Supporting Information

A Liquid Metal Composite by ZIF-8 Encapsulation

Yong Liu[a,b*], Qian Wang[c], Jinqi Deng[a,b], and Wei Zhang[a*]

a CAS Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, CAS Center for Excellence in Nanoscience, National Center for NanoScience and Technology, No. 11 Zhongguancun Beiyitiao, Beijing 100190, P. R. China
b University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing 100049, P. R. China
c College of Chemistry and Molecular Engineering, Peking University, No. 202 Chengfu Road, Beijing 100871, P. R. China

*Corresponding author: liuyong1@nanoctr.cn (Yong Liu), zhangw@nanoctr.cn (Wei Zhang)

1. Supplementary methods

1.1 Materials

Eutectic gallium indium (EGaIn) was from Beijing Hawk. poly(vinyl pyrrolidone) (PVP, M_w = 40000) was from Solarbio. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was from Xilong Scientific Co., Ltd. 2-Methylimidazole (2-MI) was from Aladdin. Methanol (> 99.7%) was from Beijing Chemical Works.

1.2 Characterizations

TEM images were obtained on a HT 7700 transmission electron microscope operated at 80 kV. HAADF-STEM images and EDX mapping were obtained on a Tecnai G2 F20 U-TWIN transmission electron microscope operated at 200 kV. SEM images were obtained on a Hitachi SU4800 electron microscope. XRD patterns were acquired at a scan rate of 5 degree/min in the 2 theta range of 10-80 degree (Cu Ka radiation, Bruker D8 Advance, German). XPS analysis was done on a Thermo Scientific ESCALAB 250XI photoelectron spectrometer. UV-Vis absorption spectra were recorded on a UV-Vis spectrophotometer (UV-2450, Shimadzu, Japan) from 190 to 850 nm. DLS and Zeta potential measurement was done on a DLS particle size and zeta potential analyzer (Zetasizer Nano ZS, Malvern, UK). ICP-AES analysis was performed on an inductively coupled plasma-atomic emission spectrometer (Prodigy 7, Leeman)

1.3 Synthesis of EGaIn@PVP NDs

In a typical synthesis, 20 mg PVP was dissolved in 2 mL DI water, followed by adding a 20 μL EGaIn droplet (~100 mg). The solution was subjected to probe sonication in an ice bath for 30 min (100 W, 3s/3s interval). The product was centrifuged at 1000 g for 10 min and the precipitated larger particles were discarded. The upper product was centrifuged at 10000 g for 15 min. After the supernatant was discarded, the smaller particles were resuspended in 2 mL methanol and washed by centrifugation at 7000 g for 10 min. The final product was resuspended in 2 mL methanol and stored at 4 ^oC. The concentration of EGaIn is 0.8 mg/mL as measured by ICP-AES. For comparison, bare EGaIn NDs without the PVP coating were synthesized in methanol using the same protocol as EGaIn@PVP NDs.

1.4 Synthesis of EGaIn@ZIF-8 NPs

The volume of reaction was fixed as 3 mL for all the experiments. Methanolic solutions of 2-MI (25 mM) and $Zn(NO_3)_2 \cdot 6H_2O$ (25 mM) were used as stock solutions. In a typical synthesis of EGaIn@ZIF-8_{N2} NPs, 500 μL EGaIn@PVP NDs was mixed with 1 mL 2-MI, followed by adding 1 mL methanol and 500 μL $Zn(NO_3)_2 \cdot 6H_2O$. The mixture was vigorously mixed and left undisturbed for 24 h at room temperature. The product was centrifuged at 5000 g for 10 min, washed twice with methanol, and resuspended in methanol or dried for further use. Details of synthesizing EGaIn@ZIF-8 NPs using different N and amount of EGaIn NDs are listed in Table S2 and Table S3.

1.5 Synthesis of ZIF-8 NPs

Methanolic solutions of 2-MI (25 mM) and $Zn(NO_3)_2 \cdot 6H_2O$ (25 mM) were used as stock solutions. In a typical synthesis of ZIF-8_{N2} NPs, 2 mL 2-MI was mixed with 1 mL $Zn(NO_3)_2 \cdot 6H_2O$ and 1 mL methanol. The mixture was vigorously mixed and left undisturbed for 24 h at room temperature. The product was centrifuged at 5000 g for 10 min, washed twice with methanol, and resuspended in methanol or dried for further use. Please refer to Table S2 for details of synthesizing ZIF-8 NPs with different L/M ratio.

1.6 Photothermal conversion of EGaIn@ZIF-8 NPs

The as-prepared EGaIn@PVP NDs were divided equally into three reaction tubes two of which were used to synthesize EGaIn@ZIF-$8_{N2/N1}$ NPs. A handheld 1500 mW 808 nm laser was used to irradiate the samples and the distance between the laser probe and the samples was fixed as 4 cm. The temperature was measured by a thermocouple.

