Supporting Information

Graphene-Based Modulation on the Growth of Urchin-Like $Na_2Ti_3O_7$ Microspheres for Photothermally-Enhanced H_2 Generation from Ammonia Borane

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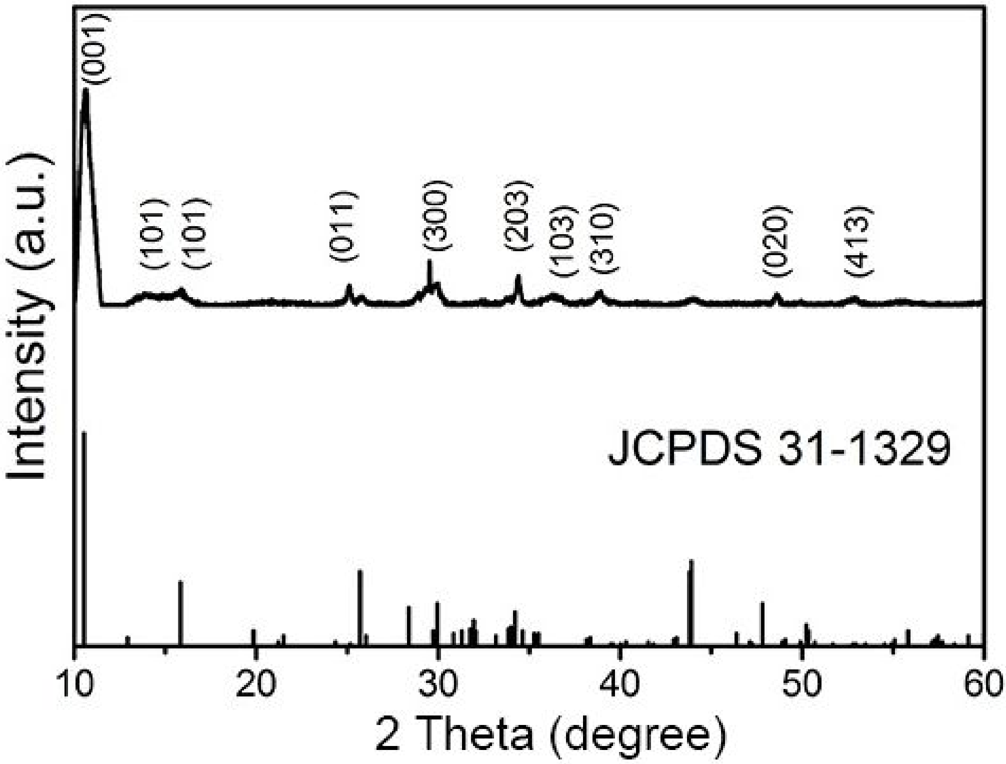

Figure S1. XRD pattern of as-prepared $Na_2Ti_3O_7$.

