Electronic Supplementary Information

Cocatalyst Engineering on a Narrow Bandgap Ga-$La_5Ti_2Cu_{0.9}Ag_{0.1}O_7S_5$ Photocatalyst Towards Effectively Enhanced Water Splitting

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Supporting Figures

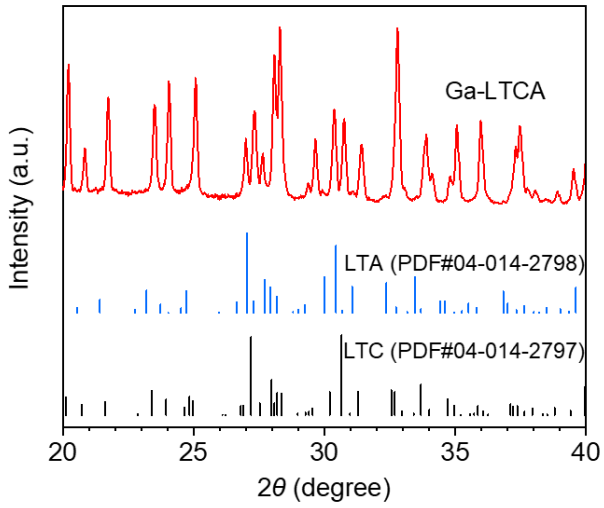

Figure S1. XRD pattern for the as-prepared Ga-LTCA sample. The reference XRD patterns for LTC and LTA refer to ICDD PDF#04-014-2797 and PDF#04-014-2798, respectively.

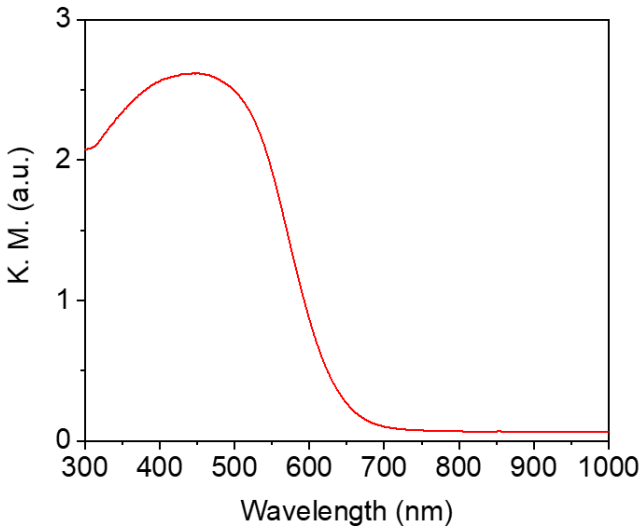

Figure S2. UV-vis DRS data obtained from the as-prepared Ga-LTCA sample.

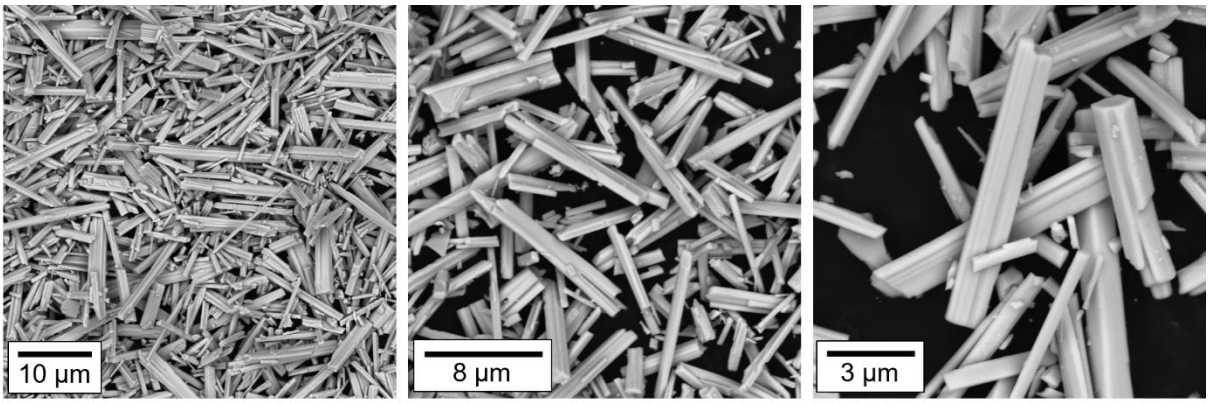

Figure S3. SEM images of the Ga-LTCA sample.

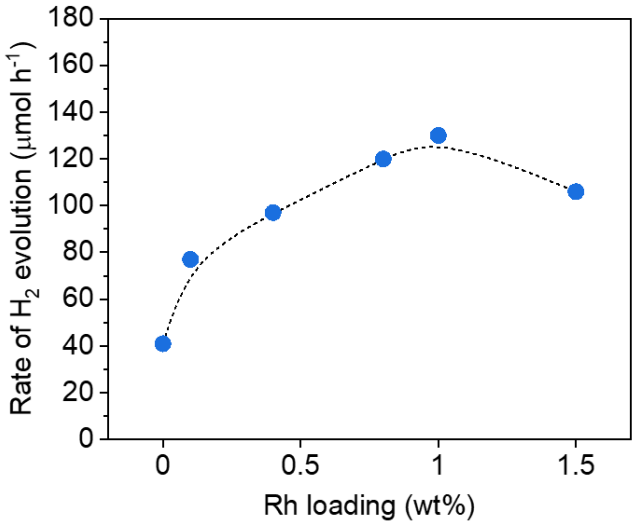

Figure S4. Photocatalytic H_2 evolution rates over Ga-LTCA photocatalysts prepared using the photodeposition method for cocatalyst loading with various Rh loading amounts.

