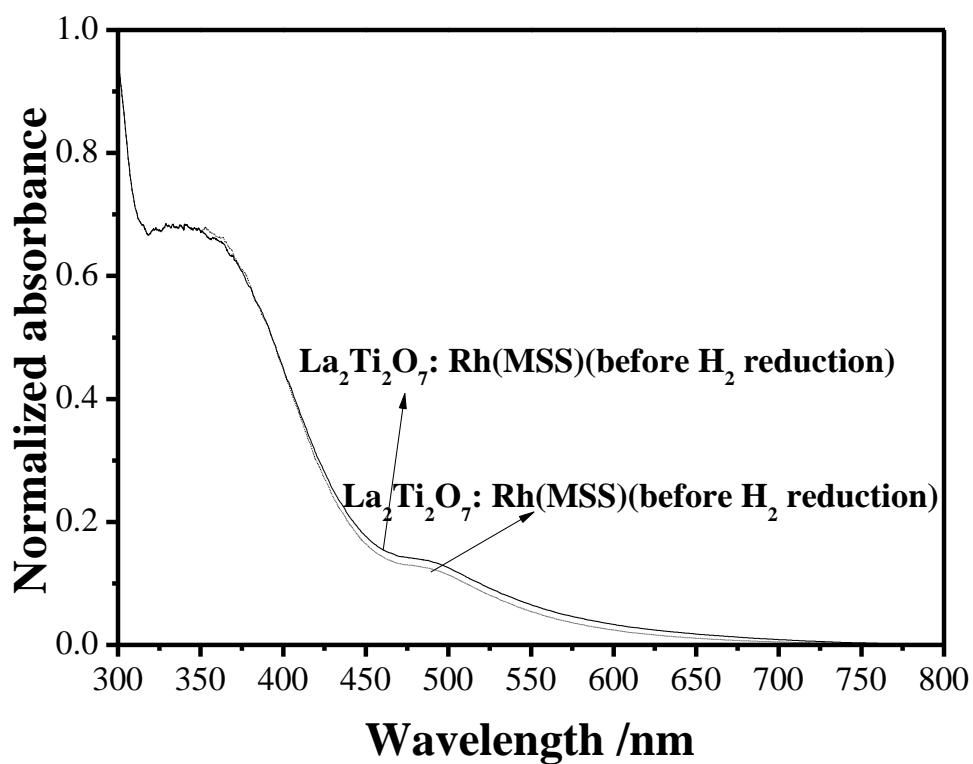
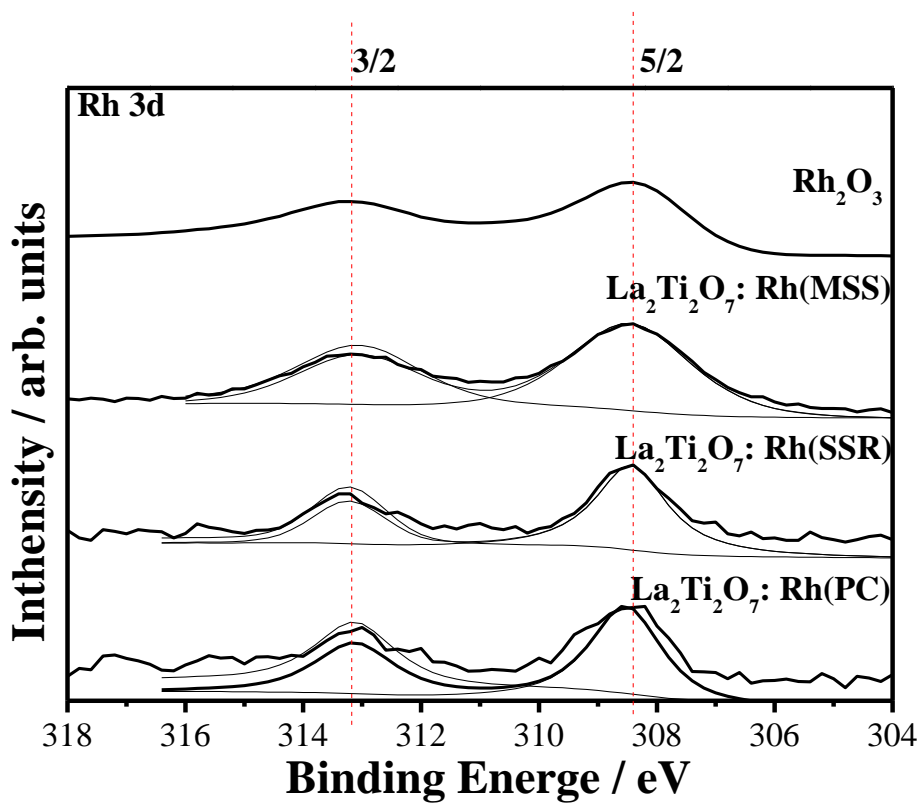


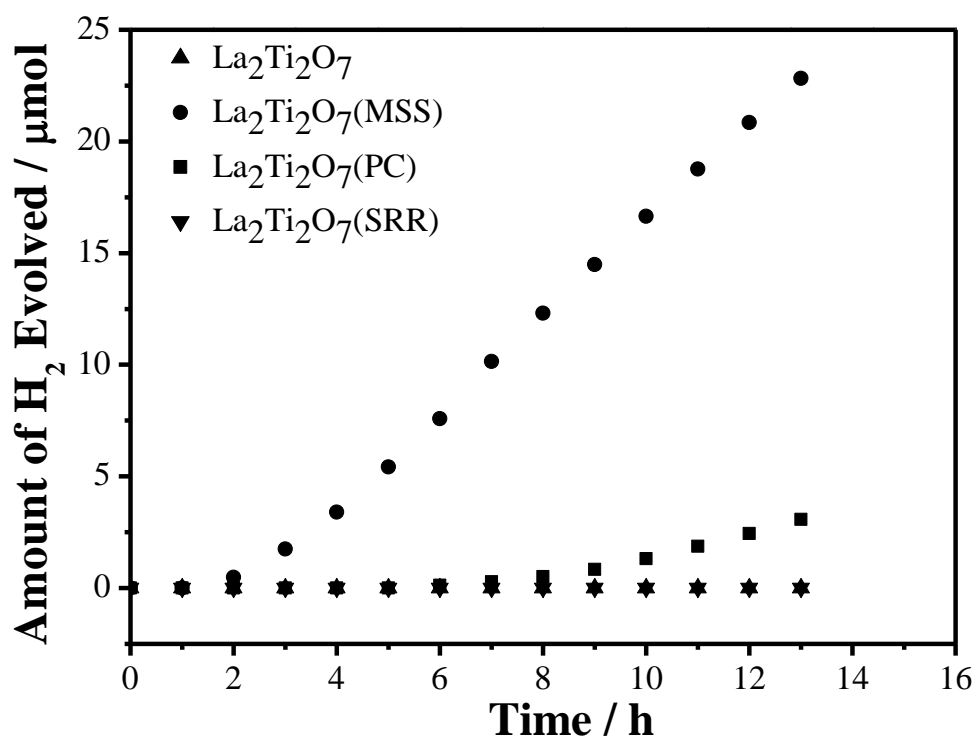
## Supporting Information



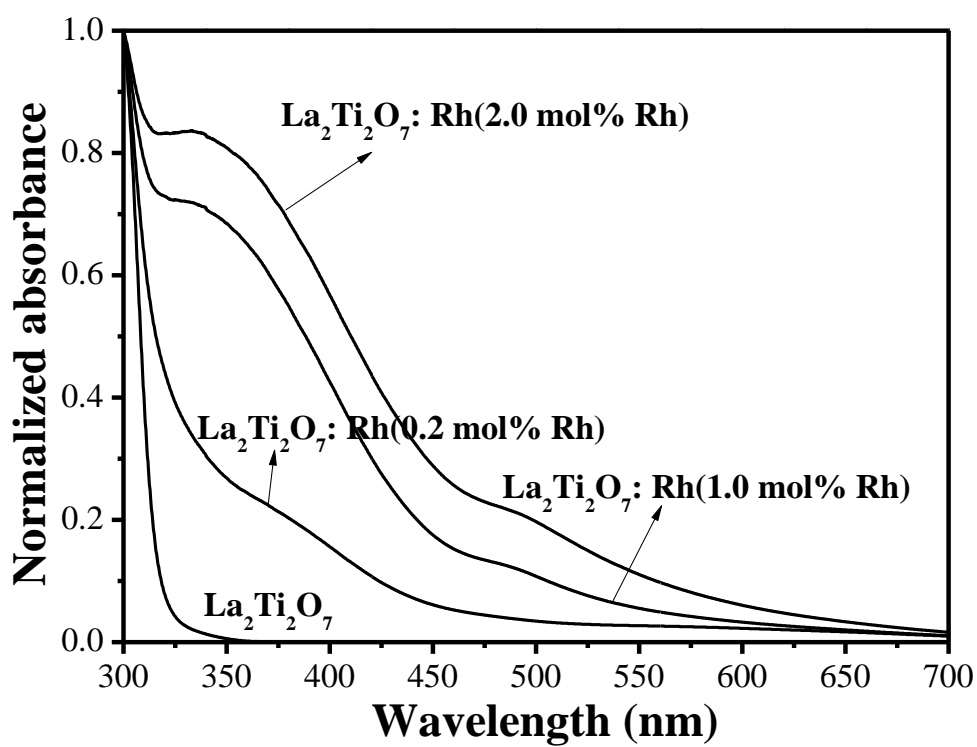
