S14.** DLS spectra of ZrO<sub>2</sub>:Er (200:1)400 MARIMO NPs (a) before and (b) after calcination at 800 °C for 60 min in air.

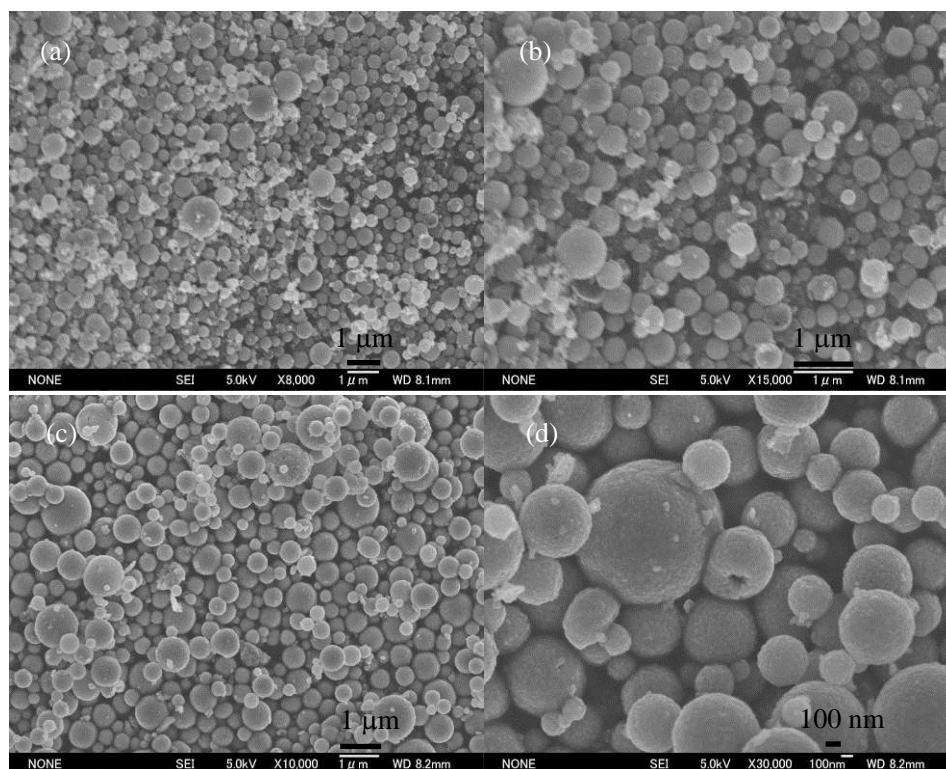


**Fig. S15.** Green light emission of ZrO<sub>2</sub>:Er (200:1)400 MARIMO NPs under irradiation of low intensity IR laser (980 nm, 10 mW) after calcination at 800 °C for 60 min.

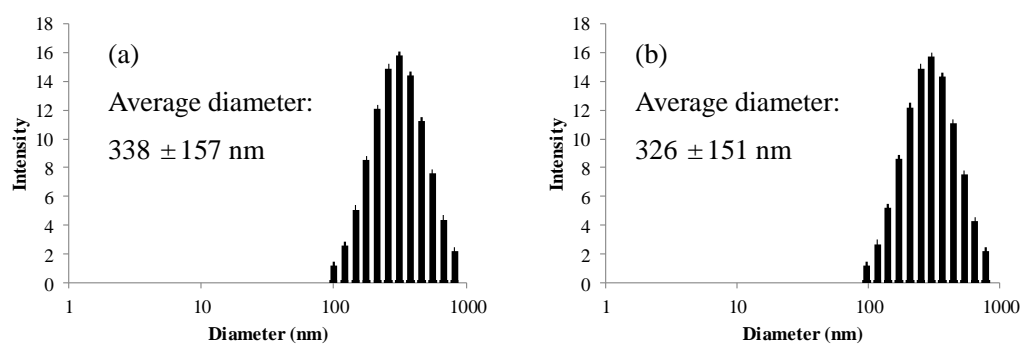
## 5. TiO<sub>2</sub>:Er MARIMO NPs



**Fig. S16.** TEM images of TiO<sub>2</sub>:Er (200:1)400 MARIMO NPs (a, b, and c) before and (d, e, and f) after calcination at 800 °C for 60 min in air.



