

Photocatalytic hydrogen production from alkanes

Collections of Pt monomers (close to each other but not directly bonded) supported on black TiO₂ exhibit superior photocatalytic performance in the nonoxidative dehydrogenation of alkanes than that of single-atom catalysts. The extent of clustering of Pt species has a decisive role in determining the reaction activity and product selectivity.

This is a summary of:

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The problem

Extracting hydrogen fuel from abundant, inexpensive alkane feedstock (such as methane and short-chain and cyclic alkanes) while converting the remaining carbon into value-added hydrocarbons has great implications for the supply of clean energy and synthetic chemistry¹. However, the stable and inert *sp*³ C–H bonds in alkanes mean that such dehydrogenation transformations are usually energy-intensive, accompanied by the release of large amounts of CO₂, and suffer from poor product selectivity and rapid catalyst deactivation². Progress over the past four decades has demonstrated that the introduction of light as a ‘green reagent’ can overcome the limitations of thermodynamic equilibrium, enabling catalytic alkane conversion under ambient conditions^{3–5}. Despite the potential, photocatalytic alkane conversion presents two pressing issues. First, most photocatalysts are inefficient and cannot operate under pure visible-light irradiation, and, second, the structure–activity relationships of the active sites need further clarification.

The solution

We approached these problems by tailoring the support and carefully controlling the arrangement of the active sites. Black TiO₂ was chosen as the support to enable the photocatalysts to maximize sunlight harvesting (>90% of solar energy). Because alkane dehydrogenation is a structure-sensitive reaction, we loaded Pt species onto black TiO₂ and finely tuned their arrangement in the subnanometre regime – from isolated single atoms to clusters, and then to nanoparticles. Among various supported Pt species, collections of Pt consisting of a few isolated Pt monomers (PtClO₃) exhibited the highest photocatalytic performance for nonoxidative dehydrogenation of cyclic alkanes, methane and short-chain alkanes under visible light irradiation at room temperature. The quantum efficiency of cyclohexane dehydrogenation exceeded 21%, and the catalyst maintained high activity for 80 cycles, with the turnover number for H₂ production exceeding 100,000 (Fig. 1). By contrast, Pt single atoms were almost inactive. Impressively, for methane conversion, the main product was propane (~65% selectivity), which is distinct from most photocatalytic methane conversion reactions, which produce ethane.

We found that the unique collections of Pt monomers only form on the surface of black TiO₂ after oxidation treatment (BT-O). Extended X-ray absorption fine

structure analysis revealed that each Pt monomer is bonded to three O ions and to one Cl ion and that no Pt–Pt bonds form. Temperature-programmed desorption measurements suggest that the distance between the Pt monomers in the collections is much smaller than that between fully isolated single-atom Pt catalysts, enabling the Pt monomers in the collection to work cooperatively to catalyse the efficient dehydrogenation of alkanes. By contrast, single-atom catalysts cannot offer the metal proximity necessary for this reaction. Our experimental and theoretical studies indicate that the Pt–Cl coordination increases the interfacial charge transfer between the substrate and Pt and lowers the energy threshold down to the near-infrared light range. Moreover, the high propane selectivity in methane conversion was found to be closely related to the size of the Pt collections.

The implications

Liquid organic hydrogen carriers are high-density and easy-to-apply systems for hydrogen storage and transport, but are currently limited by the sluggish dehydrogenation process and high operating temperature. The photocatalytic cycloalkane dehydrogenation at room temperature demonstrated by our Pt@BT-O photocatalysts represents the state of the art, comparable to the best thermal catalysts. Moreover, we propose that methyl carbene is the intermediate for methane dehydrogenation and, thus, could offer intriguing and versatile opportunities for further functionalization of methane through various well-established carbene-type reactions.

It should be noted that our photocatalytic alkane conversion is currently carried out in a batch-type reactor at the laboratory scale. How to integrate this process into flow photocatalytic systems, coupling with online hydrogen separation technologies (such as pressure swing adsorption or membrane separation), is the key to advancing the practicality of this technology, but remains a great challenge.

To extend this work, we are looking for efficient photocatalysts based on cheap metals. Furthermore, we will extend the substrates to various non-toxic saturated hydrocarbons. We are also trying to uncover the key factors in the formation of carbene intermediates with the help of theoretical calculations, to enable the regulation of the reaction path of these intermediates.

