

CO₂ capture, storage, and conversion using a praseodymium-modified Ga₂O₃ photocatalyst

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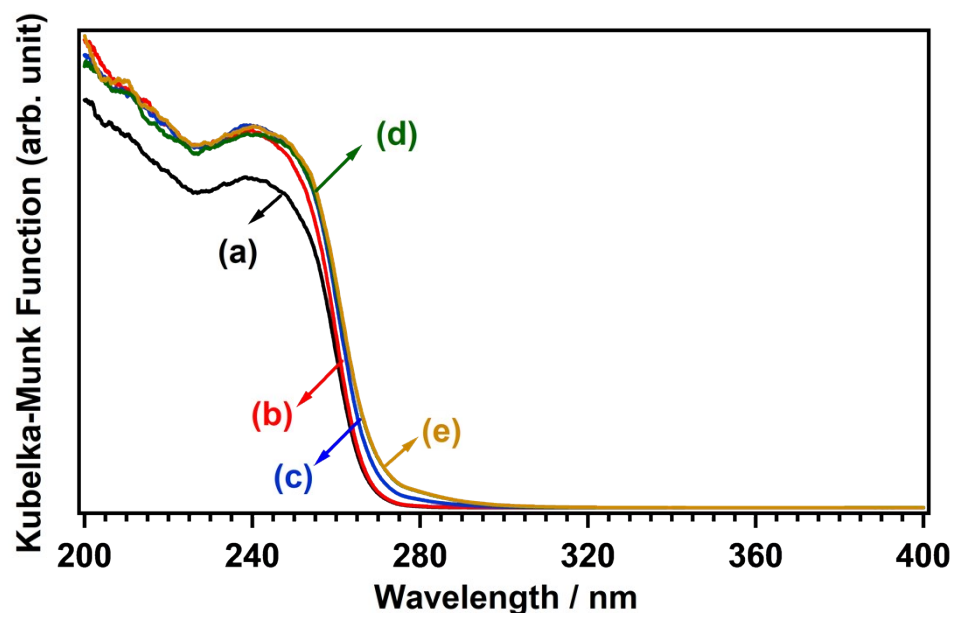


Fig. S1 UV-Vis diffuse reflectance spectra of Pr/Ga₂O₃ with different amounts of Pr: (a) 0 mol%; (b) 1.0 mol%; (c) 3.0 mol%; (d) 5.0 mol%; and (e) 10.0 mol%.