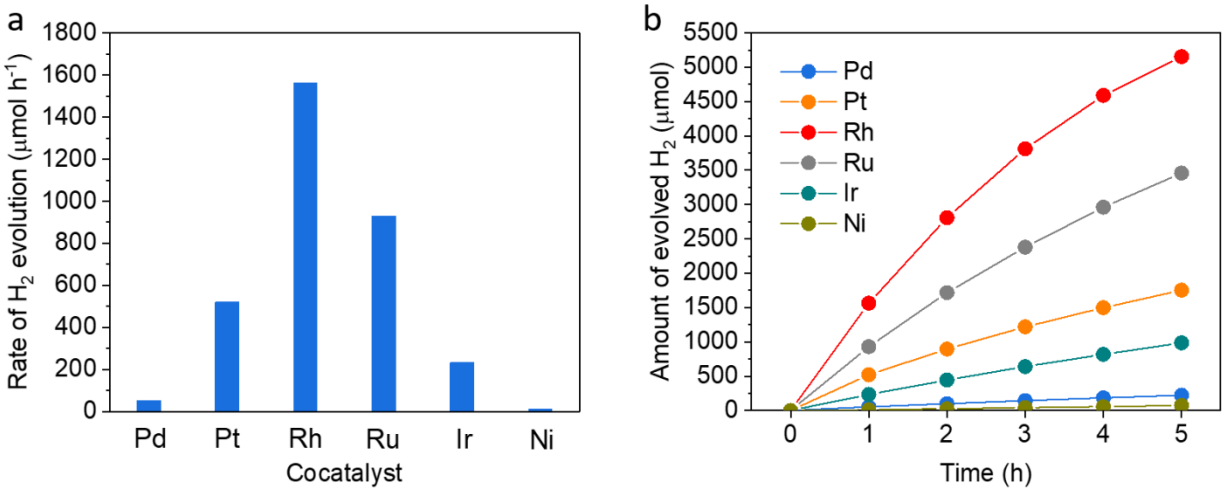

Figure S5. (a) Photocatalytic H_2 evolution rates over Ga-LTCA photocatalysts modified using the impregnation method with 0.4 wt% of different cocatalyst metals. (b) Time courses of H_2 gas evolution over Ga-LTCA photocatalysts modified using the impregnation method with different cocatalyst metals at 0.4 wt%.

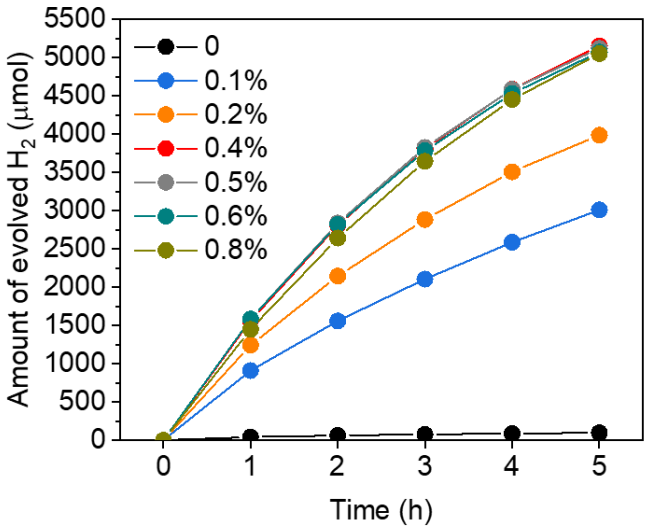

Figure S6. Time courses of H_2 gas evolution using Ga-LTCA photocatalysts modified with different amounts of the Rh cocatalyst using the impregnation method.

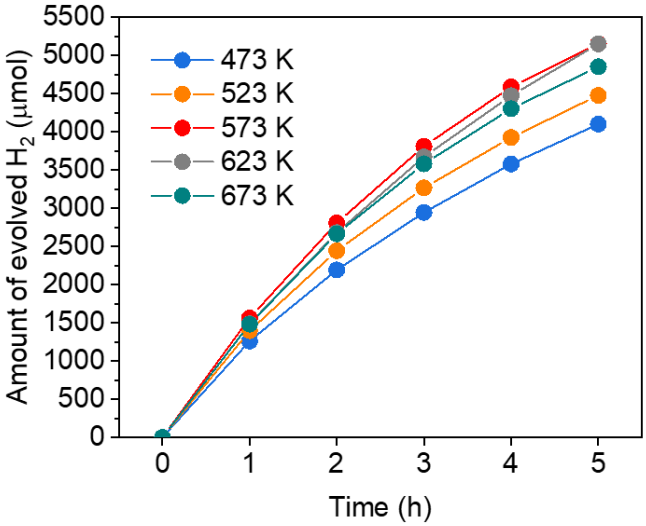

Figure S7. Time courses of H_2 gas evolution over photocatalysts loaded with a Rh cocatalyst and heated at different reduction temperatures following impregnation.