**Fig. S1.** Diffuse reflectance spectra for Rh-doped  $\text{La}_2\text{Ti}_2\text{O}_7$  (MSS) before and after  $\text{H}_2$  reduction treatment at 473 K for 2 h.



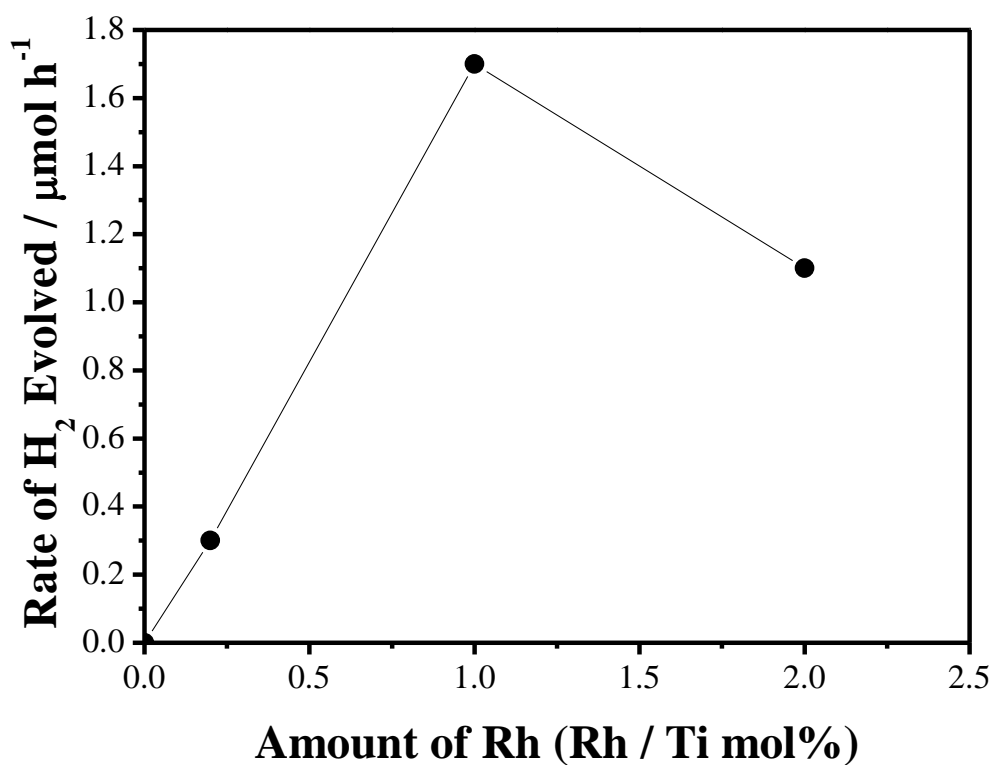
**Fig. S2.** X-ray photoelectron spectra for Rh 3d in Rh<sub>2</sub>O<sub>3</sub>, and Rh-doped La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> prepared by the molten salt synthesis (Entry 2), SSR (Entry 3), and PC (Entry 4) methods.