**Fig. S17.** SEM images of  $\text{TiO}_2\text{:Er}$  (200:1)400 MARIMO NPs (a and b) before and (c and d) after calcination at 800 °C for 60 min in air.

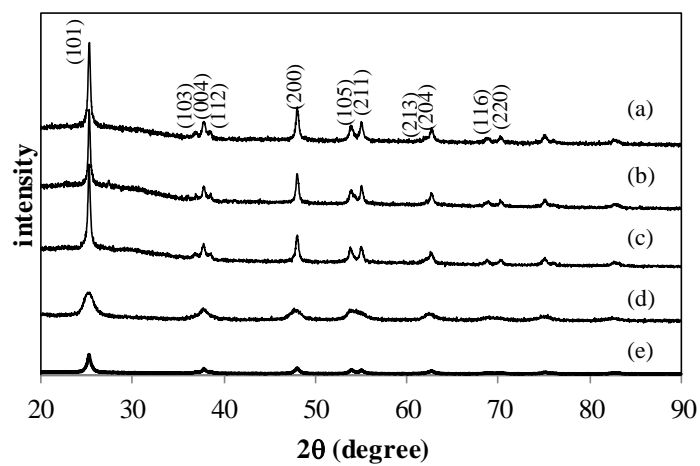


**Fig. S18.** DLS plots of  $\text{TiO}_2\text{:Er}$  (200:1)400 MARIMO NPs (a) before and (b) after calcination at 800 °C for 60 min in air.



**Fig. S19.** Green light emission of TiO<sub>2</sub>:Er (200:1)400 MARIMO NPs under irradiation of low intensity IR laser (980 nm, 10 mW) after calcination at 800 °C for 60 min.

## 6. Metal or nitrogen doped TiO<sub>2</sub> MARIMO NPs

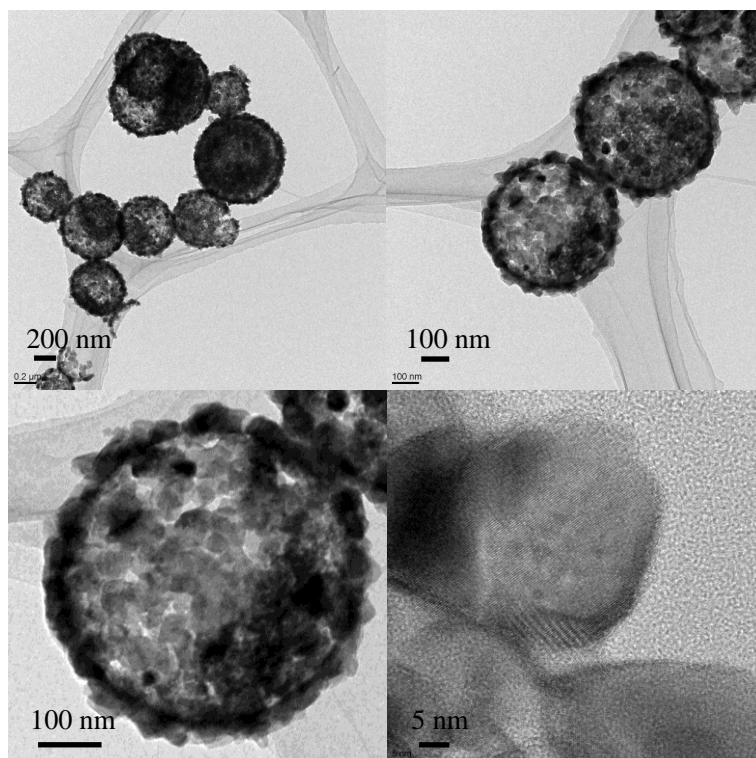


**Fig. S20.** XRD patterns of metal elements (N) doped MARIMO NPs (a) TiO<sub>2</sub>:Eu (10:1)400, (b) TiO<sub>2</sub>:Ce (10:1)400, (c) TiO<sub>2</sub>:Yb (10:1)400, (d) TiO<sub>2</sub>:Fe (10:1)300, and (e) TiO<sub>2</sub>:N (1:20)400.