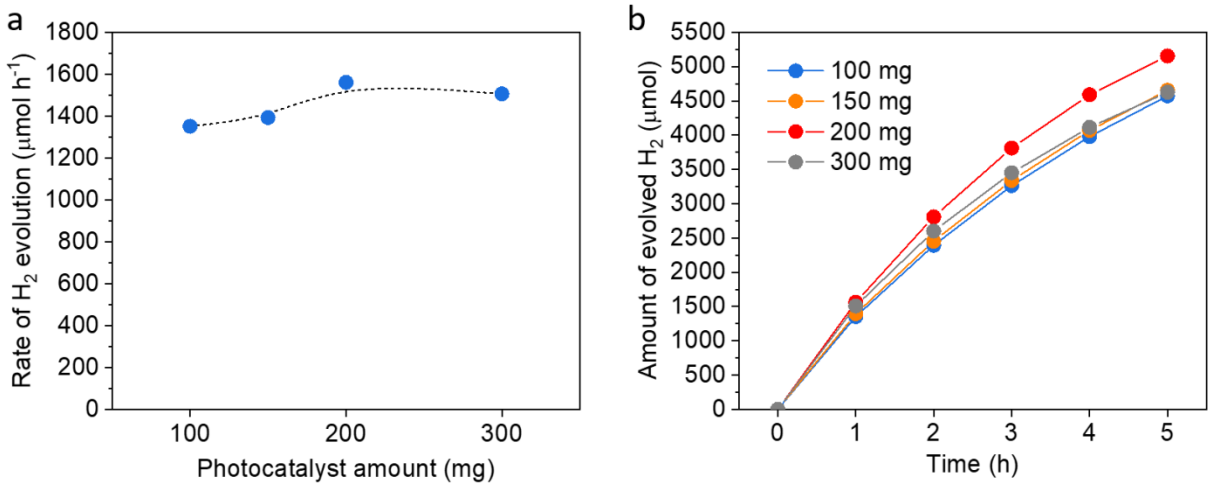

Figure S8. (a) The effect of the amount of the 0.4 wt% Rh(IMP)/Ga-LTCA photocatalyst on the photocatalytic H_2 evolution rate. (b) Time courses of H_2 gas evolution reactions using different amounts of the 0.4 wt% Rh(IMP)/Ga-LTCA photocatalyst.

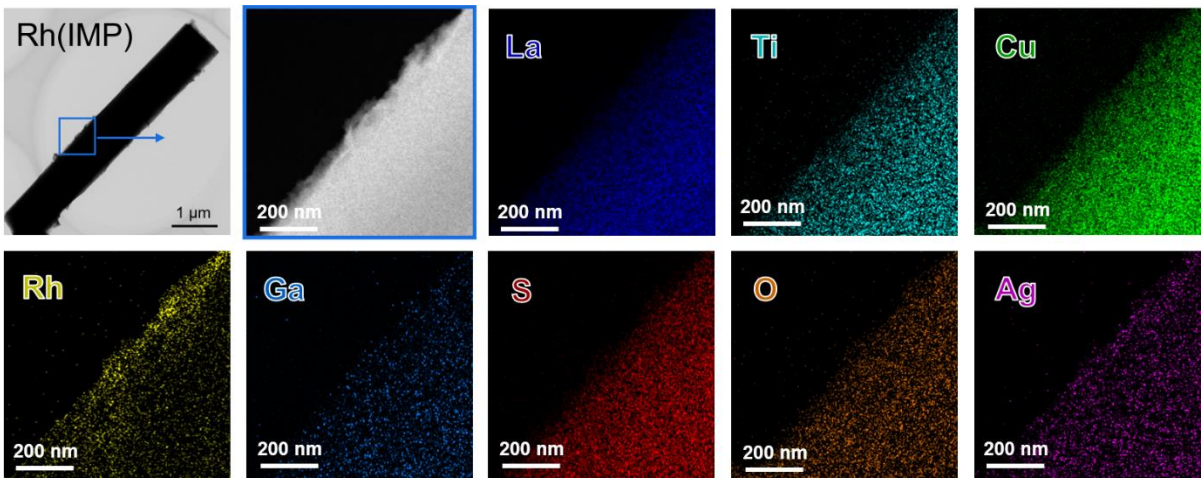

Figure S9. TEM and STEM-EDS mapping of a 0.4 wt% Rh(IMP)/Ga-LTCA sample.