2. Supplementary tables

Table S1. ICP-AES analysis of Ga, In, and Zn in EGaIn NDs and EGaIn@ZIF-8 NPs.

	EGaIn NDs	EGaIn@ZIF-8_{N2} NPs	EGaIn@ZIF-8_{N1} NPs
Ga/mg	0.272	0.199	0.239
In/mg	0.120	0.096	0.113
Zn/mg	-	0.888	0.672

Table S2. Synthesis of EGaIn@ZIF-8 NPs with different L/M ratio.

N (L/M ratio)	4	2.7	2	1.5	1.2	1
	1:0.25	1:0.375	1:0.5	1:0.67	1:0.83	1:1
$V_{2\text{-MI}}$/mL	1	1	1	1	1	1
V_{Zn}/mL	0.25	0.375	0.5	0.67	0.83	1
V_{EGaIn}/mL	0.5	0.5	0.5	0.5	0.5	0.5
V_{MeOH}/mL	1.25	1.125	1	0.83	0.67	0.5
V_{Total}/mL	3	3	3	3	3	3
Product solution	Clear	Clear	Turbid	Turbid	Turbid	Turbid
Product structure	Single core, single shell	Single core, multishell	Single core, multishell	Single core, multishell	Multicore, multishell	Multicore, single shell

Table S3. Synthesis of EGaIn@ZIF-8 NPs with different amount of EGaIn NDs.

NPs	$EGaIn_{500}$@ ZIF-8_{N2}	$EGaIn_{200}$@ ZIF-8_{N2}	$EGaIn_{100}$@ ZIF-8_{N2}	$EGaIn_{50}$@ ZIF-8_{N2}	$EGaIn_{500}$@ ZIF-8_{N1}	$EGaIn_{200}$@ ZIF-8_{N1}	$EGaIn_{100}$@ ZIF-8_{N1}	$EGaIn_{50}$@ ZIF-8_{N1}
Ga/Zn molar ratio	0.45	0.18	0.1	0.005	0.22	0.1	0.05	0.025
$V_{2\text{-MI}}$/mL	1	1	1	1	1	1	1	1
V_{Zn}/mL	0.5	0.5	0.5	0.5	1	1	1	1
V_{EGaIn}/mL	0.5	0.2	0.1	0.05	0.5	0.2	0.1	0.05
V_{MeOH}/mL	1	1.3	1.4	1.45	1	1.3	1.4	1.45
V_{Total}/mL	3	3	3	3	3	3	3	3

3. Supplementary figures

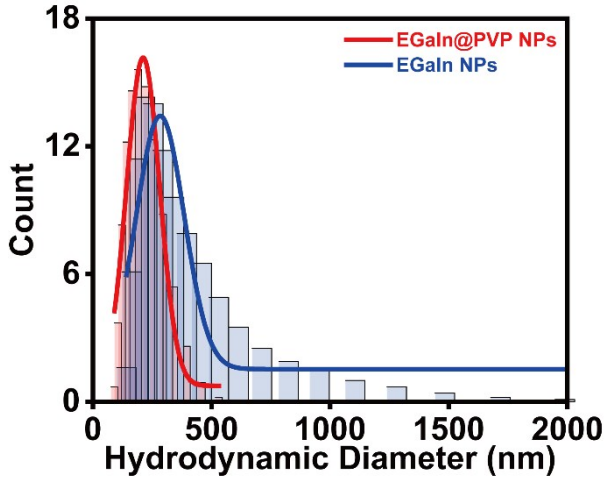

Figure S1. DLS size distributions of EGaIn@PVP NDs and EGaIn NDs. Since EGaIn cannot be processed in water in the absence of PVP because of its uncontrollable oxidation into GaOOH rods, the bare EGaIn NDs were synthesized in methanol.

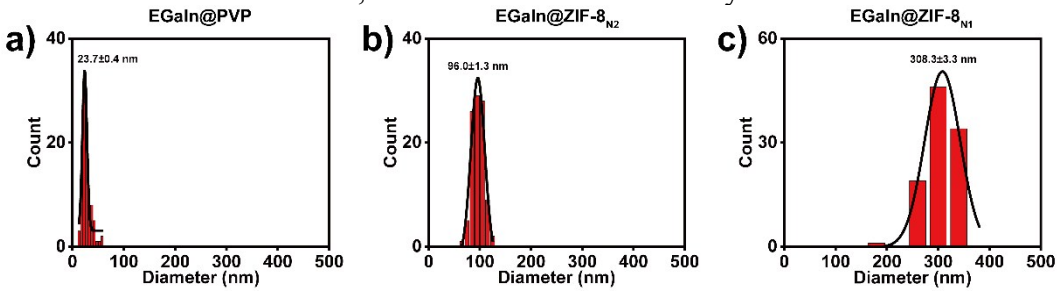

Figure S2. TEM size distributions of (a) EGaIn@PVP NDs, (b) EGaIn@ZIF-8_{N2} NPs, and (c) EGaIn@ZIF-8_{N1} NPs.