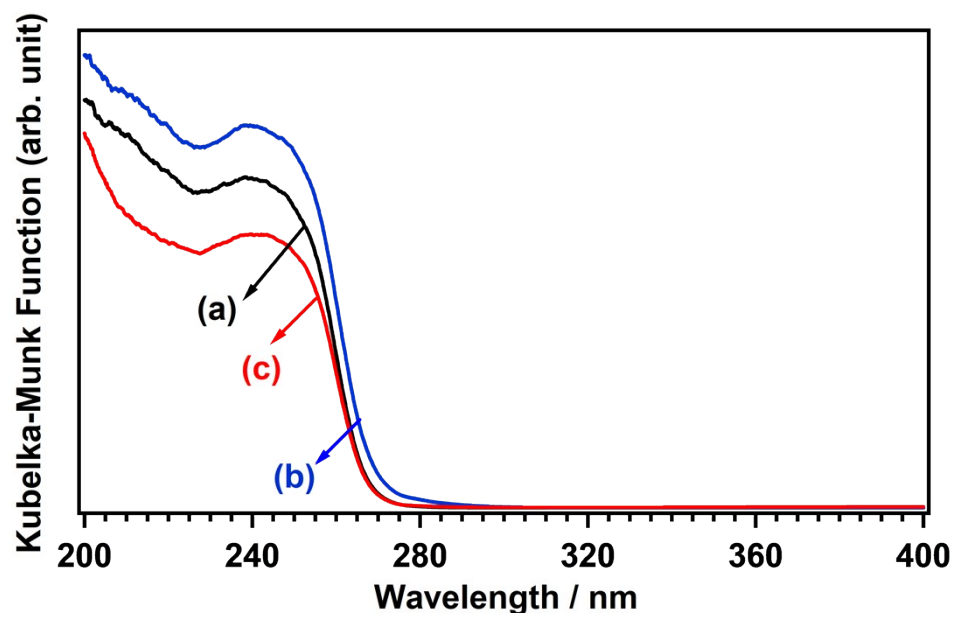


Fig. S2 UV-Vis diffuse reflectance spectra of (a) bare Ga₂O₃ and 3.0 Pr/Ga₂O₃ (b) before and (c) after reaction.

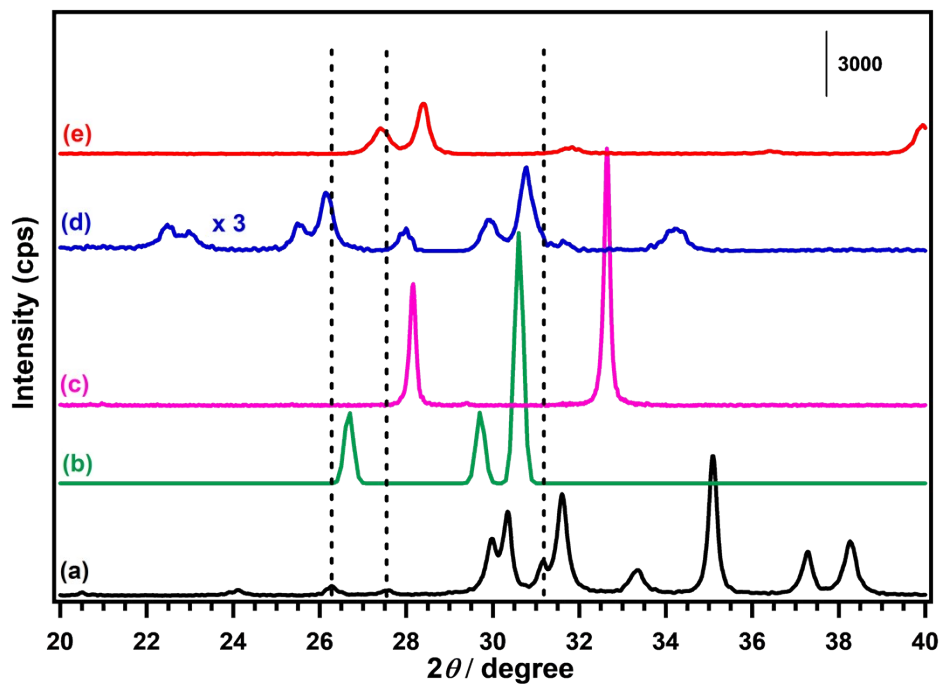


Fig. S3 XRD patterns of (a) 3.0 Pr/Ga₂O₃, (b) Pr₂O₃, (c) Pr₆O₁₁, (d) Pr₂O₂CO₃, and (e) Pr(OH)₃.