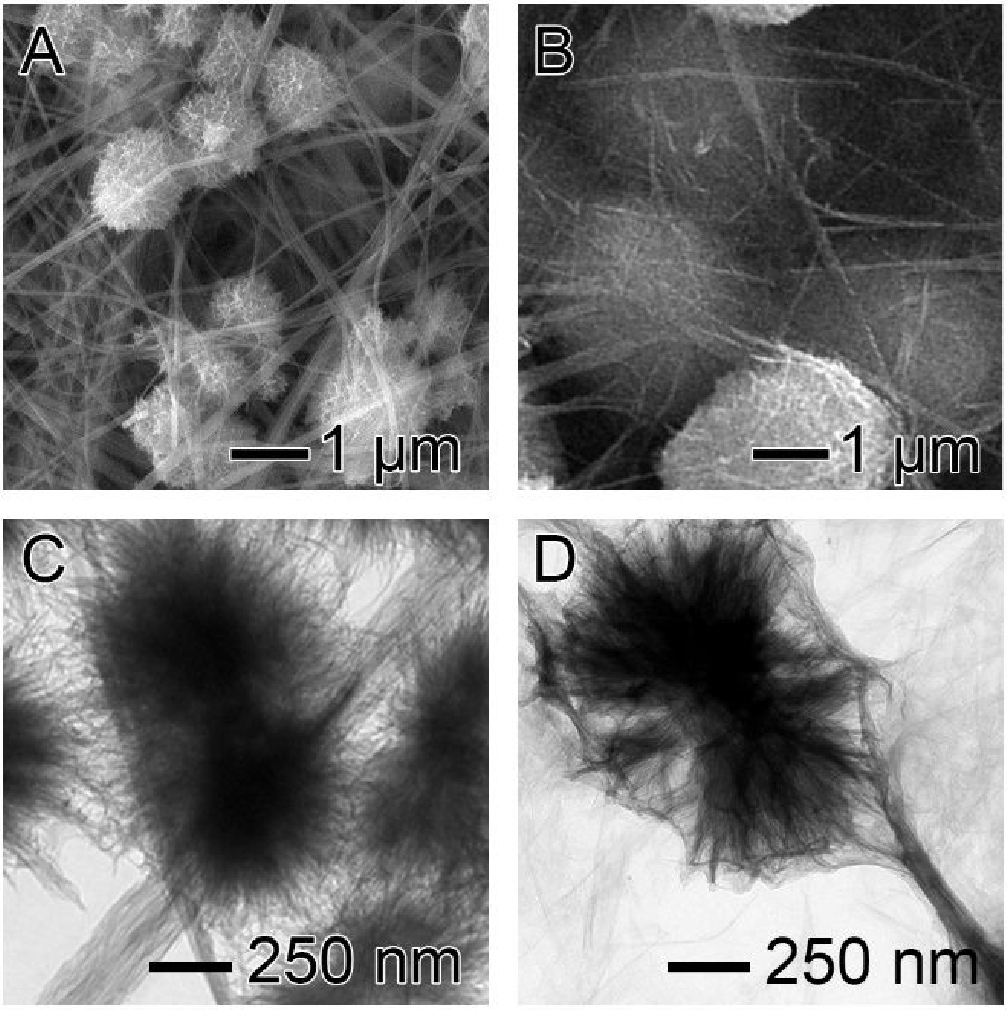

Figure S2. SEM images of (A) $Na_2Ti_3O_7$ (B) RGO/$Na_2Ti_3O_7$ and TEM images of (C) $Na_2Ti_3O_7$ (D) RGO/$Na_2Ti_3O_7$ fabricated by hydrothermal reaction for 20 h under 200 ^oC.

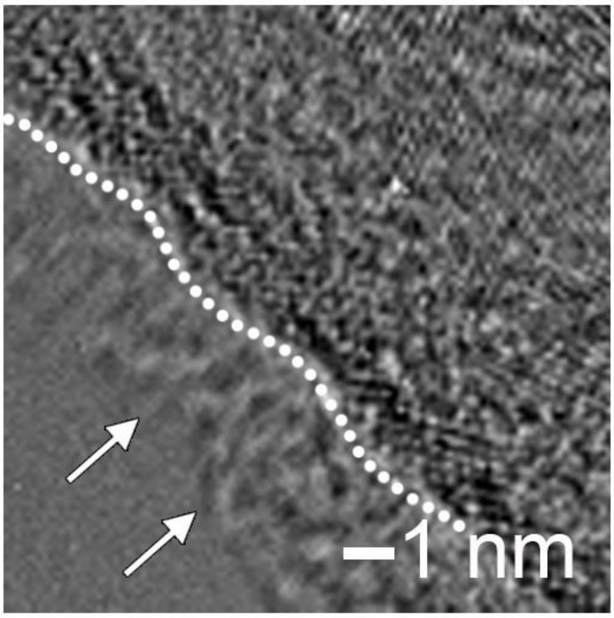

Figure S3. HRTEM images of RGO/$Na_2Ti_3O_7$. The arrows highlight the RGO sheets.