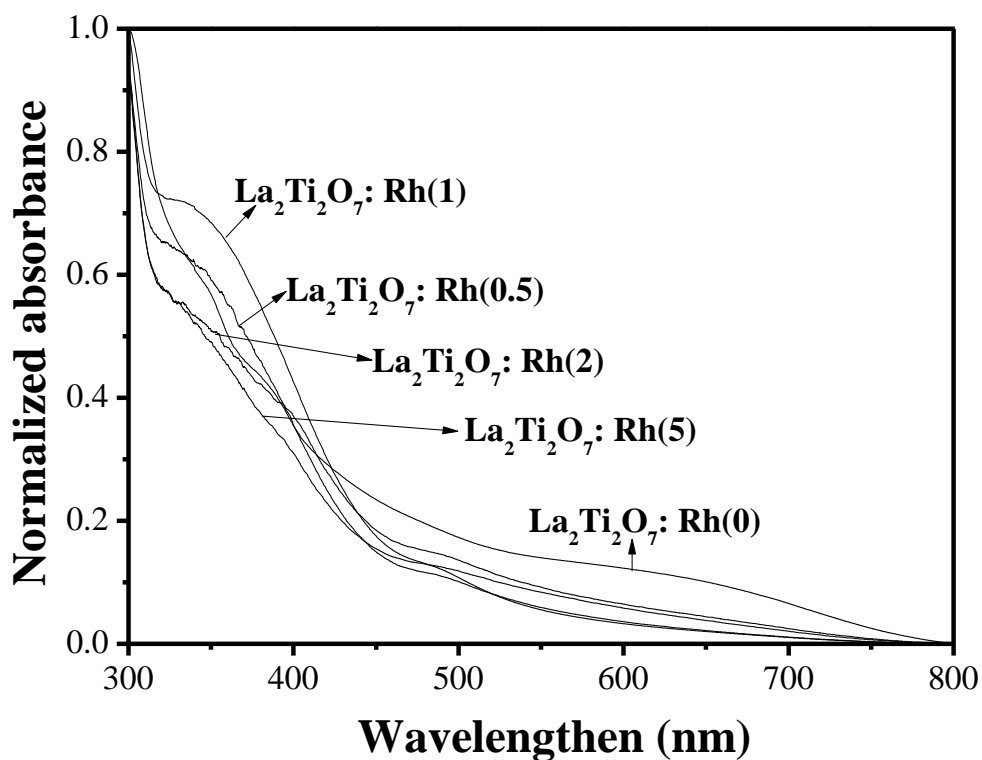
**Fig. S3.** Time courses of H<sub>2</sub> evolution over pristine La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (Entry 1), Pt/La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>: Rh (MSS) (Entry 2), Pt/La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>: Rh (SSR) (Entry 3), and Pt/La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>: Rh (PC) (Entry 4). Reaction conditions: Catalyst, 0.3 g; cocatalyst, Pt (0.5 wt%); reactant solution, 150 mL of 10 vol% aqueous methanol solution; light source, 300 W xenon lamp ( $\lambda > 420$  nm).