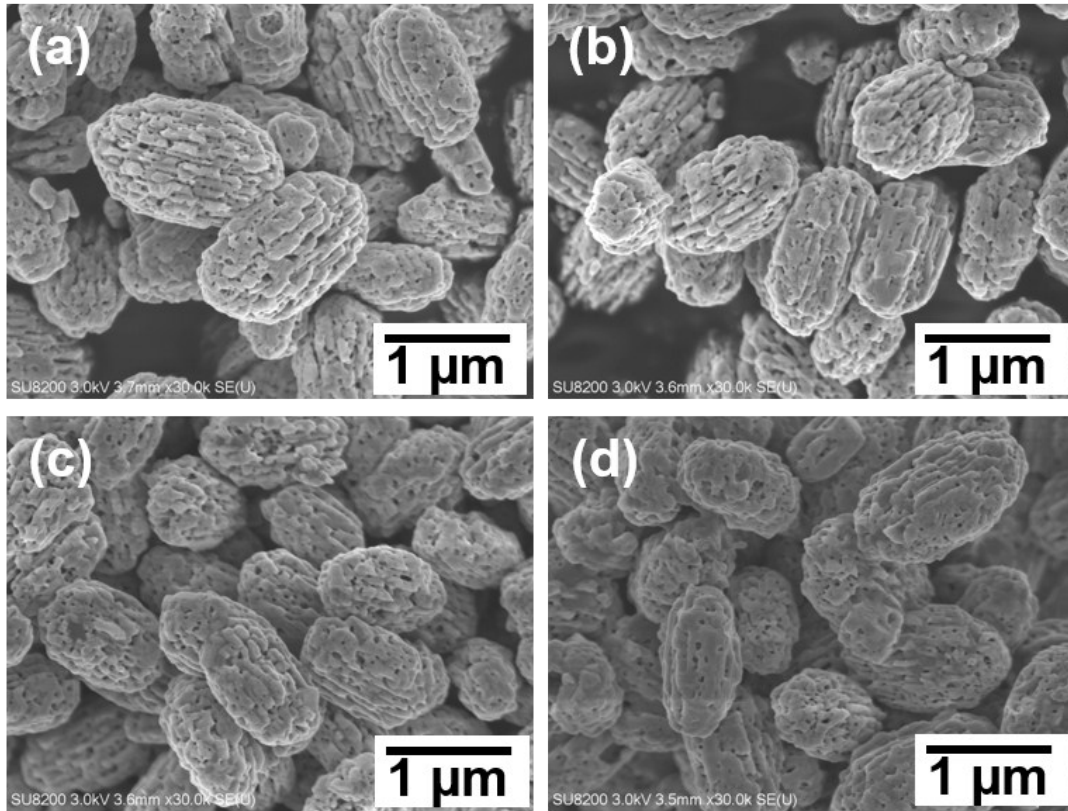


Fig. S4 SEM images of Ga_2O_3 with different degrees of Pr modification: (a) 0 mol%; (b) 1.0 mol%; (c) 5.0 mol%; and (d) 10.0 mol%.