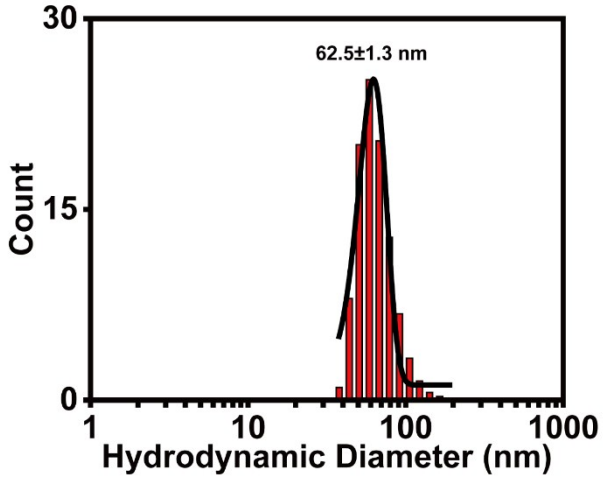

Figure S3. DLS size distribution of EGaIn@PVP NDs.

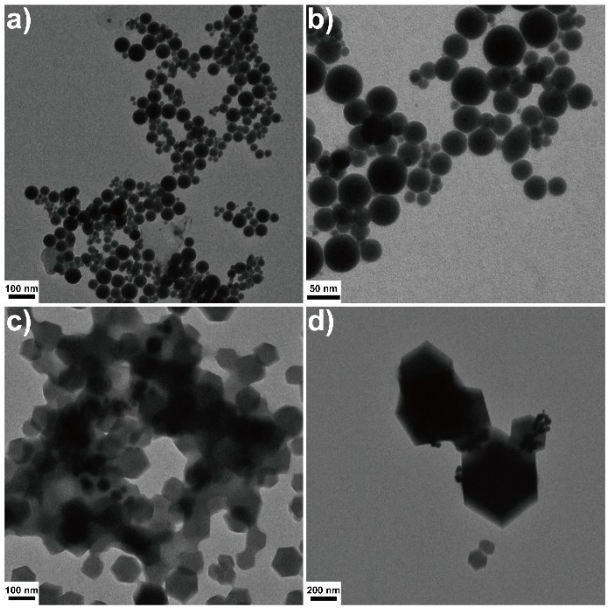

Figure S4. TEM images of bare EGaIn NDs (a-b) and their ZIF-8 composites with different L/M ratio N2 (c) and N1 (d). EGaIn NDs cannot be encapsulated in ZIF-8 in the absence of the PVP coating.

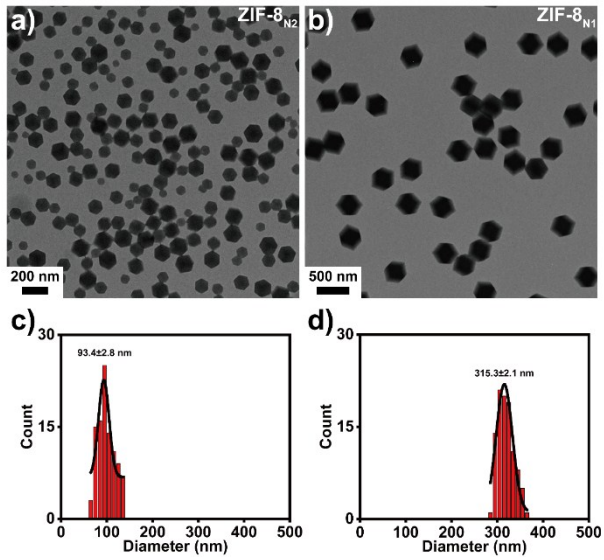

Figure S5. TEM images and size distributions of ZIF-8_{N2} NPs (a, c) and ZIF-8_{N1} NPs (b, d). Scale bar: 200 nm in (a), 500 nm in (b).

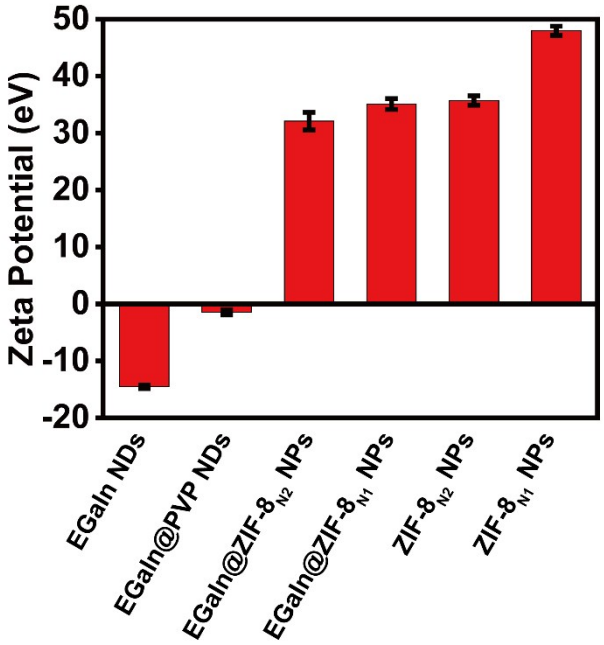

Figure S6. Zeta potential analysis. EGaIn NDs refers to bare EGaIn NDs synthesized in methanol.