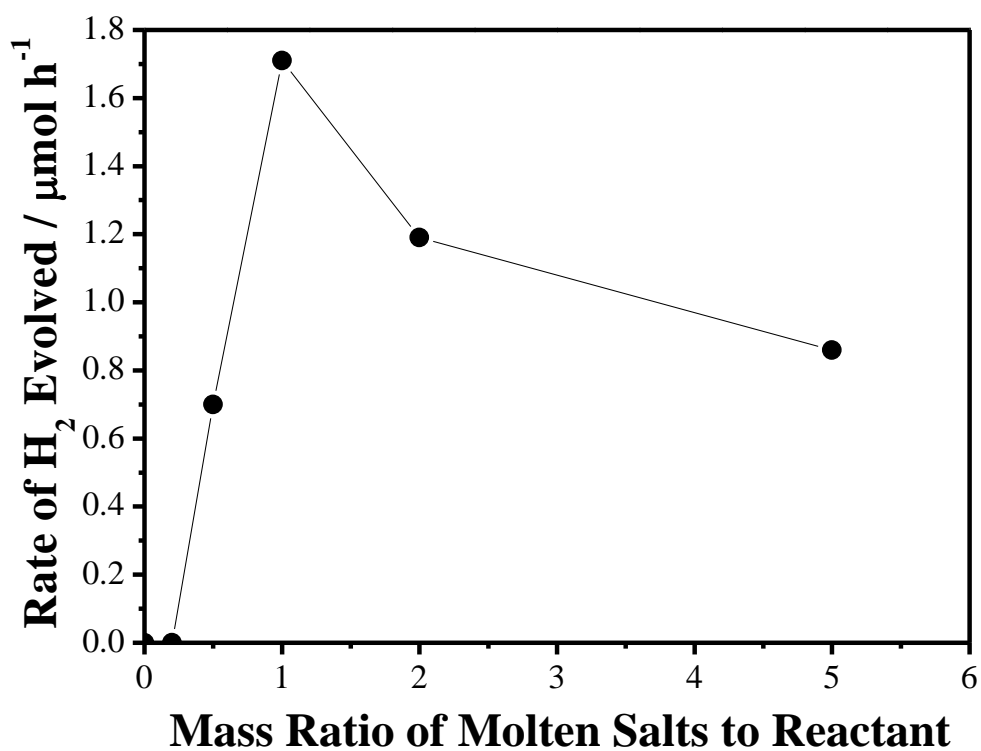
**Fig. S4.** Diffuse reflectance spectra for pristine  $\text{La}_2\text{Ti}_2\text{O}_7$  and  $\text{La}_2\text{Ti}_2\text{O}_7$  doped with 0.2, 1.0, and 2.0 mol% Rh with respect to Ti.



**Fig. S5.** Dependence of H<sub>2</sub> evolution activity of Rh-doped La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> on the doping amount. Reaction conditions: Catalyst, 0.3 g; cocatalysts, Pt (0.5 wt%); reactant solution, 150 mL of 10 vol% aqueous methanol solution; light source, 300 W xenon lamp ( $\lambda > 420$  nm).



**Fig. S6.** Diffuse reflectance spectra for Rh-doped  $\text{La}_2\text{Ti}_2\text{O}_7$  (1.0 mol% with respect to Ti) prepared with different amounts of molten salts. Mass ratio of molten salt to reactant: 0, 0.5, 1, 2, and 5.



**Fig. S7.** Dependence of H<sub>2</sub> evolution activity of Rh-doped La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> on the amount of molten salt. Reaction conditions: Catalyst, 0.3 g; cocatalysts, Pt (0.5 wt%); reactant solution, 150 mL of 10 vol% aqueous methanol solution; light source, 300 W xenon lamp ( $\lambda > 420$  nm).