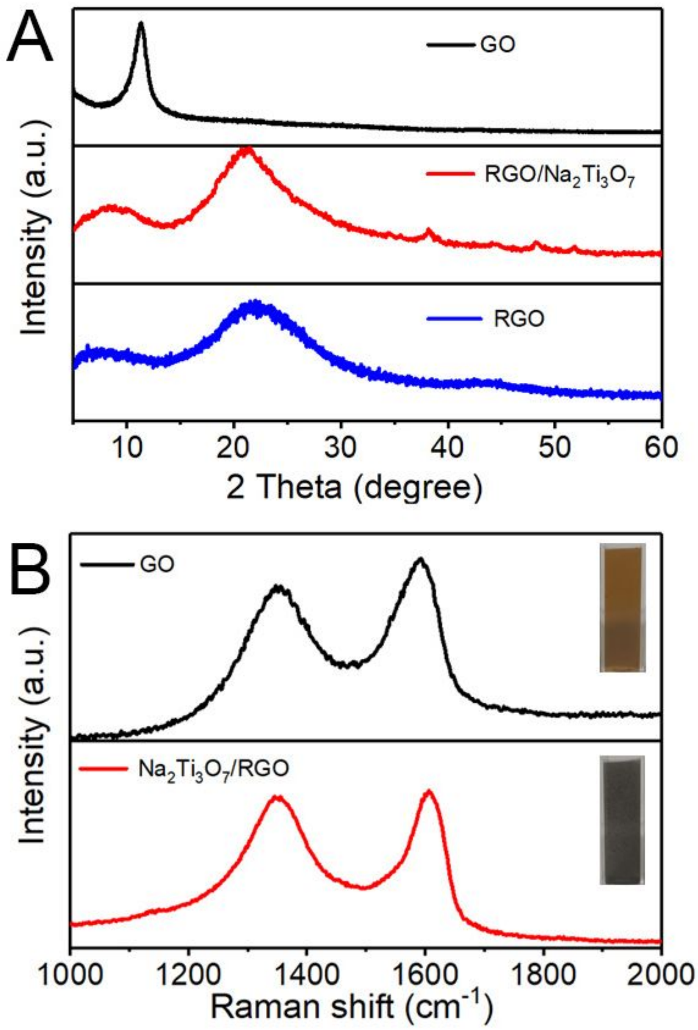

Figure S4. (A) The XRD patterns of GO, RGO/$Na_2Ti_3O_7$ and RGO. (B) Raman spectra of GO and RGO/$Na_2Ti_3O_7$. The insets in B are the photographs of the pristine GO and RGO/$Na_2Ti_3O_7$ dispersed in water, respectively.