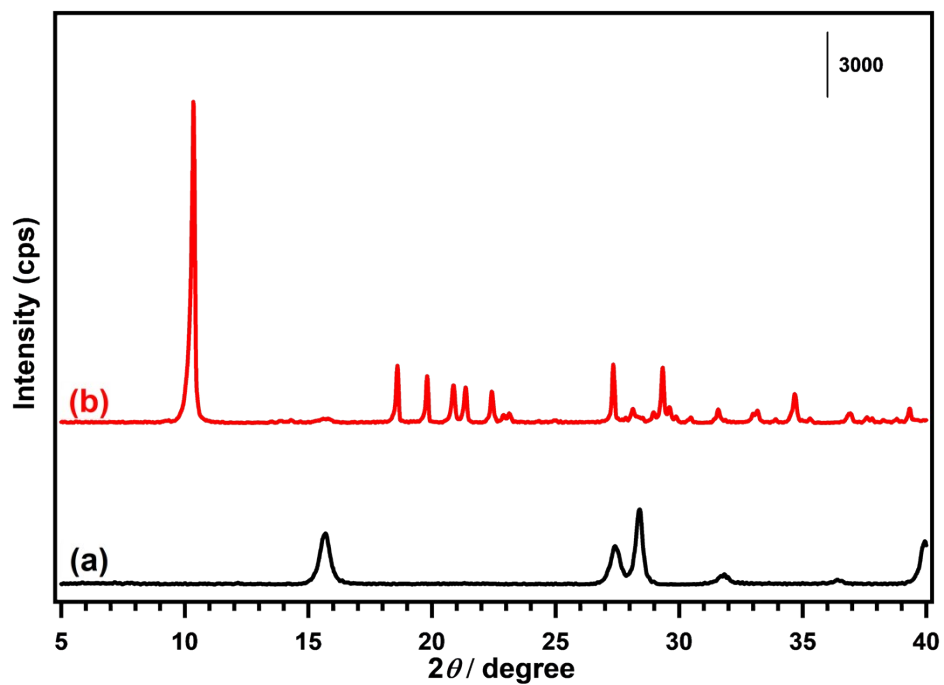


Fig. S5 XRD patterns of (a) as-prepared Pr(OH)_3 , (b) treated in 0.1 M NaHCO_3 with flowing CO_2 for 20 h.

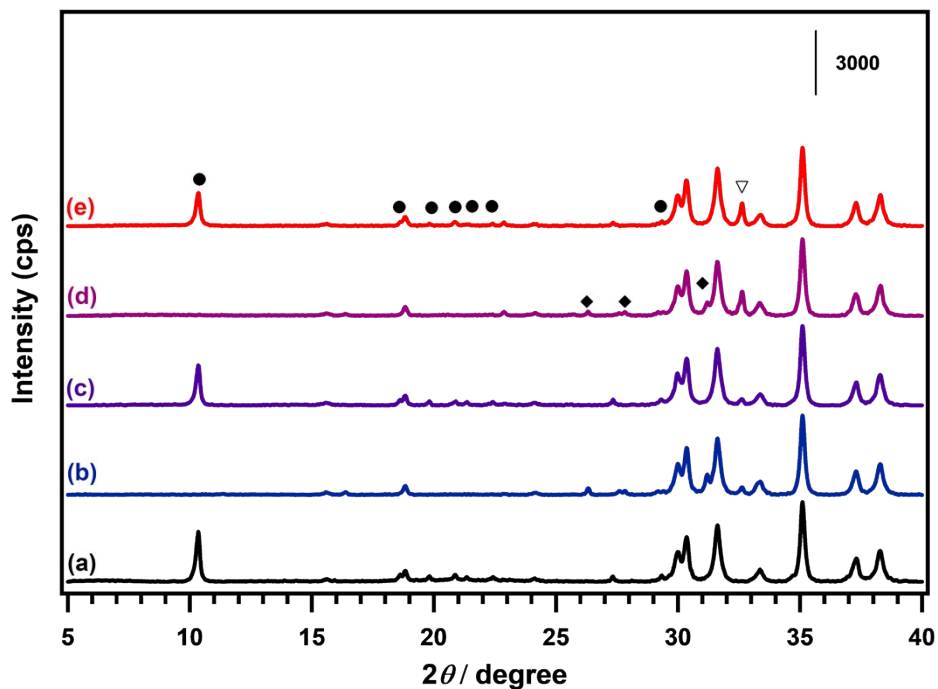


Fig. S6 XRD patterns of 3.0 Pr/Ga₂O₃ (a) after reaction, (b) after calcination of sample (a) at 1223 K for 1 h, (c) after treatment of sample (b) in an aqueous solution of NaHCO₃ under CO₂ flow for 5 h, (d) after calcination of sample (c) at 1223 K for 1 h, and (e) after treatment of sample (d) in an aqueous solution of under CO₂ flow for 5 h. Closed circle: Pr₂(CO₃)₃·8H₂O. Closed diamond: Pr-derived species. Open triangle: PrGaO₃.

