

Electronic Supplementary Information

**Preparation and enhanced photocatalytic hydrogen-evolution
activity of ZnGa₂O₄/N-rGO heterostructures**

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Table S1. The synthesis parameters of the samples

| Samples | ZnGa ₂ O ₄ -x | ZnGa ₂ O ₄ /rGO | ZnGa ₂ O ₄ /N-rGO |
|---|-------------------------------------|---------------------------------------|---|
| Zn(NO ₃) ₂ ·6H ₂ O/mg | 0.298 | \ | \ |
| Ga(NO ₃) ₃ ·xH ₂ O/mg | 0.512 | \ | \ |
| C ₆ H ₅ Na ₃ O ₇ ·2H ₂ O/g | x | \ | \ |
| deionized water/mL | 80 | 30 | 30 |
| pH | 8.86 | \ | \ |
| ZnGa ₂ O ₄ nanospheres/g | \ | 0.120 | 0.120 |
| GO solution (1 mg/mL) | \ | 3 mL | \ |
| NGO suspension(1 mg/mL) | \ | \ | 3 mL |

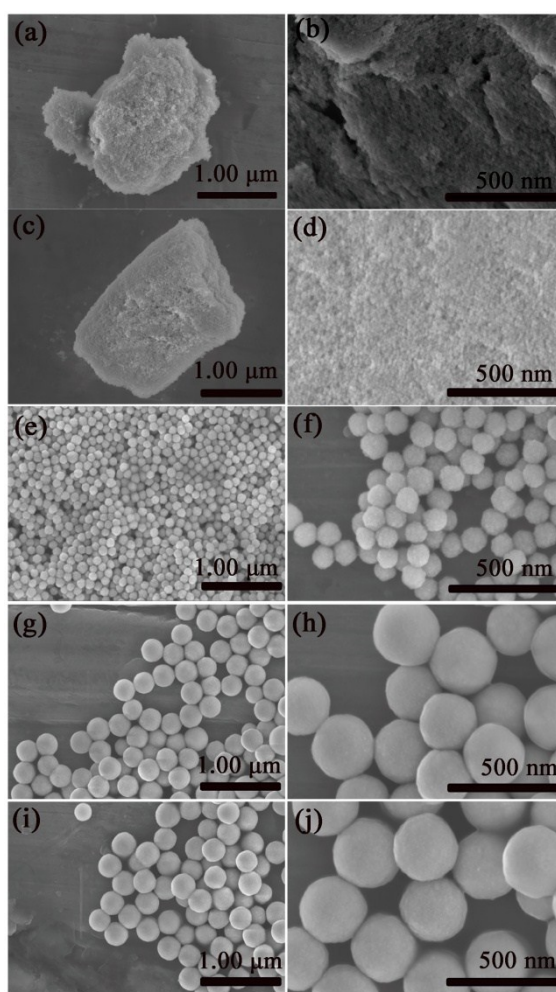


Fig. S1 SEM images of the ZnGa₂O₄ with different amount of surfactant trisodium citrate: (a, b) ZnGa₂O₄-0; (c, d) ZnGa₂O₄-0.25; (e, f) ZnGa₂O₄-0.30; (g, h) ZnGa₂O₄-0.35 and (i, j) ZnGa₂O₄-0.40.

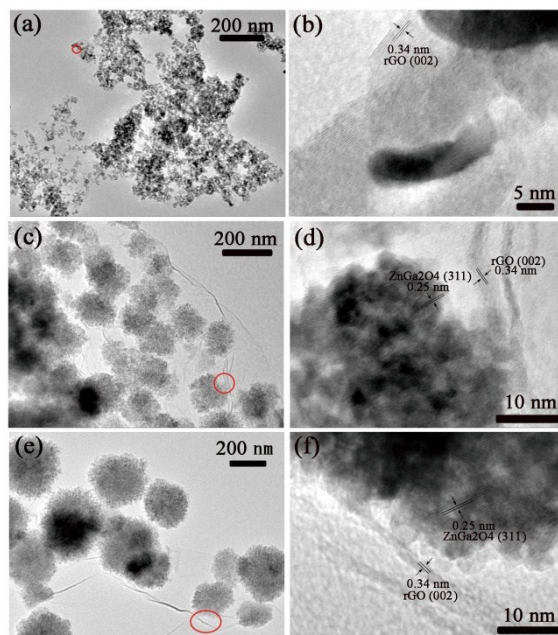


Fig. S2 TEM and HRTEM images of the samples: (a, b) ZnGa_2O_4 -0.25/rGO; (c, d) ZnGa_2O_4 -0.30/rGO; (e, f) ZnGa_2O_4 -0.35/rGO.