### 6.1 $\text{TiO}_2\text{:Eu}$ MARIMO NPs



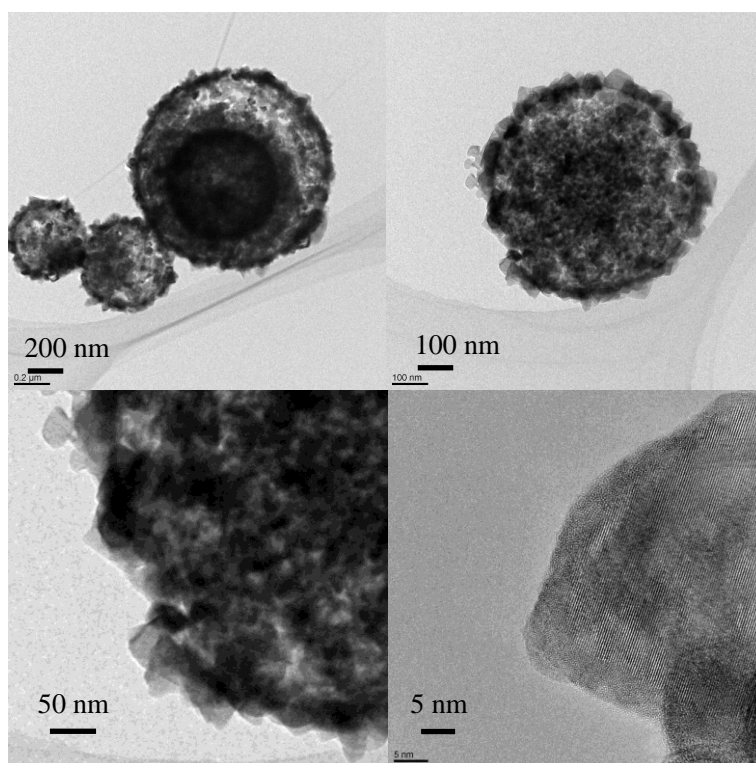
$\text{TiO}_2\text{:Er}$  hollow MARIMO nanoparticles