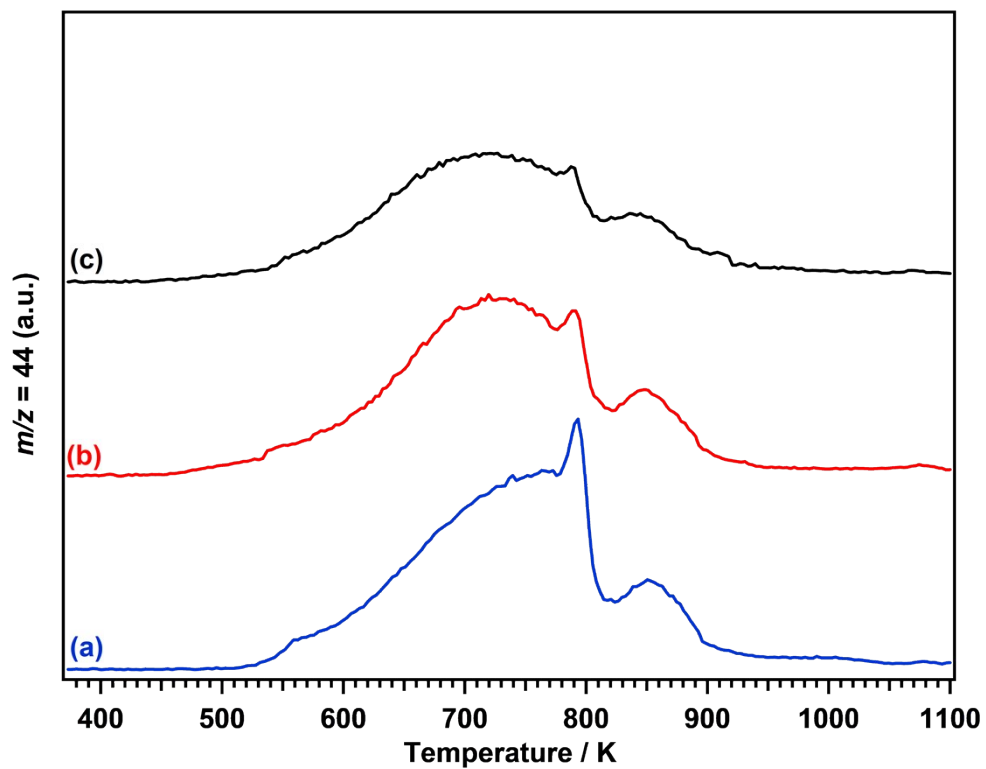


Fig. S7 CO₂-TPD profiles ($m/z = 44$) of 3.0 Pr/Ga₂O₃ (a) after reaction (the first run), (b) the second run, and (c) the third run after calcination at 1223 K for 1 h and treatment in an aqueous solution of NaHCO₃ under CO₂ flow.

