Highly stable Pt single atoms on TiO_2 for efficient photocatalytic H_2 production

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Semiconductors have been widely used as photocatalysts and/or photoelectrodes for solar-driven water splitting. In the context of solar-driven H_2 production, effective utilization of many semiconductors typically requires co-catalyst functionalization. While noble metal nanoparticles have traditionally served as co-catalysts, a more promising approach involves the use of noble metal single atoms (SAs). This strategy has the potential to achieve maximum atom utilization efficiency and exceptional catalytic performance due to the spatial atomic isolation, distinct electronic structures, and unsaturated coordination centers.[1-3] However, achieving the stabilization of isolated atoms on semiconductors for practical applications remains a considerable challenge, mainly due to the insufficient trapping sites available on unmodified semiconductor surfaces.

Recently, we developed a fluorine stabilization strategy for the synthesis of Pt SAs on fluoride-modified TiO_2, a method applicable to TiO_2 with different morphologies.[4] The modulation of fluorine speciation on TiO_2 has emerged as a critical factor for achieving uniform and stable dispersion of Pt SAs, resulting in high efficiency of Pt SA co-catalyzed photocatalytic H_2 production. Remarkably, maximum photocatalytic activity is achieved with fluorine-stabilized Pt SAs on TiO_2 catalysts even at low Pt SA loading levels, surpassing the performance of Pt nanoparticles on TiO_2 despite equivalent or higher loading levels. Pt SAs on TiO_2 exhibit superior photocatalytic activity and photocurrent compared to conventional Pt nanoparticles on TiO_2. Furthermore, Pt SAs on TiO_2 exhibit exceptional photocatalytic stability during prolonged photocatalytic reactions. This study provides an effective approach to exploit the interaction of stable fluorine in TiO_2 to design stable and active single atom catalysts on semiconductors for applications in photocatalysis and photoelectrocatalysis.

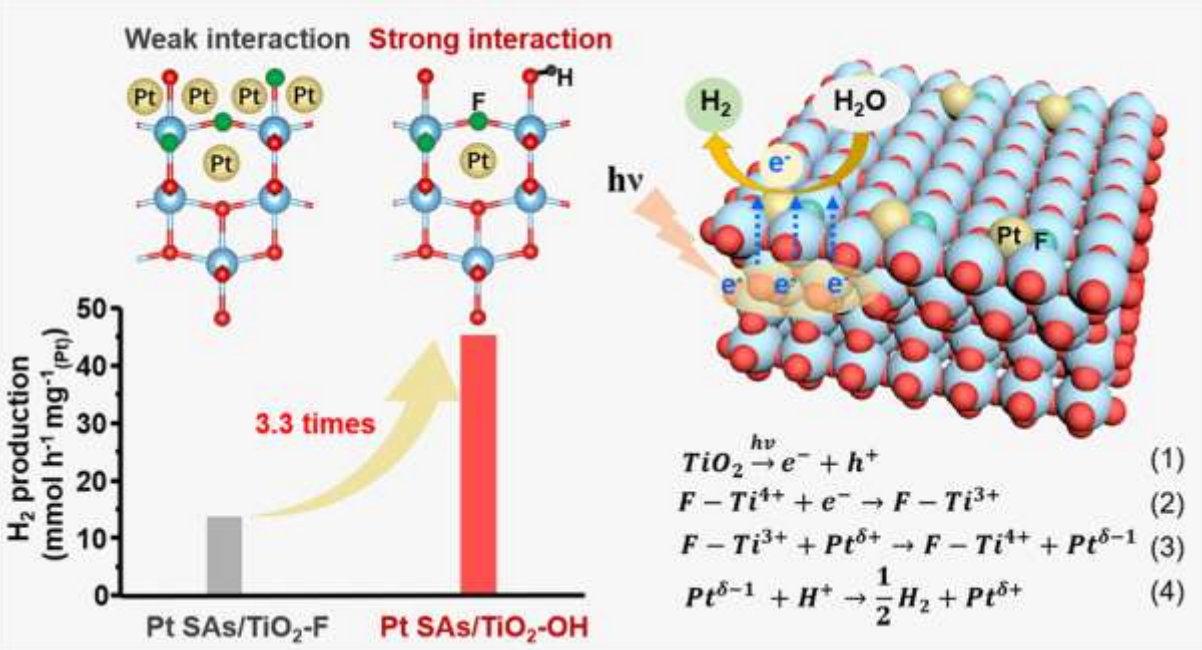

Figure 1. Schematic illustration of the fluorine-aided stabilization of Pt SAs and corresponding photocatalytic H_2 production performance and photocatalytic mechanism.

References

1. Y. Wang, S. Qin, N. Denisov, H. Kim, Z. Bad'ura, B. B. Sarma, P. Schmuki, *Adv. Mater.* **35** (2023) 2211814. https://doi.org/10.1002/adma.202211814
2. N. Denisov, S. Qin, J. Will, B. N. Vasiljevic, N. V. Skorodumova, I. A. Pašti, B. B. Sarma, B. Osuagwu, T. Yokosawa, J. Voss, J. Wirth, E. Spiecker, P. Schmuki, *Adv. Mater.* **35** (2023) 2206569. https://doi.org/10.1002/adma.202206569
3. S. Hejazi, S. Mohajernia, B. Osuagwu, G. Zoppellaro, P. Andryskova, O. Tomanec, S. Kment, R. Zbořil, P. Schmuki, *Adv. Mater.* **32** (2020) 1908505. https://doi.org/10.1002/adma.201908505.
4. S.-M. Wu, I. Hwang, B. Osuagwu, J. Will, Z. Wu, B. B. Sarma, F.-F. Pu, L.-Y. Wang, Z. Badura, G. Zoppellaro, E. Spiecker, P. Schmuki, *ACS Catal.* **13** (2023) 33. https://pubs.acs.org/doi/10.1021/acscatal.2c04481