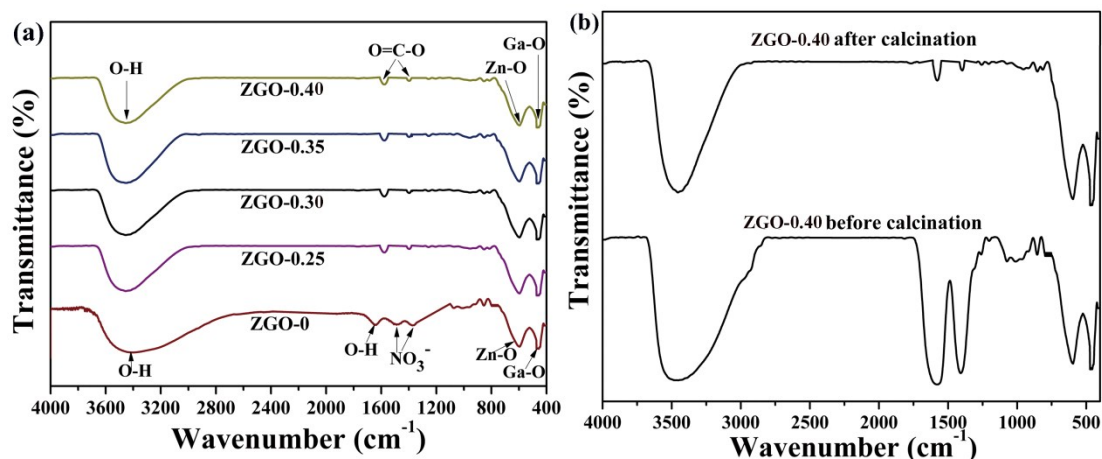


Fig. S3 FT-IR spectra of (a) the ZnGa_2O_4 with different size: ZnGa_2O_4 -0; ZnGa_2O_4 -0.25; ZnGa_2O_4 -0.30; ZnGa_2O_4 -0.35; ZnGa_2O_4 -0.40 and (b) ZnGa_2O_4 -0.40 before and after calcinations at 400 °C.

The FT-IR spectra of the as-prepared ZnGa_2O_4 with different size are shown in Fig. S3. The broad and strong band centered at 3425-3454 and 1629-1676 cm^{-1} is attributed to the O-H stretching and bending vibration of H_2O absorbed by the samples. The bands at 1578 and 1408 cm^{-1} are ascribed to the vibration of the COO^- group from surfactant trisodium citrate.¹ In our system, Citrate ion (Cit^{3-}) as a structure-directing reagent could form Zn^{2+} - Cit^{3-} - Ga^{3+} complexes to control the nucleation and growth of the crystals, resulting in the formation of ZnGa_2O_4 nanospheres.² The two obvious bands at 589 and 436 cm^{-1} can be ascribed to the

characteristic metal-oxygen (Zn-O and Ga-O) vibrations, respectively.³ We calcined ZnGa₂O₄ nanospheres to remove the COO⁻ group, and the result is shown in Fig. S3 b. After calcination, the vibration of COO⁻ group significantly diminished, indicating an effective removal of the COO⁻ group.