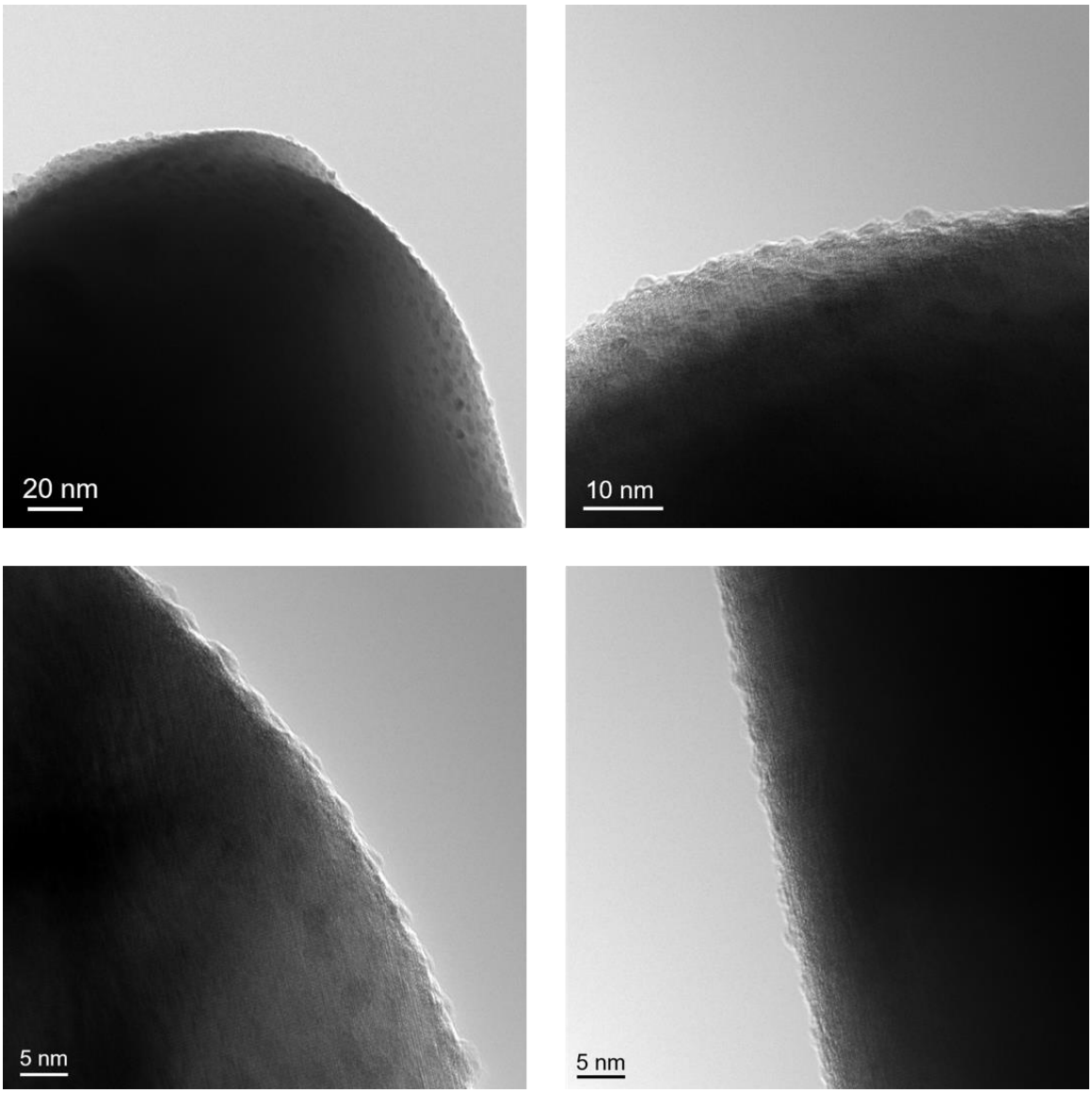

Figure S10. Additional HRTEM images of a 0.4 wt% Rh(IMP)/Ga-LTCA sample showing that the Rh particles had hemispherical shapes and intimate contact with the Ga-LTCA surface.