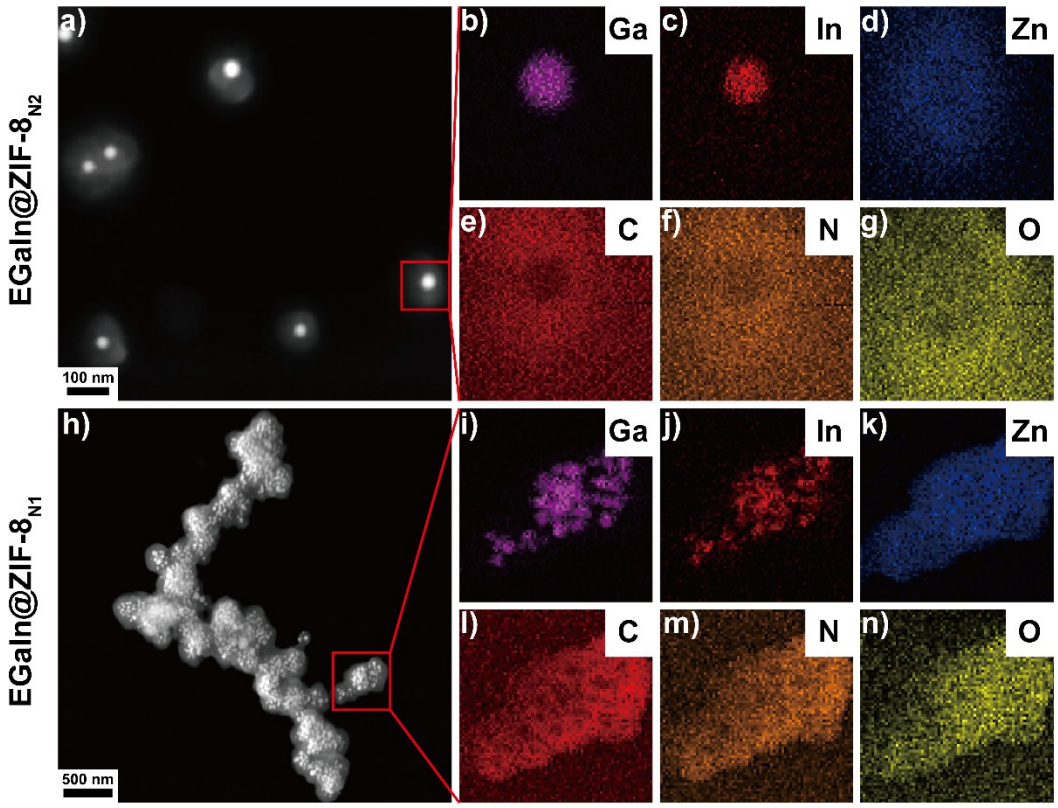

Figure S7. HAADF-STEM images and EDX mapping of EGaIn@ZIF-8_{N2} NPs (a-g) and EGaIn@ZIF-8_{N1} NPs (h-n). Scale bar: 100 nm in (a), 500 nm in (h).