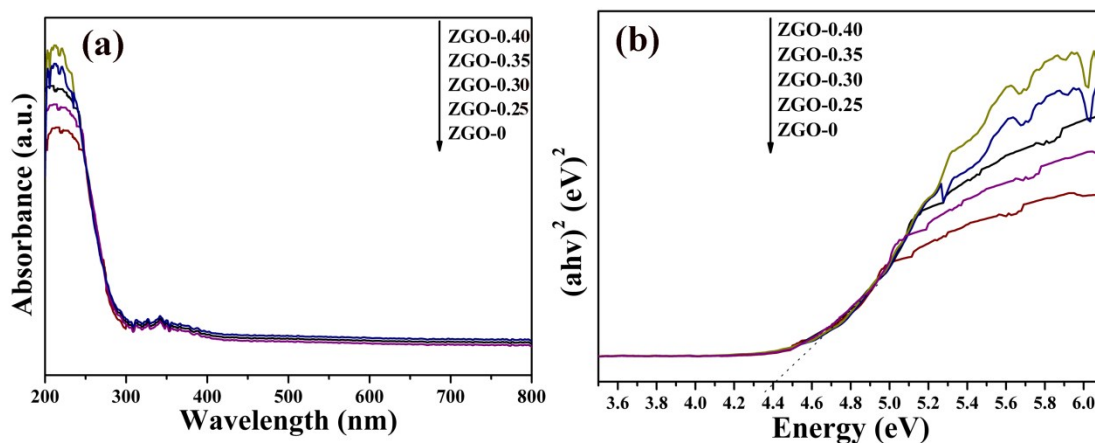


Fig. S4 (a) UV-vis diffuse reflectance spectra and (b) the plot of transformed Kubelka-Munk function versus the energy of the ZnGa₂O₄ with different size: ZnGa₂O₄-0; ZnGa₂O₄-0.25; ZnGa₂O₄-0.30; ZnGa₂O₄-0.35 and ZnGa₂O₄-0.40.

Table S2. The BET surface area of the samples

| Samples | A _{BET} (m ² ·g ⁻¹) | Average pore size/nm |
|----------------|---|----------------------|
| ZGO-0 | 57.767 | 13.52 |
| ZGO-0.25 | 50.131 | 21.33 |
| ZGO-0.30 | 41.448 | 28.28 |
| ZGO-0.35 | 35.627 | 26.32 |
| ZGO-0.40 | 30.081 | 26.78 |
| ZGO-0.25/rGO | 65.258 | 22.72 |
| ZGO-0.25/N-rGO | 66.117 | 23.42 |
| ZGO-0.30/rGO | 57.785 | 29.56 |
| ZGO-0.30/N-rGO | 56.308 | 31.12 |
| ZGO-0.35/rGO | 53.41 | 27.74 |
| ZGO-0.35/N-rGO | 53.767 | 27.98 |

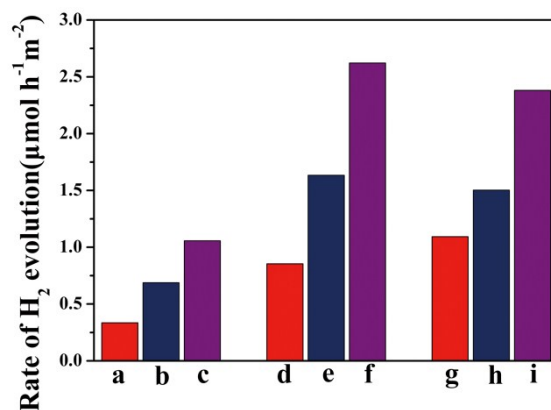


Fig. S5 Photocatalytic water splitting activity normalized by the BET surface areas of (a-c) ZnGa₂O₄-0.25, ZnGa₂O₄-0.25/rGO, ZnGa₂O₄-0.25/N-rGO; (d-f) ZnGa₂O₄-0.30, ZnGa₂O₄-0.30/rGO, ZnGa₂O₄-0.30/N-rGO; (g-i) ZnGa₂O₄-0.35, ZnGa₂O₄-0.35/rGO, ZnGa₂O₄-0.35/N-rGO.

Table S3. Photocatalytic water splitting activity normalized by the BET surface areas and parameters of equivalent circuits for the impedance data of the samples

| Samples | Rate of H ₂ evolution (μmol h ⁻¹ m ⁻²) | R _{ct} (10 ⁵ , Ω cm ²) |
|----------------|--|--|
| ZGO-0 | 0.084 | 17.22 |
| ZGO-0.25 | 0.335 | 10.22 |
| ZGO-0.30 | 0.781 | 4.69 |
| ZGO-0.35 | 1.093 | 3.98 |
| ZGO-0.40 | 1.104 | 4.06 |
| ZGO-0.25/rGO | 0.687 | 5.52 |
| ZGO-0.25/N-rGO | 1.056 | 4.04 |
| ZGO-0.30/rGO | 1.634 | 2.70 |
| ZGO-0.30/N-rGO | 2.621 | 1.44 |
| ZGO-0.35/rGO | 1.533 | 2.84 |
| ZGO-0.35/N-rGO | 2.381 | 1.80 |