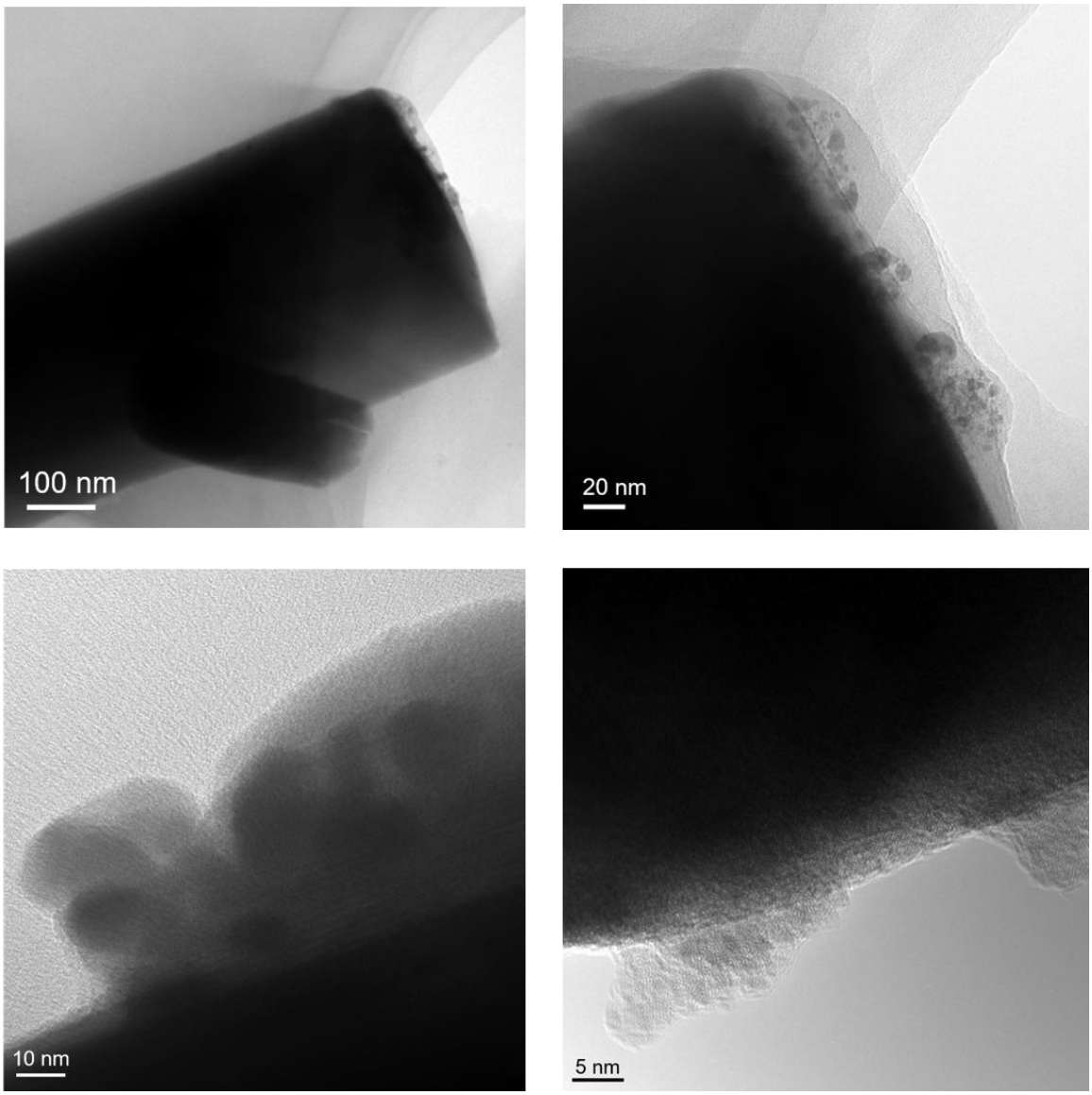

Figure S11. Additional TEM images of a 1.0 wt% Rh(PD)/Ga-LTCA sample showing that the Rh particles were aggregated on the top surfaces of the Ga-LTCA particles.

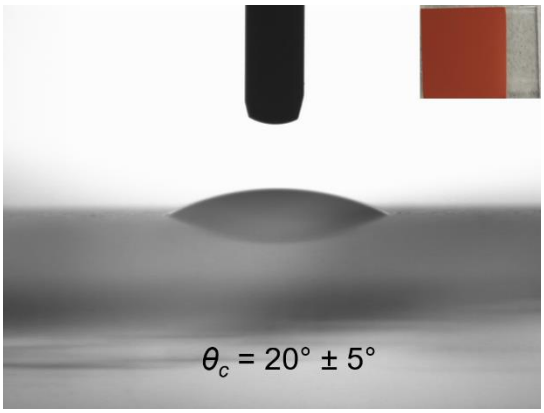

Figure S12. Photograph showing a Ga-LTCA photocatalyst film and associated water contact angle (ϑ_c).

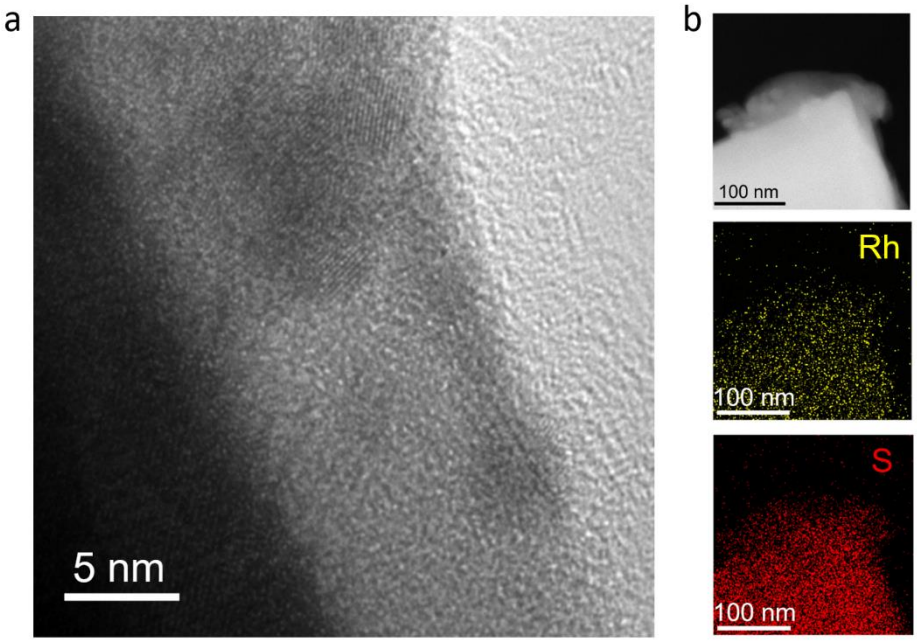

Figure S13. HRTEM image and STEM-EDS mapping of a 1.0 wt% Rh(PD)/Ga-LTCA sample.