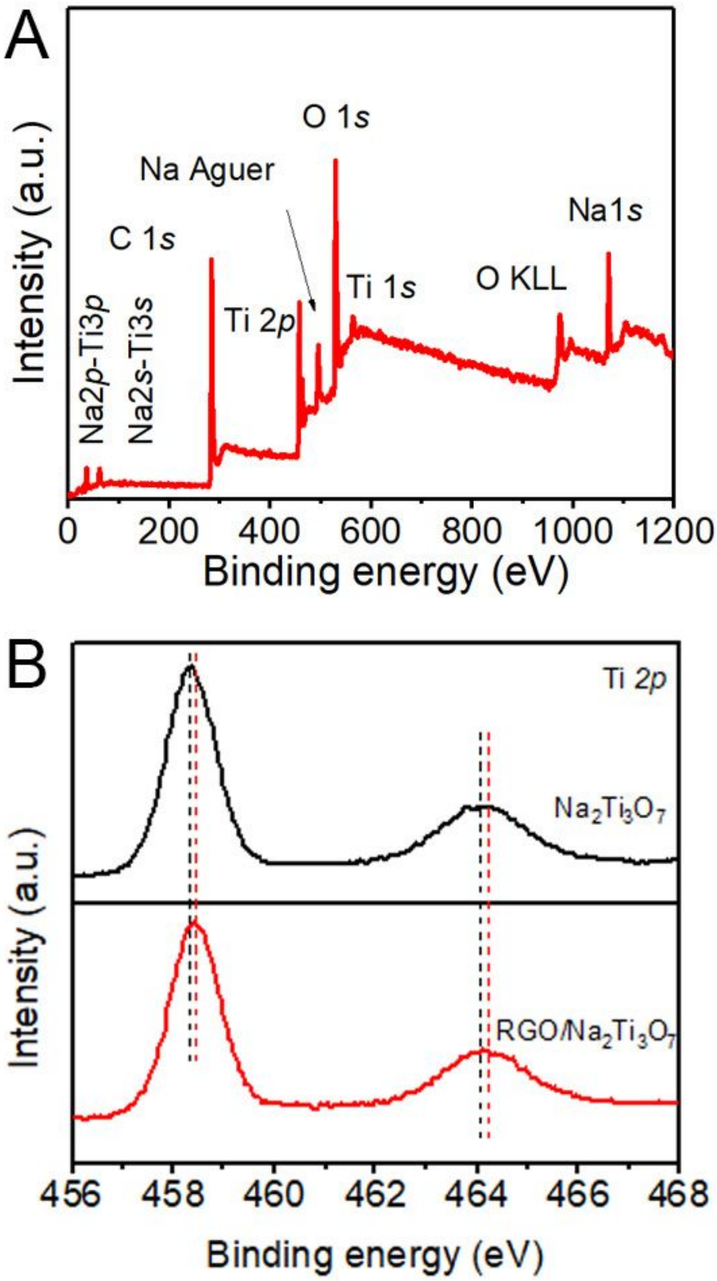

Figure S5. (A) Full and (B) high-resolution Ti 2*p* XPS spectra of RGO/$Na_2Ti_3O_7$.

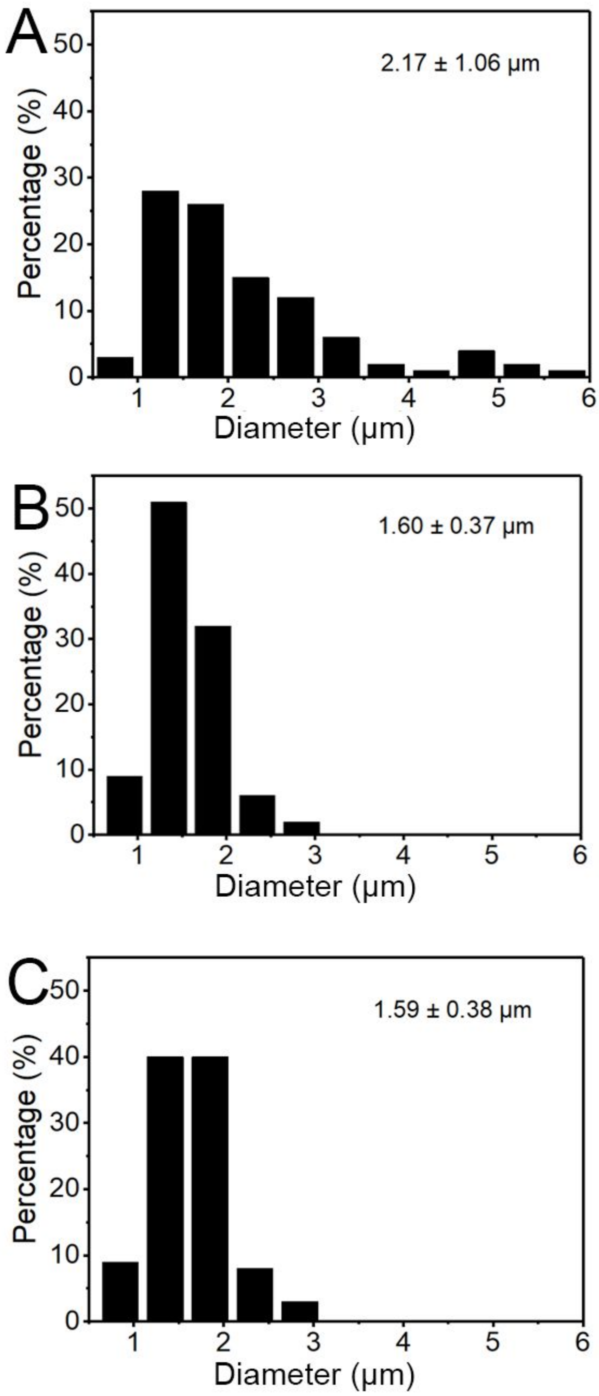

Figure S6. Histogram of diameters of $Na_2Ti_3O_7$ microspheres in RGO/$Na_2Ti_3O_7$ under 200 ^oC for 15 h in the presence of GO sheets sonicated for (A) 16, (B) 32, and C) 64 min.

