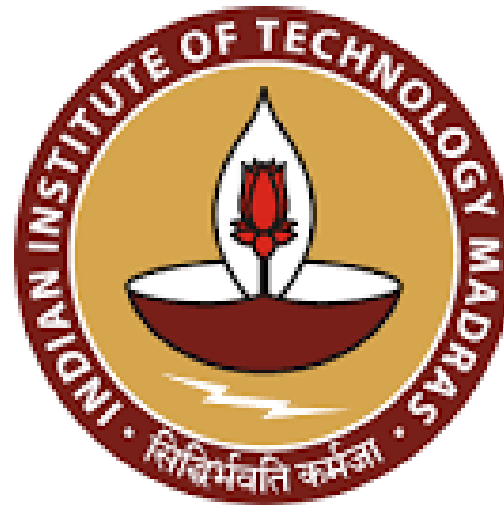


Paper Presentation



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Embedding Ultrasmall Au Clusters into the Pores of a Covalent Organic Framework for Enhanced Photostability and Photocatalytic Performance

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Abstract: Gold clusters loaded on various supports have been widely used in the fields of energy and biology. However, the poor photostability of Au clusters on support interfaces under prolonged illumination usually results in loss of catalytic performance. Covalent organic frameworks (COFs) with periodic and ultrasmall pore structures are ideal supports for dispersing and stabilizing Au clusters, although it is difficult to encapsulate Au clusters in the ultrasmall pores. In this study, a two-dimensional (2D) COF modified with thiol chains in its pores was prepared. With $-SH$ groups as nucleation sites, Au nanoclusters (NCs) could grow in situ within the COF. The ultrasmall pores of the COF and the strong $S-Au$ binding energy combine to improve the dispersibility of Au NCs under prolonged light illumination. Interestingly, $Au-S-COF$ bridging as observed in this artificial Z-scheme photocatalytic system is deemed to be an ideal means to increase charge-separation efficiency.

stability and thus a tendency to aggregate and loss of catalytic performance.^[5]

Loading of nanomaterials on high-surface-area supports to give heterogeneous catalysts is a feasible strategy to improve stability and catalytic performance.^[6] In recent years, as promising metal supports, covalent organic frameworks (COFs) have attracted much attention and been continually developed.^[7] As compared with some traditional supports (g- C_3N_4 , metal oxide, etc.), the highly ordered structure and ultrasmall pores of COFs can not only limit the growth of NCs but also enable uniform dispersion of NCs on COF supports.^[8] Through a simple post-treatment process, Wang and co-workers prepared a palladium(II)-containing COF showing excellent catalytic performance for the Suzuki–Miyaura coupling reaction.^[9] Zhang and co-workers embedded Pd NPs and Pt NPs inside the pores of a COF with a size distribution of (1.7 ± 0.2) nm, which exhibited enhanced

Why this paper ?

- The first report on utilising Au clusters supported with covalent organic framework to enhance the photostability and photocatalytic performance
- Application of this novel strategy in the purification of flowing waste water.