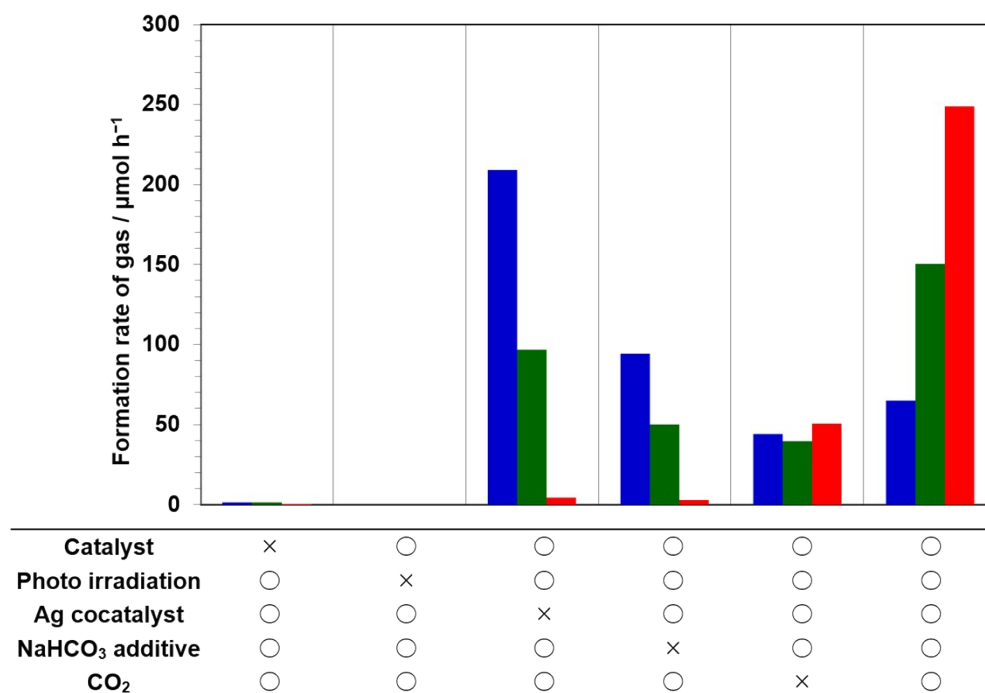


Fig. S8 Formation rates of H₂ (blue), O₂ (green), and CO (red) in the absence of each component in the photocatalytic conversion of CO₂ by H₂O over Ag/3.0 Pr/Ga₂O₃. Photocatalyst weight: 0.5 g, CO₂ flow: 30 mL min⁻¹, solution volume: 1.0 L, additive: 0.1 M NaHCO₃, light source: 400 W Hg lamp.

We performed blank tests for the photocatalytic conversion of CO₂ by H₂O over Ag/3.0 mol% Pr/Ga₂O₃ with the omission of one of five system components; the photocatalyst, photoirradiation, CO₂ flow, the Ag cocatalyst, and the NaHCO₃ additive, to confirm that these components are important for high CO evolution in our system (Figure S4). Tiny amounts of H₂ and O₂ are evolved without the photocatalyst. No product is obtained in the

absence of photoirradiation. Without the Ag cocatalyst, H₂ is evolved as the main product. It is known that the electrochemical reduction of CO₂ to CO occurs selectively on a Ag metal electrode in aqueous solution. Similarly, the metallic Ag particles on the 3.0 Pr/Ga₂O₃ function as active sites to capture the photoexcited electrons for the reduction of CO₂. Without NaHCO₃, mainly H₂ is evolved. The positive effects of various additives including NaHCO₃ have been reported in our recent work.¹ One function of NaHCO₃ is to increase the solubility of CO₂ in water. Here, NaHCO₃ does not accelerate the rate of H₂ formation but rather that of CO. In addition, the Pr species on the surface of Ga₂O₃ are not stable without NaHCO₃ (Figure 5(b)). Thus, the function of NaHCO₃ is also beneficial for maintaining the Pr species. Interestingly, the formation of CO was achieved at 50.4 μmol h⁻¹ with a selectivity of 53.3% toward CO, and this result is totally different to those of previously reported catalysts such as Zn/Ga₂O₃,² Sr₂KTa₅O₁₅,³ and ZnTa₂O₆.⁴ This can be explained as follows: NaHCO₃ can decompose to form CO₂ under flowing Ar, and the CO₂ is easily captured by Pr species on the surface of Ga₂O₃, which are then used for the formation of CO during photoirradiation. However, the other catalysts reported do not have a strong ability for CO₂ capture, thus they do not form CO without flowing CO₂.

References

1. K. Teramura, K. Hori, Y. Terao, Z. Huang, S. Iguchi, Z. Wang, H. Asakura, S. Hosokawa and T. Tanaka, *The Journal of Physical Chemistry C*, 2017, **121**, 8711-8721.

2. K. Teramura, Z. Wang, S. Hosokawa, Y. Sakata and T. Tanaka, *Chemistry-A European Journal*, 2014, **20**, 9906-9909.
3. Z. Huang, K. Teramura, S. Hosokawa and T. Tanaka, *Applied Catalysis B: Environmental*, 2016, **199**, 272-281.
4. S. Iguchi, K. Teramura, S. Hosokawa and T. Tanaka, *Catalysis Science & Technology*, 2016, **6**, 4978-4985.