**Fig. S21.** TEM images of  $\text{TiO}_2\text{:Eu}$  (10:1)400 MARIMO NPs.



## 6.2 $\text{TiO}_2\text{:Ce}$ MARIMO NPs

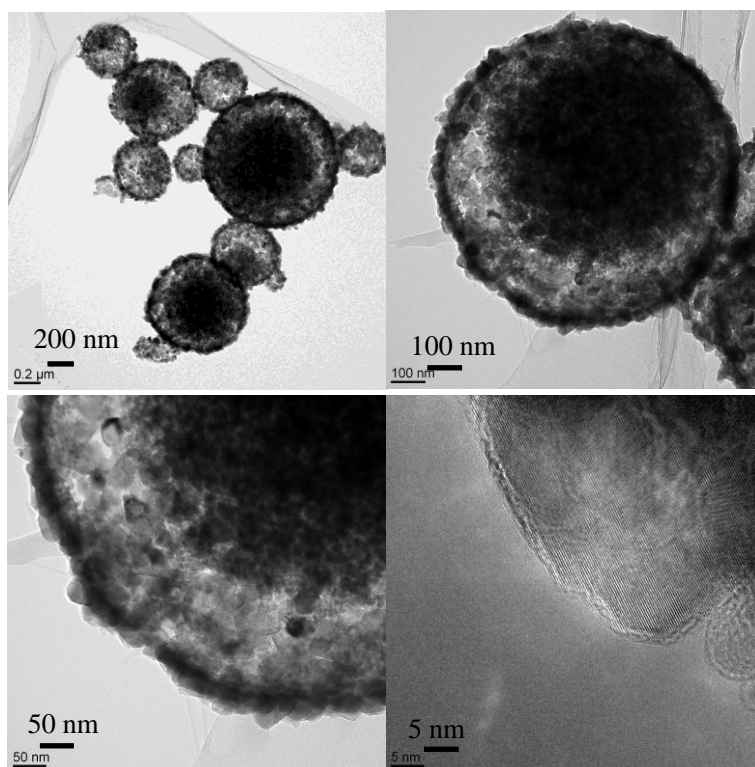


**Fig. S22.** TEM images of  $\text{TiO}_2\text{:Ce}$  (10:1)400 MARIMO NPs.

### 6.3 $\text{TiO}_2\text{:Yb}$ doped MARIMO NPs



$\text{TiO}_2\text{:Yb}$  hollow MARIMO nanoparticles

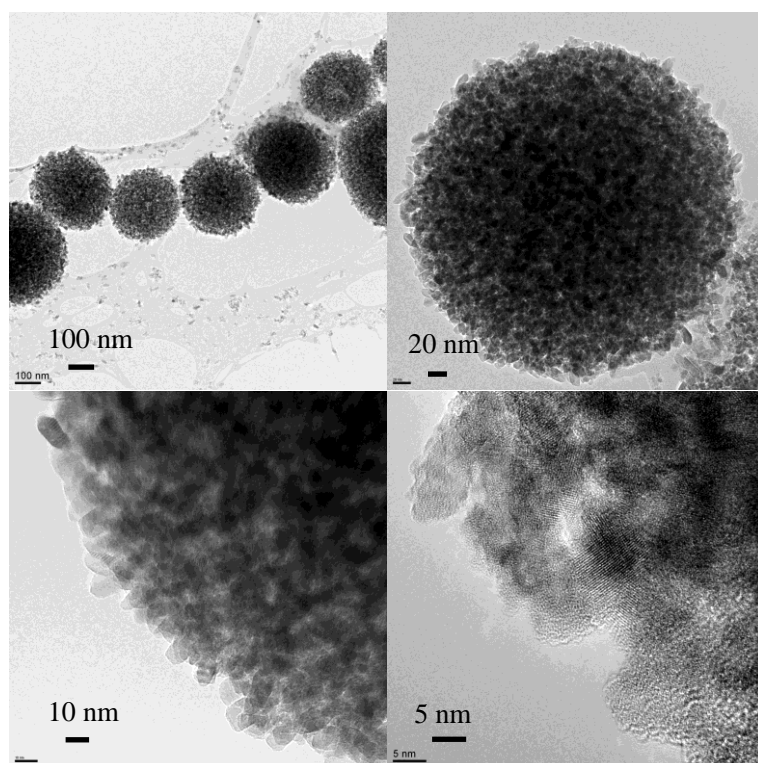


**Fig. S23.** TEM images of  $\text{TiO}_2\text{:Yb}$  (10:1)400 MARIMO NPs.

#### 6.4 $\text{TiO}_2\text{:Fe}$ MARIMO NPs



$\text{TiO}_2\text{:Fe}$  solid MARIMO nanoparticles

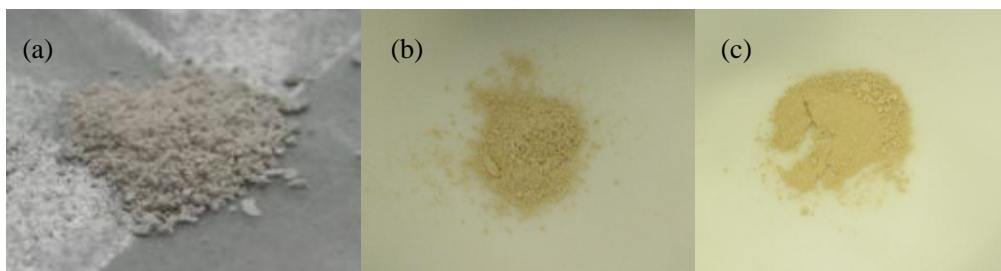


**Fig. S24.** TEM images of  $\text{TiO}_2\text{:Fe}$  (10:1)300 MARIMO NPs.

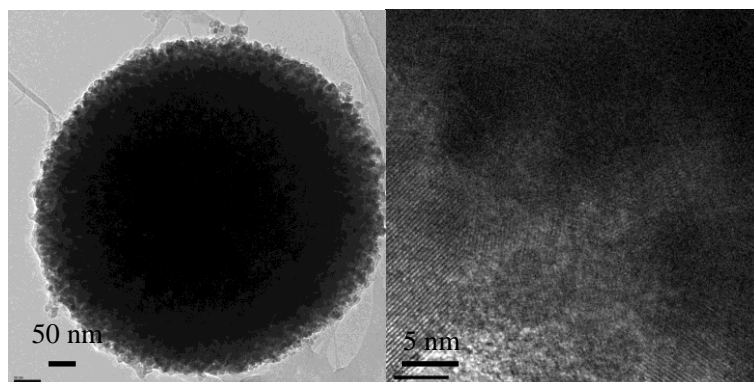
### 6.5 $\text{TiO}_2\text{:N}$ MARIMO NPs



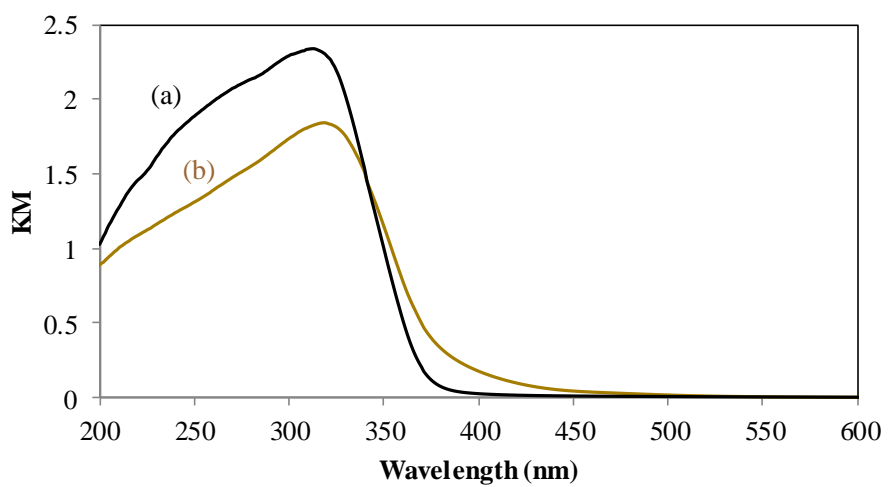
$\text{TiO}_2\text{:N}$  solid MARIMO



**Fig. S25.** (a) Prototype  $\text{TiO}_2$  MARIMO NPs prepared under the conditions of 400 °C, 10 min, and 0.28 g mL<sup>-1</sup> MeOH density in the presence of benzoic acid;  $\text{TiO}_2\text{:N}$  (1:20)400 MARIMO NPs (b) before and (c) after calcination at 500 °C for 60 min in air.



**Fig. S26.** TEM images of  $\text{TiO}_2\text{:N}$  (1:20)400 MARIMO NPs.



**Fig. S27.** (a) UV-vis absorption spectrum of TiO<sub>2</sub> MARIMO NPs prepared under the conditions of 400 °C, 10 min, and 0.28 g mL<sup>-1</sup> MeOH density in the presence of benzoic acid. (b) UV-vis absorption spectrum of TiO<sub>2</sub>:N (1:20)400 MARIMO prepared at 400 °C for 60 min in 0.28 g mL<sup>-1</sup> MeOH density in the presence of benzamide and benzoic acid.