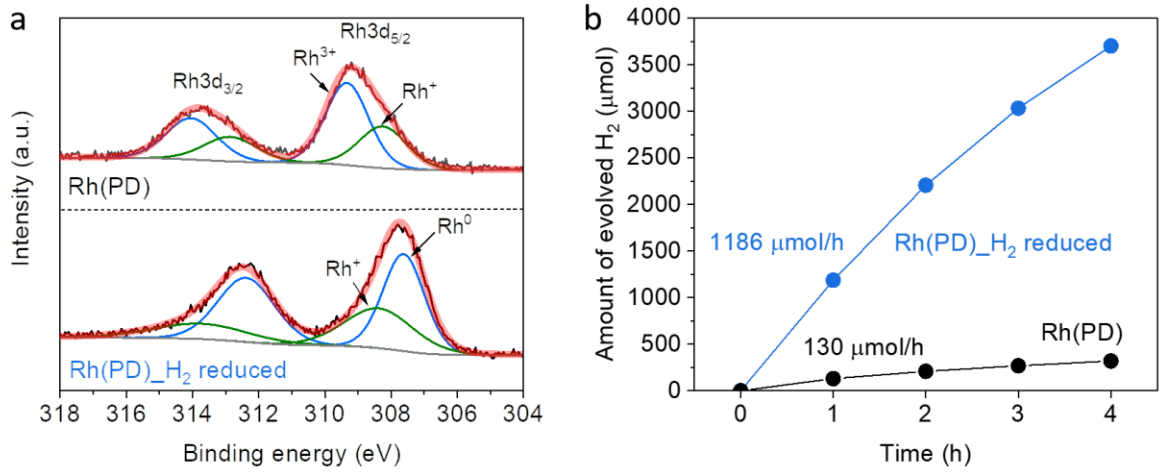

Figure S14. (a) XPS spectra of Rh species on Ga-LTCA loaded by photodeposition method (PD) and the same photocatalyst treated with H_2 reduction at 573 K for 1 h (H_2 reduced). (b) Time courses of H_2 gas evolution on Ga-LTCA loaded with a Rh cocatalyst using photodeposition (PD) and the same photocatalyst treated with H_2 reduction at 573 K for 1 h (H_2 reduced).

The 1.0 wt% Rh(PD)/Ga-LTCA sample was treated with H_2 reduction at 573 K for 1 h. As shown in the XPS spectra, the H_2-reduced sample showed significant metallic Rh^0 species with minor Rh^+ species, which was similar with the XPS data of the Rh(IMP)/Ga-LTCA sample (Figure 2e in the main text). Moreover, the H_2 reduced sample was significantly improved HER activity (1186 μmol/h) compared with original PD sample (130 μmol/h). This result suggests that the metallic Rh^0 species are important for the improved photocatalytic activity. However, this activity is still lower than the HER activity of the 0.4 wt% Rh(IMP)/Ga-LTCA sample (1562 μmol/h). This is because the Rh loading amount and cocatalyst distribution are also important for the photocatalytic performance as is discussed in this work.