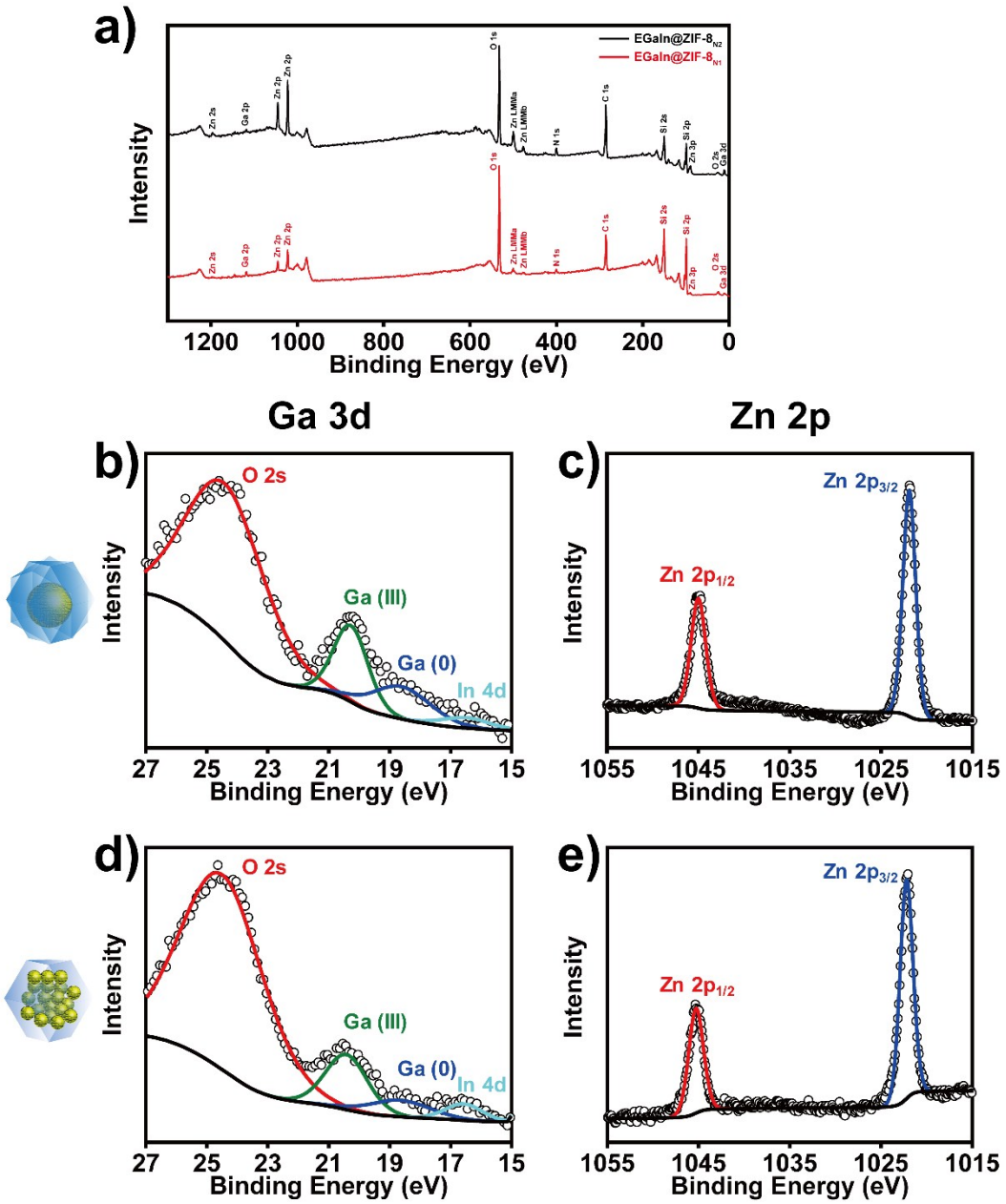

Figure S8. (a) XPS spectra of EGaIn@ZIF-8_{N2} NPs and EGaIn@ZIF-8_{N1} NPs. (b-e) Ga 3d and Zn 2p analysis of EGaIn@ZIF-8_{N2} NPs (b-c) and EGaIn@ZIF-8_{N1} NPs (d-e).

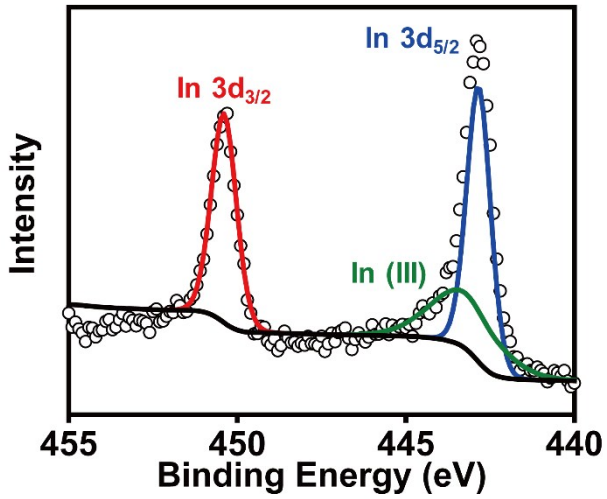

Figure S9. In 3d region of EGaIn@PVP NDs. The two In $3d_{3/2,\ 5/2}$ peaks at 450.4 and 442.9 eV belong to In (0) and the In (III) peak at 443.5 eV is from In^{3+}.

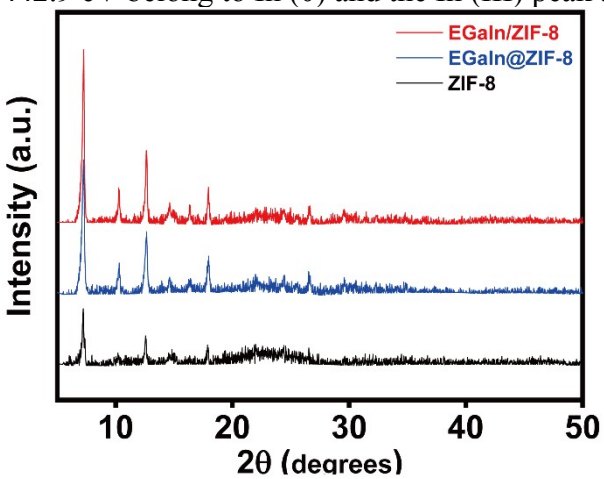

Figure S10. XRD patterns of LM@MOF composites and ZIF-8 nanoparticles.