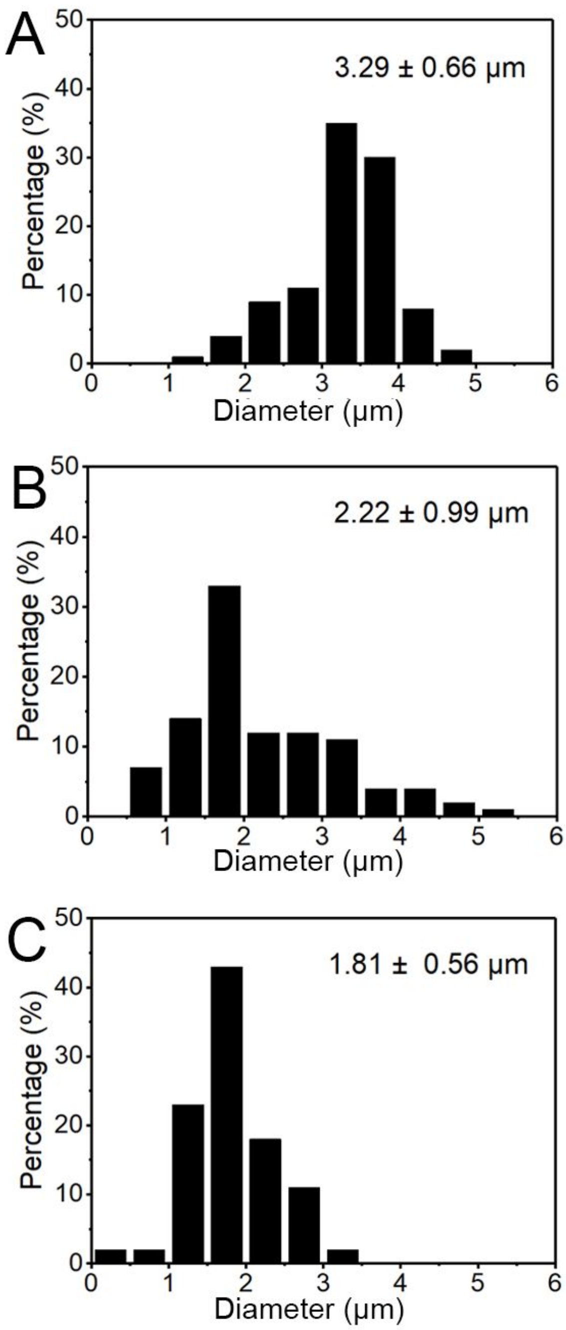

Figure S7. Histogram of diameters of $Na_2Ti_3O_7$ microspheres in RGO/$Na_2Ti_3O_7$ composites synthesized with (A) 33, (B) 60, (C) 66 wt% of GO under 200 °C for 1 h.

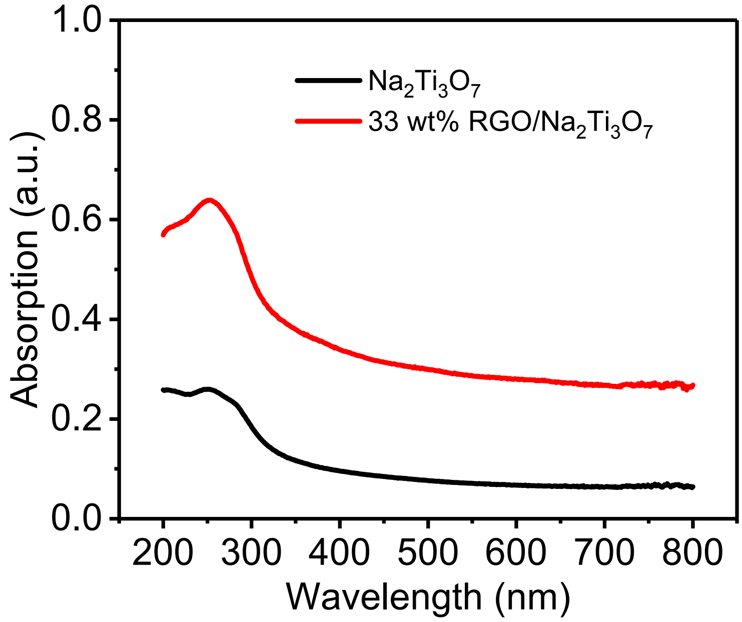

Figure S8. The UV–vis spectra of $Na_2Ti_3O_7$ and RGO/$Na_2Ti_3O_7$ microspheres with 33 wt% of GO.

Table S1. Comparison of the photoelectrochemical performance with similar photoelectrochemical systems.