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EXPERT OPINION

"Solar energy must be used to reduce the huge energy consumption of chemical processes. Here, a specially designed photocatalyst consisting of titanium dioxide and platinum successfully realized the dehydrogenation of chemically inert alkanes to more useful alkenes with

hydrogen formation by using visible light energy under ambient conditions. This fundamental discovery in the photocatalysis field could contribute to the development of our sustainable society." **Hisao Yoshida, Kyoto University, Kyoto, Japan.**

FIGURE

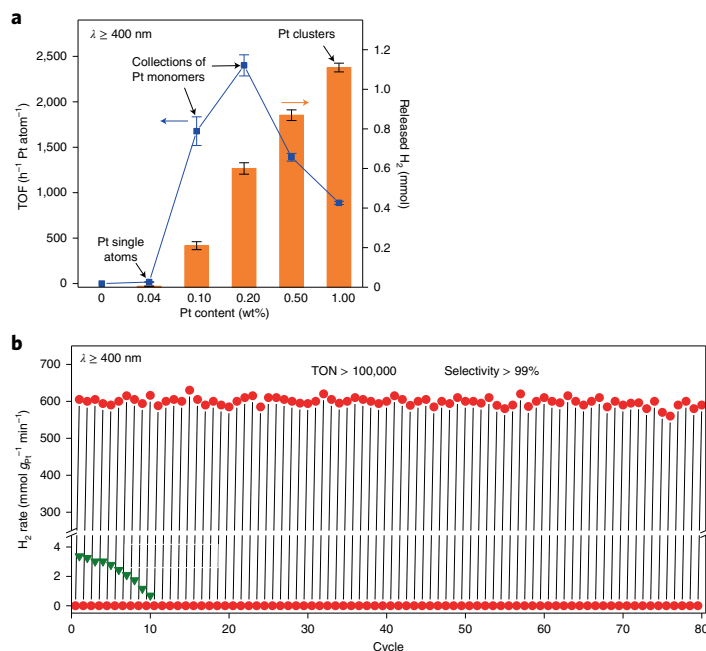


Fig. 1 | Visible-light-driven cyclohexane dehydrogenation at room temperature. a, Comparison of the turnover frequency (TOF) and amount of released H_2 by using Pt@BT-O photocatalysts with different Pt loadings under visible light irradiation ($\geq 400 \text{ nm}$). b, Cycling tests over 0.2Pt@BT-O (0.2 wt% Pt, corresponding to collections of Pt monomers) and 1.0Pt $^{\circ}$ _{NPS}@TiO $_2$ (1.0 wt% Pt, corresponding to Pt nanoparticles, a previously reported cyclohexane dehydrogenation photocatalyst). The error bars in a represent the standard deviation of measurements of three different batches of sample. All data in a are presented as mean values \pm the standard deviation. λ , wavelength; TON, turnover number. © 2022, Zhang, L. et al.

BEHIND THE PAPER

Since it was established in 2018, our research group has been working on developing light-driven approaches to activate inert C–H bonds under mild conditions. Initially, we tried to replace the white TiO $_2$ support used in my previous work with black TiO $_2$ to enhance the light-absorption capacity of the catalyst. However, the performance of black TiO $_2$ -supported Pt was even worse than that of white TiO $_2$ -supported Pt, and this

problem plagued us for some time. After a vacation, we found that when we deposited Pt on old black TiO $_2$ that had been exposed to air for about a month, the photocatalytic performance was dramatically improved. This phenomenon inspired us to deeply study the interaction between the various active groups of the black TiO $_2$ surface and the supported Pt species, and after 3 years of research, the initial progress made is reported in this study. **L.L.**

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A review article that presents the latest progress, challenges and potential solutions for photocatalytic methane conversion.

FROM THE EDITOR

"Catalysts with highly-dispersed metal atoms at the surface have been a target in recent years as they promise more efficient usage of precious metals. This paper is eye-catching as it suggests that, in this case, catalytic function is not only influenced by high atomic dispersion, but also how the isolated active atoms are arranged at greater length scales" **James Gallagher, Senior Editor, Nature Energy.**