Chemists discover fundamental catalyst protonation process to promote solar-driven water splitting

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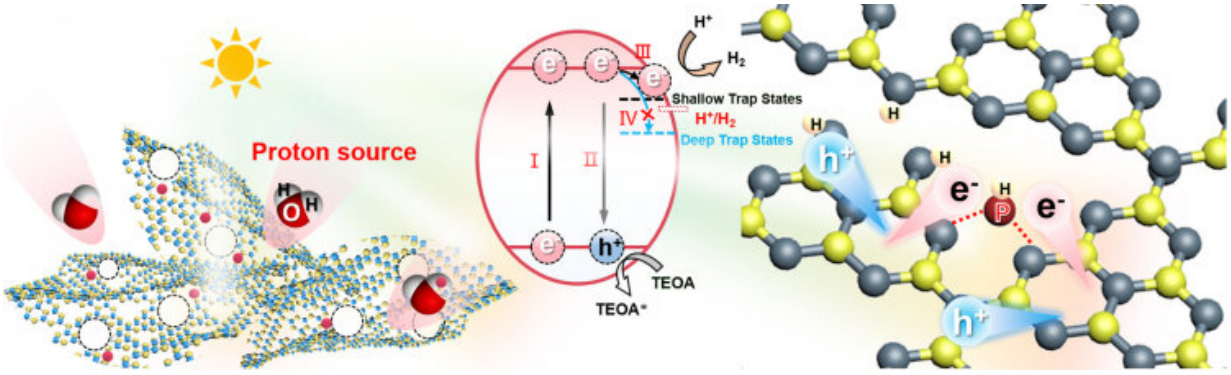

Chemists at HKU discover a fundamental catalyst protonation process to enhance productivity of solar-driven water-splitting for hydrogen by eight times, catalysing green energy without CO2 emissions. Credit: The University of Hong Kong

Hydrogen is a promising green energy carrier for a sustainable future. However, it is mostly locked in water. Energy is required to liberate it from water for practical use. Solar energy is abundantly renewable and ideal for direct water-splitting to generate hydrogen using a "photocatalyst." However, despite considerable effort, practical adoption has been slow due to relatively low efficiency and the high cost of the catalyst.

A research team led by Professor Zheng-Xiao Guo and Professor David Lee Phillips from the HKU-CAS Joint Laboratory on New Materials and the Department of Chemistry of The University of Hong Kong (HKU), has reported the discovery of an important in-situ protonation process that improves the photodynamics and separation of charge carriers in a photocatalyst, leading to efficient hydrogen generation from water using visible solar light.

The process is enabled in an interstitial phosphorus-doped carbon nitride structure, with only earth-abundant non-metallic elements, for its cost-effectiveness and high potential for practical applications. The research findings are recently published online in *Energy & Environmental Science*.

Extensive research efforts have been devoted to the development of photocatalysts for solar-driven energy conversion with improved activity, efficiency and durability, mostly via charge separation, transfer and utilization. However, the complex multi-electron transfer, proton coupling and intermediate dynamics can all influence the photocatalytic pathway, kinetics and efficiency, which have not been well understood.

It is thus highly desirable to foster in-depth investigations integrating innovative synthesis design, microscopic and spectroscopic characterizations and atomic simulations at the molecular level.

Appreciating the current efforts and the challenges in photocatalysis, the HKU team examined the fundamental issues from a different angle and proposed a new fundamental process of a proton-mediated photocatalytic mechanism to enhance the photo-dynamics, charge separation and hence the overall efficiency of an interstitial phosphorus-doped carbon-nitride, g-C_3N_4.

The in-situ proton-mediated mechanism points to a new role for the

water molecule, not just as a solvent or reactant but as an effective band-structure modifier of the catalyst in the overall design of effective photocatalytic processes.

In essence, the team has developed an effective atomic heterojunction by porosity-stabilized interstitial P-doping and in-situ protonation to induce shallow trap states, which effectively enhance the lifetime of the excited states and also restrain undesirable deep charge trapping, leading to efficient water decomposition.

For the first time, the team has identified that the in-situ protonation of an interstitially anchored phosphorus in a holey g-$C_{3-x}N_4$ is a very effective structural configuration of the catalyst for highly efficient and stable visible-light hydrogen generation.

"We expect that our discovery will open up a new line of thinking in the future design of photocatalysts for effective solar energy utilization, by paying more attention to operando structural dynamism as a viable handle to pump up the conversion efficiency," said Professor Zheng-Xiao Guo.

"Spectroscopic investigations show a colorful world of nanomaterials, and it will cast more light on the mechanistic insights of science and technologies," echoed Professor David Lee Phillips.

More information: Wenchao Wang et al, In-Situ Protonated-Phosphorus Interstitial Doping Induces Long-Lived Shallow Charge Trapping in Porous C3-xN4 Photocatalyst for Highly Efficient H2 Generation, *Energy & Environmental Science* (2022). DOI: 10.1039/D2EE02680E

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