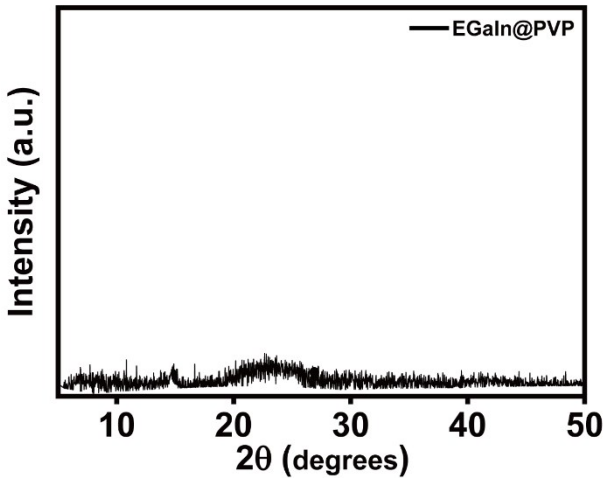

Figure S11. XRD pattern of EGaIn@PVP NDs.

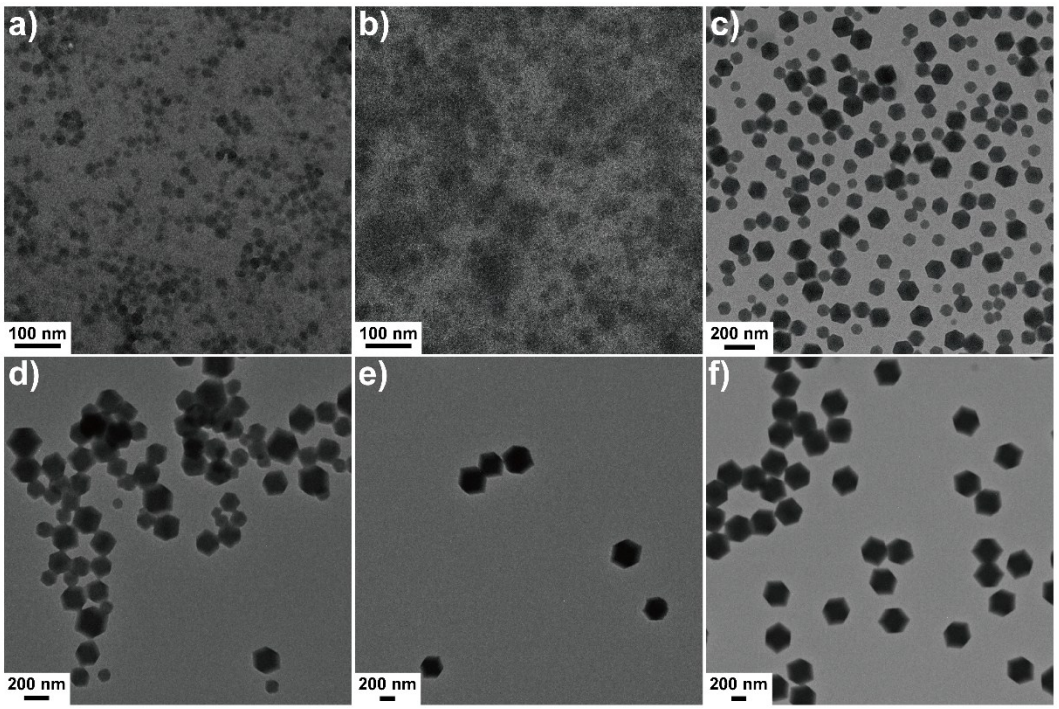

Figure S12. TEM images of ZIF-8 NPs with different L/M ratio: 4 (a), 2.7 (b), 2 (c), 1.5 (d), 1.2 (e), and 1 (f).