Sample	J_{st} (μA/cm^2)	Reference
50 wt% RGO/$Na_2Ti_3O_7$	2.31	In this work
N-doped graphene quantum dots	0.400	1
Au/TiO_2	<0.900	2
Fe_3O_4/g-C_3N_4	<0.400	3
graphene-TiO_2	<0.120	4

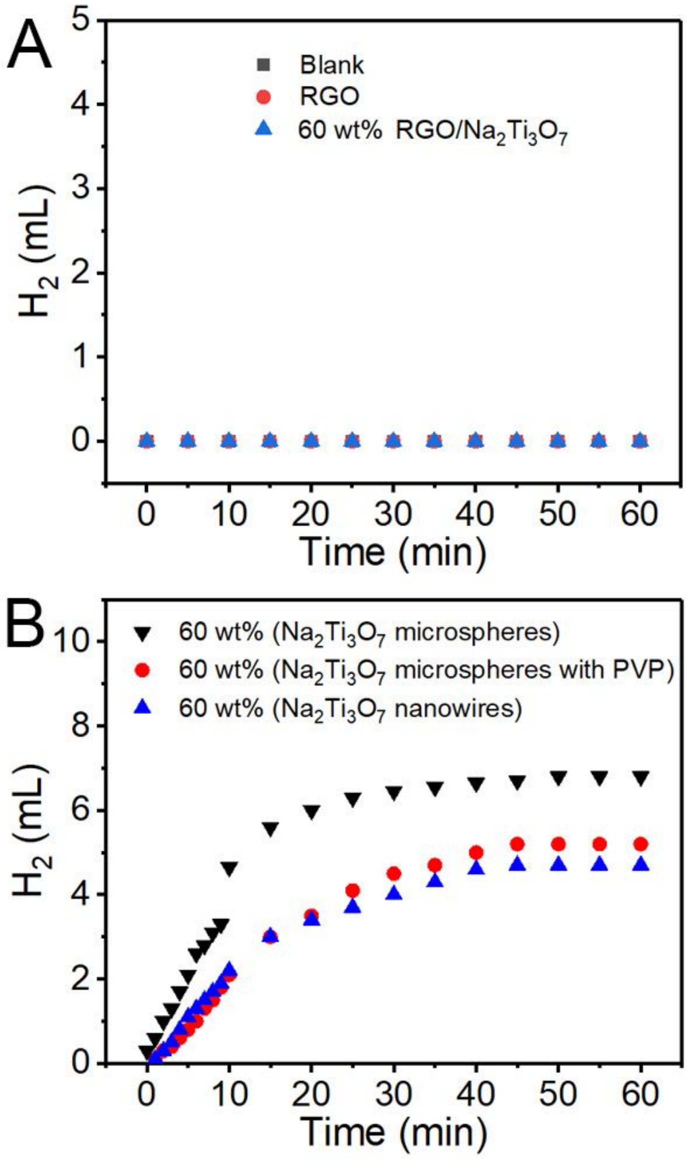

Figure S9. (A) Time course of H_2 evolution from AB without using catalyst or using 60 wt% RGO/$Na_2Ti_3O_7$ and RGO without visible-light irradiation. (B) Time course of H_2 evolution from AB using different catalyst under visible light irradiation. The RGO/$Na_2Ti_3O_7$ nanowires is a mixture of RGO and $Na_2Ti_3O_7$ nanowires with the same mass ratio of 3: 2 as that of RGO/$Na_2Ti_3O_7$ microspheres.