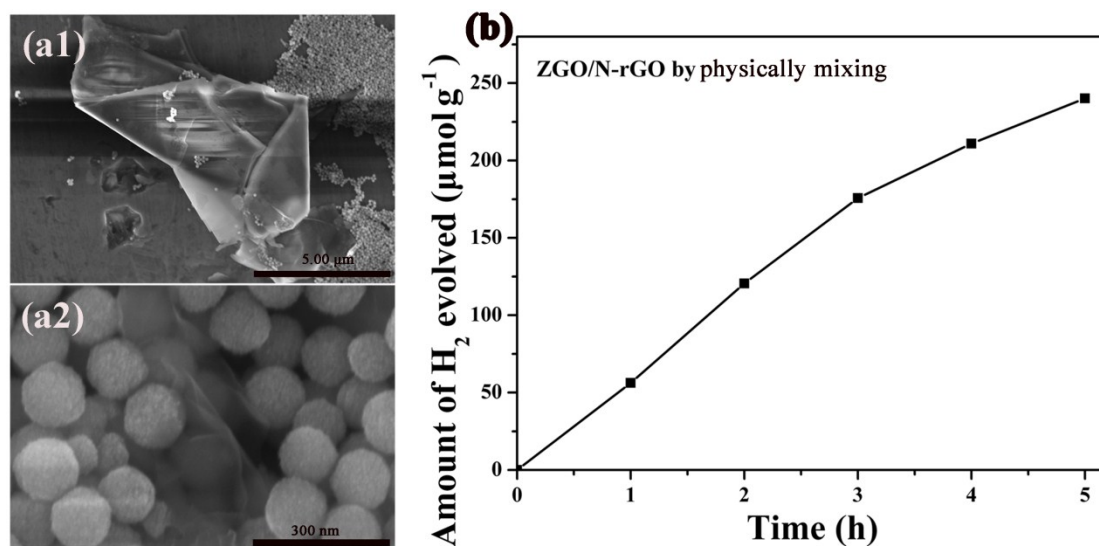


Fig. S6 (a) SEM images and (b) photocatalytic water splitting activity (under the same photocatalytic reaction conditions) of the ZnGa₂O₄-0.30/N-rGO sample by physically mixing.

For comparison, the sample of ZnGa₂O₄-0.30 and N-rGO composites was prepared by stirred mixing 6 h, which based on the same weight ratio with the ZnGa₂O₄-0.30/N-rGO by hydrothermal method. Fig. S6a shows typical SEM images of the ZnGa₂O₄-0.30/N-rGO by physically mixing, in which we can clearly see that ZnGa₂O₄ spheres were not deposited on the surface of the N-rGO sheet. There is no intimate interfacial contact between the ZnGa₂O₄ spheres and N-rGO for ZnGa₂O₄-0.30/N-rGO by physically mixing. Fig. S6b shows the photocatalytic activities of ZnGa₂O₄-0.30/N-rGO by physically mixing. The average rate of H₂ production in 5 h was 48.52 μmol h⁻¹ g⁻¹, which was much lower than ZnGa₂O₄-0.30/N-rGO by hydrothermal method (147.61 μmol h⁻¹ g⁻¹). The result indicating that intimate interfacial contact between the ZnGa₂O₄ spheres and N-rGO was beneficial for the separation of photoinduced charge carriers, resulting in enhanced photocatalytic H₂ generation from water splitting.

Notes and references

- 1 I. F. Li, C.-H. Su, H.-S. Sheu, H.-C. Chiu, Y.-W. Lo, W.-T. Lin, J.-H. Chen and C.-S. Yeh, *Advanced Functional Materials*, 2008, **18**, 766-776.
- 2 Y. Zhang, Z. Wu, D. Geng, X. Kang, M. Shang, X. Li, H. Lian, Z. Cheng and J. Lin, *Advanced Functional Materials*, 2014, **24**, 6581-6593.
- 3 M. Yu, J. Lin, Y. H. Zhou and S. B. Wang, *Materials Letters*, 2002, **56**, 1007-1013.