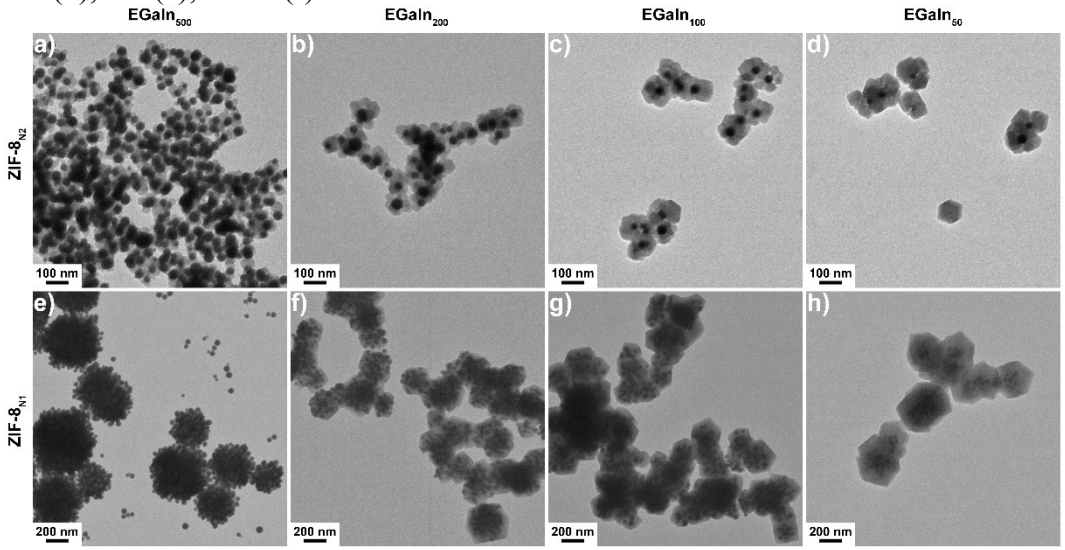

Figure S13. TEM images of EGaIn@ZIF-8 NPs synthesized using different amount of EGaIn (indicated by volume 500, 200, 100, and 50 μL) and L/M ratio (indicated by N2 and N1).

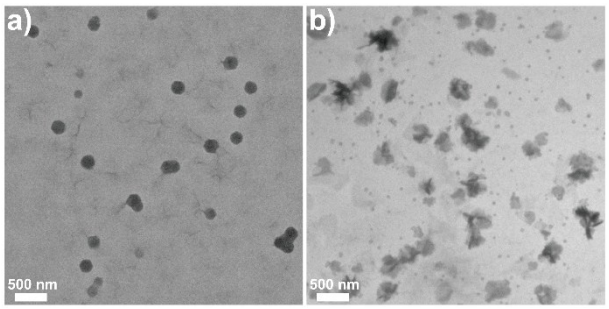

Figure S14. TEM images of ZIF-8_{N2} clusters (a) and ZIF-8_{N1} clusters (b) after 2 min reaction. Scale bar: 500 nm in (a-b).

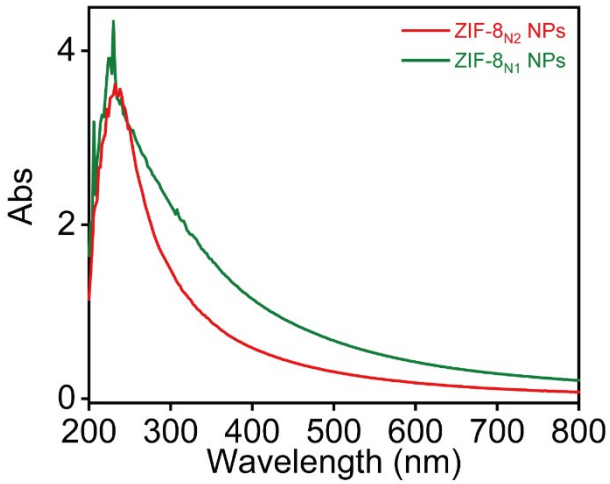

Figure S15. UV-Vis adsorption spectrum of ZIF-8 NPs.