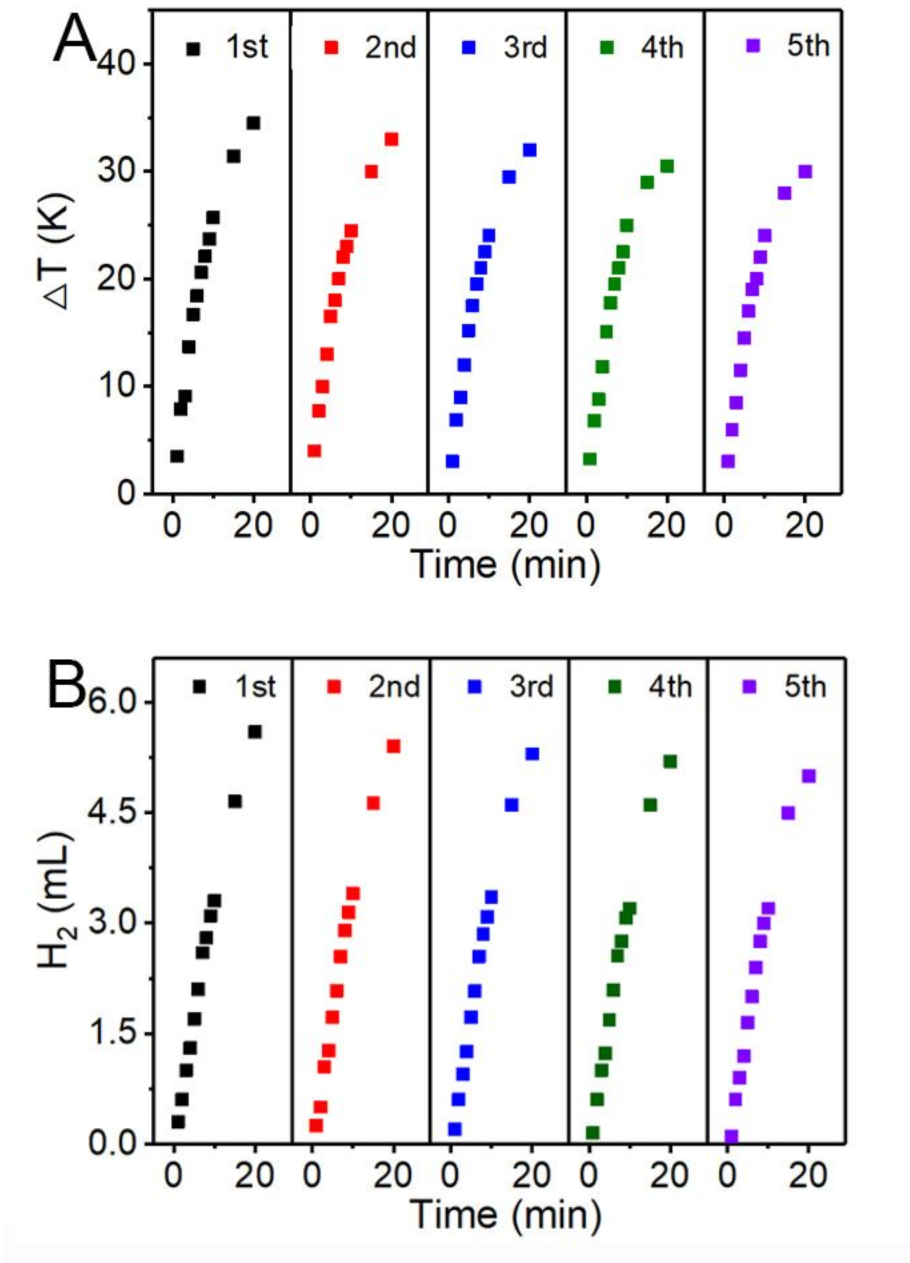

Figure S10. Stability of (A) temperature variation, and (B) time course of H_2 evolution from AB using 60 wt% RGO/$Na_2Ti_3O_7$ as catalyst.