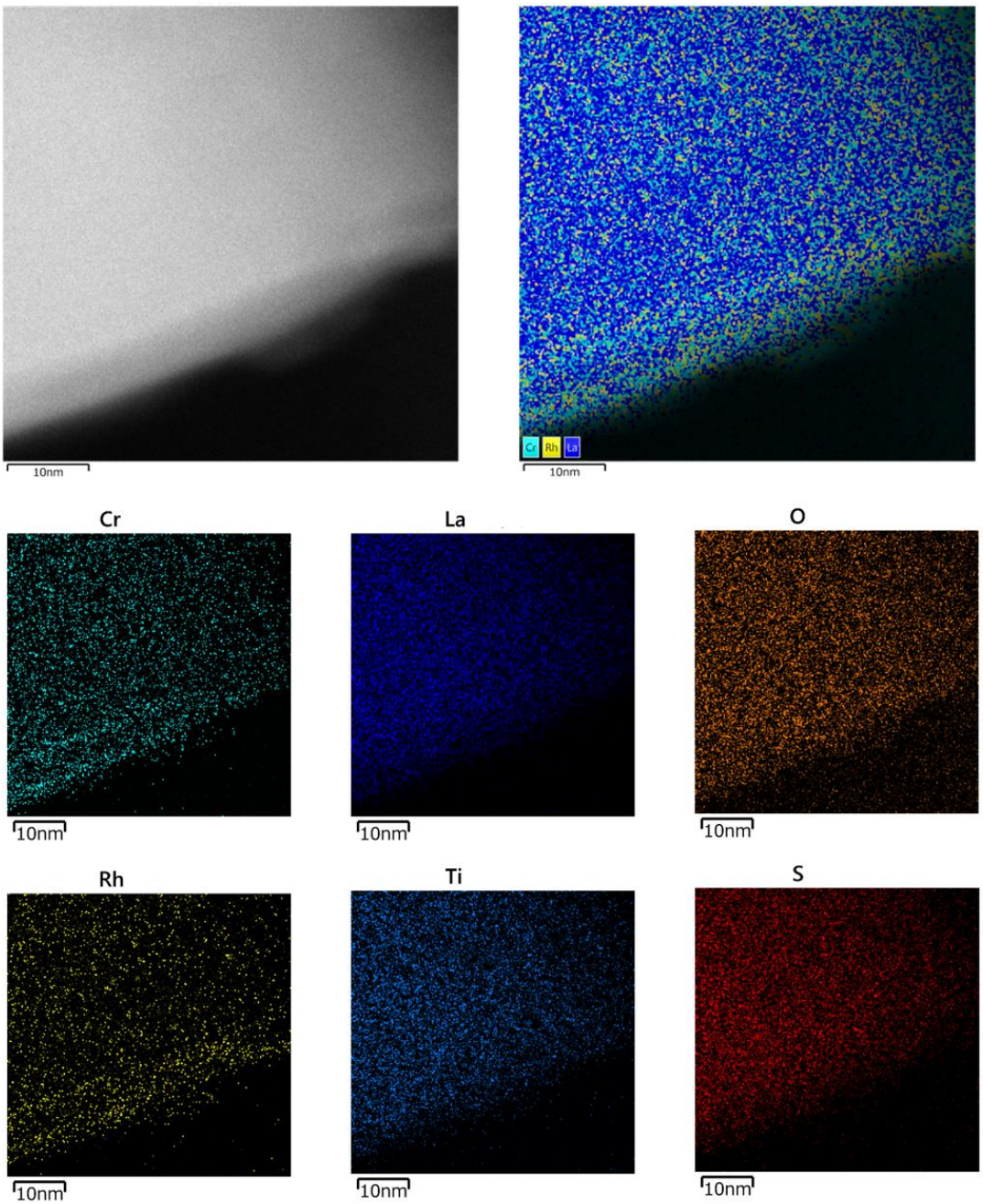

Figure S15. STEM-EDS mapping analysis of the 0.2 wt% Cr_2O_3/0.4 wt% Rh(IMP)/Ga-LTCA sample showing that Cr was in close proximity to the Rh, suggesting that the photoexcited electrons acted on the lateral surfaces of the Ga-LTCA particles.

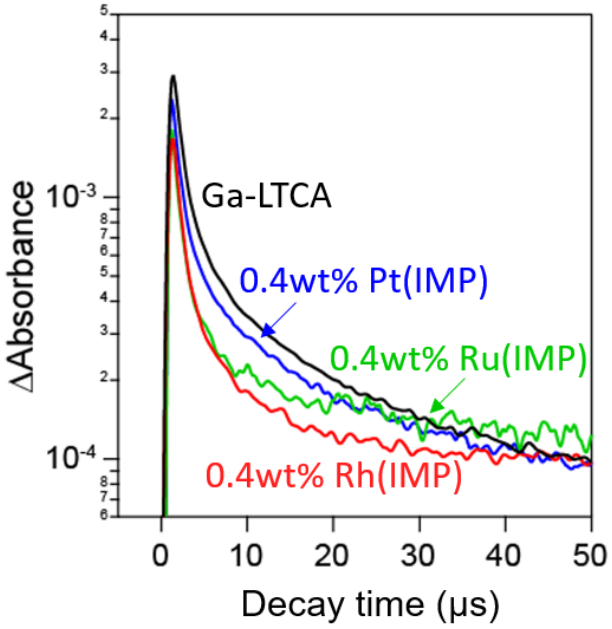

Figure S16. TA kinetic profiles of surviving electrons probed at 5000 cm^{-1} (2000 nm) in various samples under 470 nm excitation (3 mJ $pulse^{-1}$) for different cocatalysts: bare Ga-LTCA, 0.4 wt% Pt(IMP)/Ga-LTCA, 0.4 wt% Ru(IMP)/Ga-LTCA and 0.4 wt% Rh(IMP)/Ga-LTCA. The electron transfer efficiency increased in the order of Rh > Ru > Pt at the same loading amount (0.4 wt%). This result is in good agreement with the H_2 evolution activity data obtained from Ga-LTCA loaded with different cocatalysts (**Figure S5**).