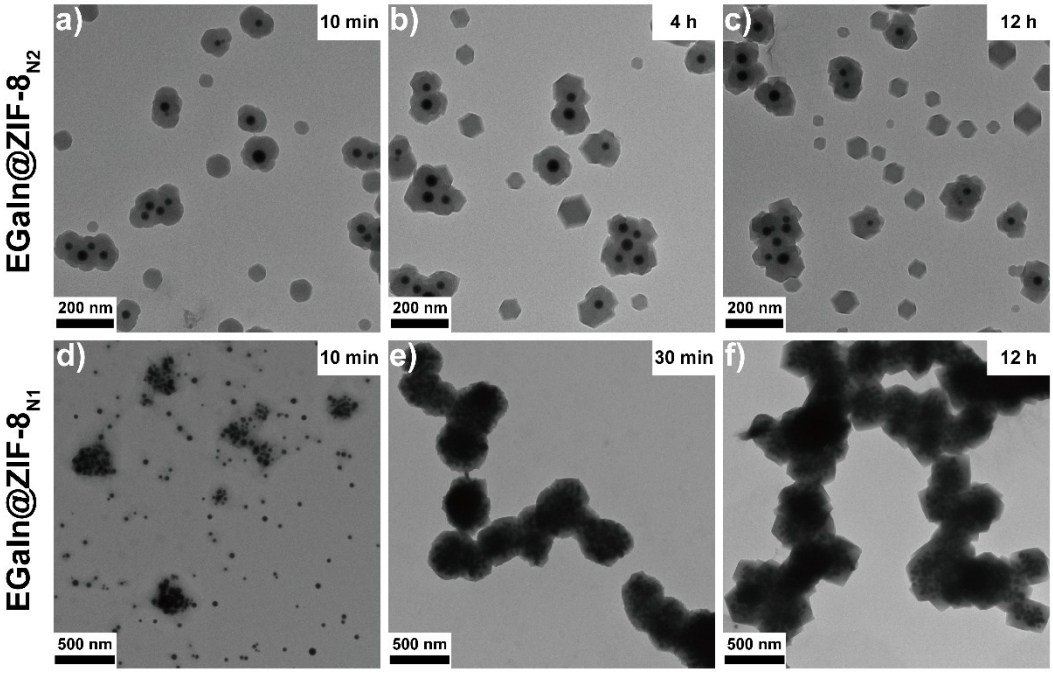

Figure S16. Structural evolution of EGaIn@ZIF-8 NPs. Time-dependent TEM images of EGaIn@ZIF-8_{N2} NPs (a-c) and EGaIn@ZIF-8_{N1} NPs (d-f). Scale bar: 200 nm in (a-c). 500 nm in (d-f).

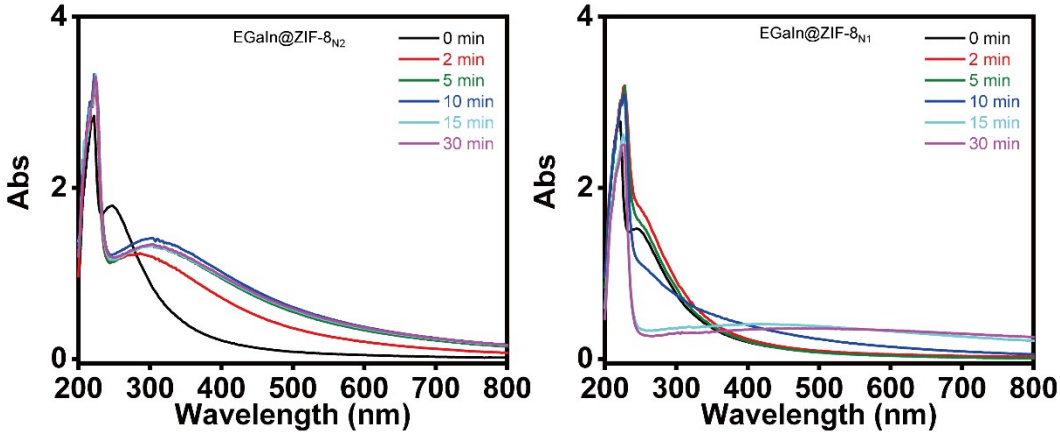

Figure S17. Time-dependent UV-Vis spectra of EGaIn@ZIF-8_{N2} NPs (a) and EGaIn@ZIF-8_{N1} NPs (b).

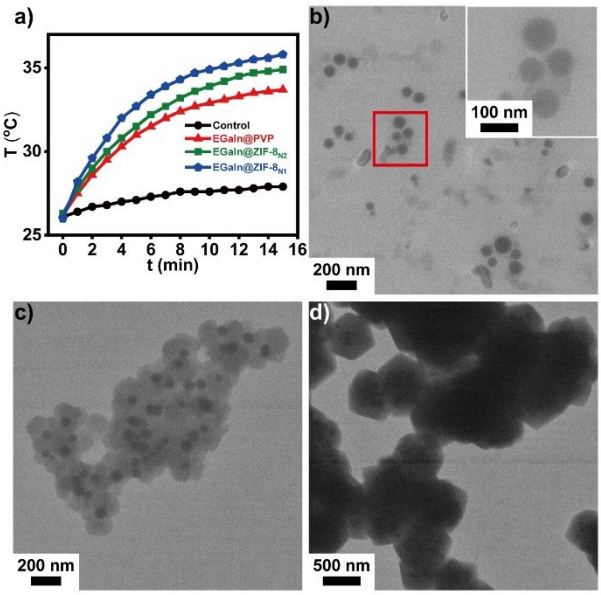

Figure S18. NIR light-activated photothermal conversion of LM@MOF composites. (a) Temperature increases of EGaIn NDs, EGaIn@ZIF-8_{N2} NPs, EGaIn@ZIF-8_{N1} NPs, and methanol upon light irradiation. (b-d) TEM images of EGaIn NDs (b), EGaIn@ZIF-8_{N2} NPs (c), and EGaIn@ZIF-8_{N1} NPs after light irradiation. Scale bar: 200 nm in (b) and (c), 100 nm in (b, inset), 500 nm in (d).