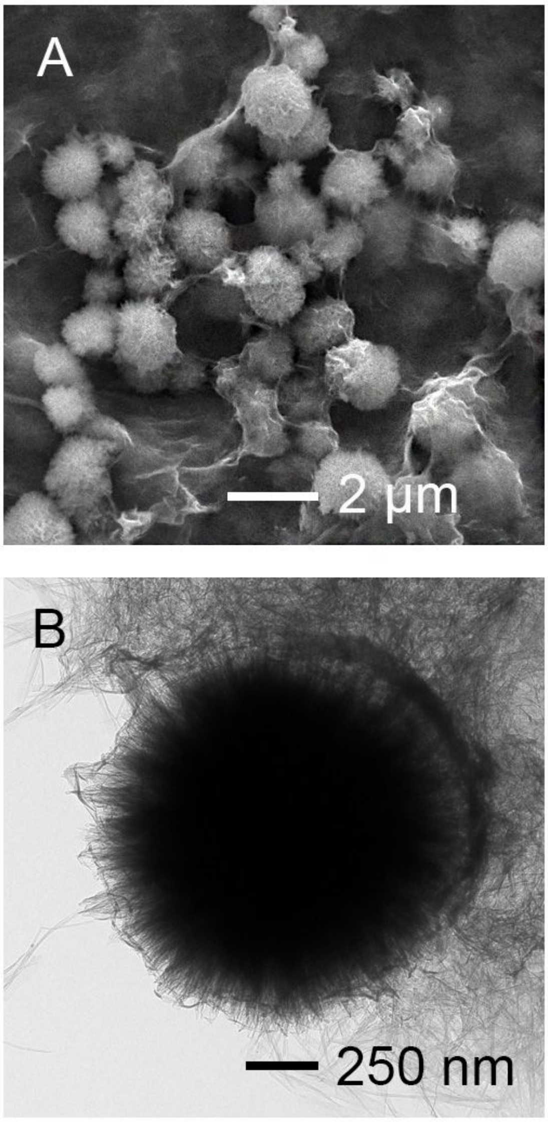

Figure S11. (A) SEM and (B) TEM images of 60 wt% RGO/$Na_2Ti_3O_7$ after the catalytic reaction.

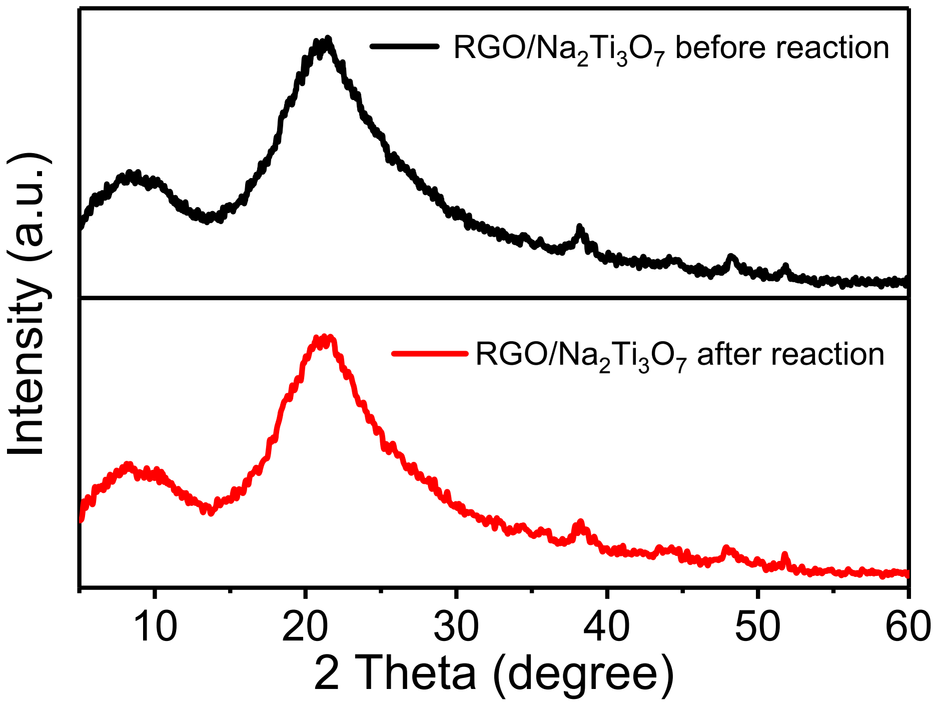

Figure S12. The XRD patterns of the RGO/$Na_2Ti_3O_7$ before and after catalytic reaction.

Reference

(1) Dai, Y.; Long, H.; Wang, X.; Wang, Y.; Gu, Q.; Jiang, W.; Wang, Y.; Li, C.; Zeng, T. H.; Sun, Y.; Zeng, J. Versatile Graphene Quantum Dots with Tunable Nitrogen Doping. *Part. Part. Syst. Charact.* **2014**, *31* (5), 597−604.

(2) Jung, H.; Song, J.; Lee, S.; Lee, Y. W.; Wi, D. H.; Goo, B. S.; Han, S. W. Hierarchical Metal-Semiconductor-Graphene Ternary Heteronanostructures for Plasmon-Enhanced Wide-Range Visible-Light Photocatalysis. *J. Mater. Chem. A* **2019**, *7* (26), 15831−15840.

(3) Zeng, D.; Zhou, T.; Ong, W. J.; Wu, M.; Duan, X.; Xu, W.; Chen, Y.; Zhu, Y. A.; Peng, D. L. Sub-5 nm Ultra-Fine FeP Nanodots as Efficient Co-Catalysts Modified Porous g-C_3N_4 for Precious-Metal-Free Photocatalytic Hydrogen Evolution under Visible Light. *ACS Appl. Mater. Interfaces* **2019**, *11* (6), 5651−5660.

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