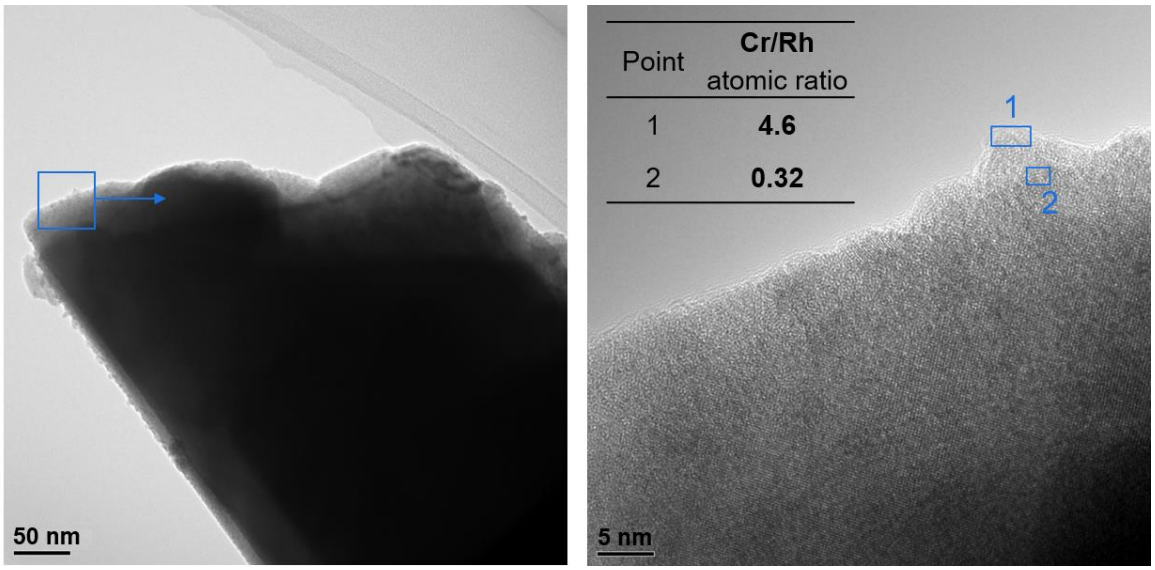

Figure S17. TEM images and EDS elemental analysis results for selected areas that confirm the Rh/Cr_2O_3 core-shell structure in a 0.2 wt% Cr_2O_3/0.4 wt% Rh(IMP)/Ga-LTCA sample.

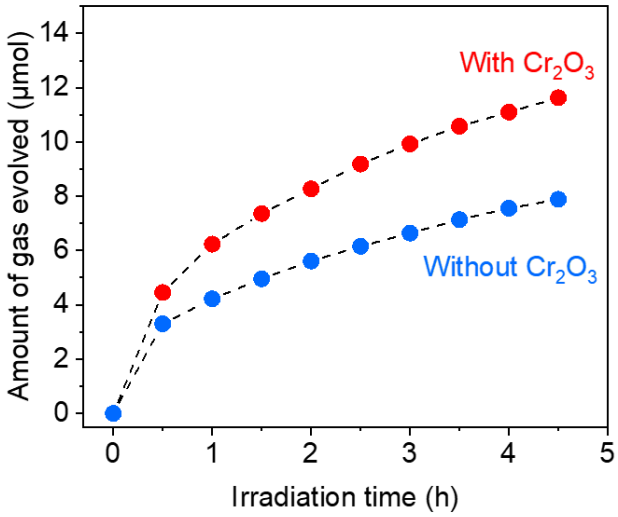

Figure S18. Time courses of H_2 gas evolution reactions using the 0.4 wt% Rh(IMP)/Ga-LTCA photocatalyst with and without Cr_2O_3 in a 15 mM aqueous NaI solution under visible light (λ > 420 nm). Reaction conditions: photocatalyst 50 mg, NaI aqueous solution (15 mM, 100 mL) adjusted to pH 4 by adding a 0.1 M aqueous H_2SO_4 solution, Ar 5 kPa background pressure.

Supporting Table

Table S1. Comparison of reported hydrogen evolution reaction activities over various oxysulfide photocatalysts.

Photocatalyst (*Absorption edge*)	**Cocatalyst**	**HER activity (μmol h^{-1})**	**AQY (%)**	**Reference**
Ga-$La_5Ti_2Cu_{0.9}Ag_{0.1}O_7S_5$ (*700 nm*)	Rh	464	3.1 (420 nm)	[1]
$La_5Ti_2AgO_7S_5$ (*600 nm*)	Pt/NiS	250	No data	[2]
Ga-$La_5Ti_2Cu_{0.9}Ag_{0.1}O_7S_5$ (*700 nm*)	Pt/NiS	130	No data	[2]
$La_5Ti_2AgO_7S_5$ (*600 nm*)	Pt	225	1.2 (420 nm)	[3]
$La_5Ti_2CuO_7S_5$ (*650 nm*)	Pt-PD/NiS	170	1.3 (420 nm)	[4]
$La_5Ti_2CuO_7S_5$ (*650 nm*)	Pt-IMP/NiS	280	1.8 (420 nm)	[5]
$Sm_2Ti_2O_5S_2$ (*650 nm*)	Rh	350	No data	[6]
Ag-$Sm_2Ti_2O_5S_2$ (*650 nm*)	Rh	949	8.8 (440 nm)	[7]
$Y_2Ti_2O_5S_2$ (*650 nm*)	Rh	125	5.3 (420 nm)	[8]
Ga-$La_5Ti_2Cu_{0.9}Ag_{0.1}O_7S_5$ (*700 nm*)	Rh	1562	11.2 (420 nm)	This work

References

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