PHOTOCATALYSIS

Small but strong

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Credit: Wiley

Metal nanoclusters (NCs) with precise atomic composition feature very interesting optical properties and can be regarded as small band-gap semiconductors. However, their application in the area of photocatalysis has not yet received much attention. Now, Yu Wang, Qing-Yun Chen, Nicola Pinna and colleagues introduce a composite material based on titania-supported silver nanoclusters that behaves as a type-II heterojunction and shows high activity for the photocatalytic evolution of hydrogen under UV-vis light.

The composite is obtained by depositing atomically precise silver NCs — that is, Ag₄₄(SR)₃₀ where SR represents thiolate ligands — onto TiO₂ nanoparticles (NPs). Through a combination of UV-vis and transient spectroscopy analyses, the authors obtain information on the energy level diagram of the composite (pictured, panel a). The formation of the heterojunction results in the surface band bending of TiO₂. Moreover, unlike TiO₂, small silver clusters are capable of absorbing visible light, broadening the absorption properties of the composite. The cluster can therefore function as a photosensitizer. In fact, under visible light irradiation, hydrogen evolution from a methanol/water solution can be observed. In this case, the reactivity is attributed to photoinduced electrons excited from the HOMO to the LUMO+1 of the cluster

and further injected to TiO₂ — the latter has a conduction band with lower energy and can thus attract the electrons. The situation, however, changes under UV-vis irradiation as both the cluster and the semiconductor are excited and the system behaves as a type-II heterojunction. Accordingly, holes formed on TiO₂ are transferred to the HOMO of the cluster, while electrons are transferred from the cluster to the TiO₂ conduction band. This improved charge-carrier separation boosts the photocatalytic activity of the composite, which features a three-order-of-magnitude increase in the production of hydrogen when moving from visible light to simulated sunlight irradiation.

The use of Ag clusters with precise composition (panel b, 1-TiO₂) proves crucial for the activity of the composite, as shown by control experiments using regular supported silver nanoparticles (Ag NP-TiO₂) or bare TiO₂ NPs. Moreover, recycling experiments confirmed that the catalyst largely retains its activity over multiple reaction cycles (panel c). These findings showcase the potential of NCs with precise composition in the preparation of tunable heterogeneous photocatalysts.

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