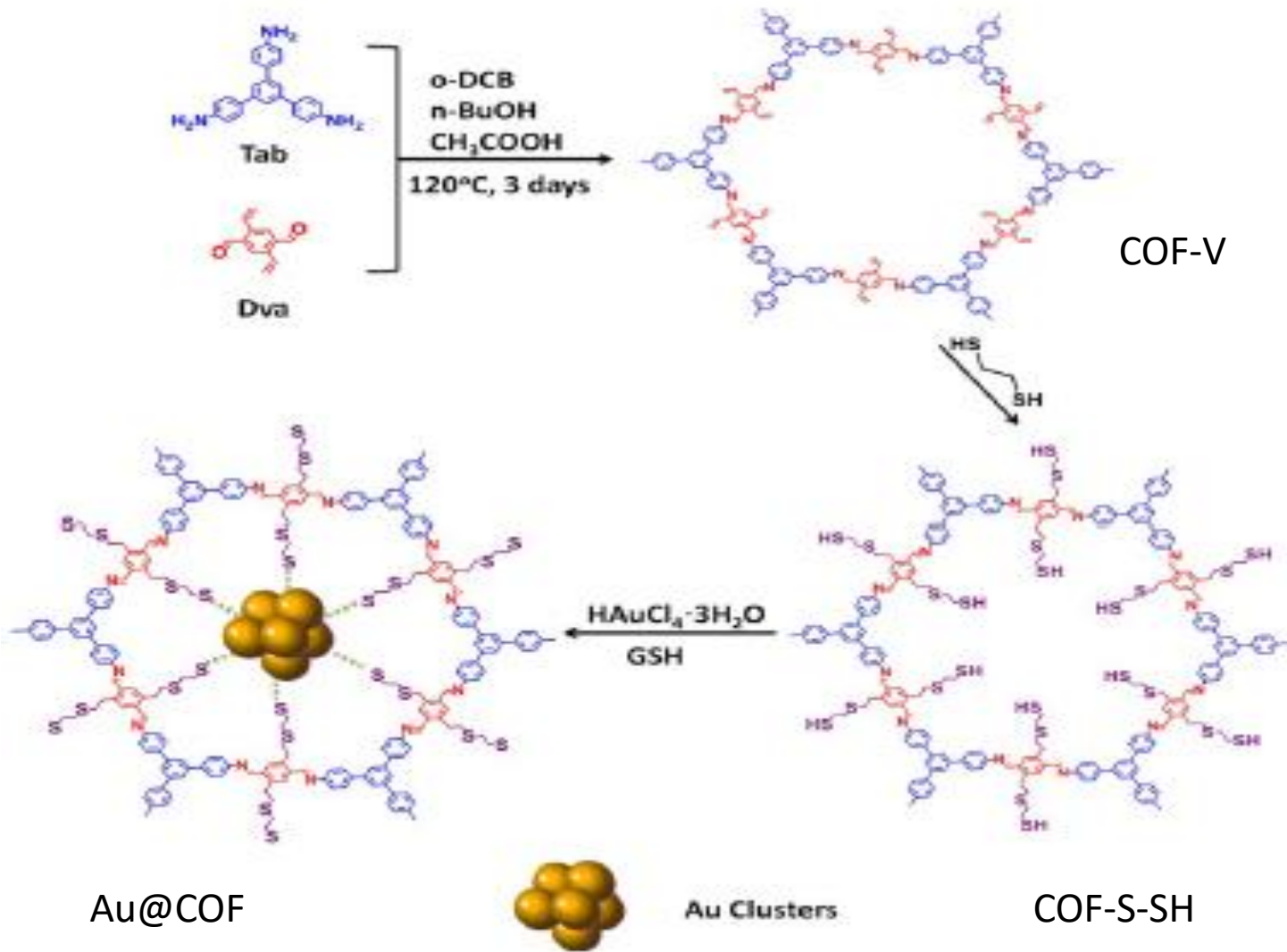
Introduction

- Controllable adjustment of catalytic performance in metal nanoparticles and nanoclusters is a significant goal
- The surface free energy will be enhanced when their size is minimized, which further causes poor stability and catalytic performance
- Nanomaterials on high-surface-area supports to give heterogeneous catalysts is a feasible strategy to improve stability and catalytic performance
- Some traditional supports are C_3N_4 , metal oxide, etc.
- Covalent organic frameworks (COFs) have attracted much attention
- The highly ordered structure and ultra small pores of COFs , limit the growth of NCs and enable uniform dispersion of NCs on COF supports

Introduction

- Au Nanoparticles is a prototype with adjustable size, and excellent catalytic performance
- Au NCs can be aggregated more readily than various other NCs and NPs for higher surface energy
- Traditional strategy of loading Au NCs on a metal oxides has difficulty to maintain the stability of the composite under in situ photo irradiation conditions
- In this paper, a covalent organic framework postmodified with thiol chains, COF-S-SH, was selected as the support for Au NCs
- Ultrasmall pores (2.8 nm) of this COF limit the growth of Au NCs
- Thiol chains were chosen to build a bridge between COF and Au NCs
- Formation of Au–S–COF bonding bridges, increases the charge-separation efficiency

Synthesis



Morphology

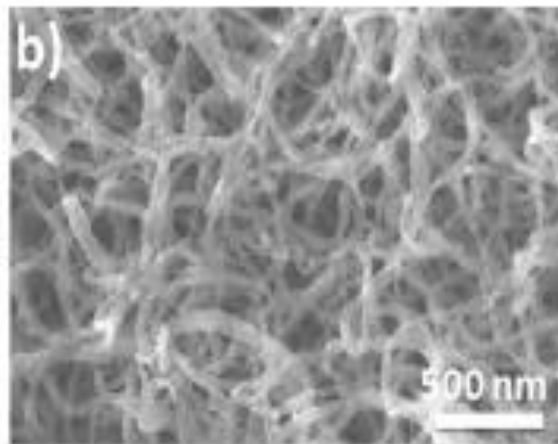
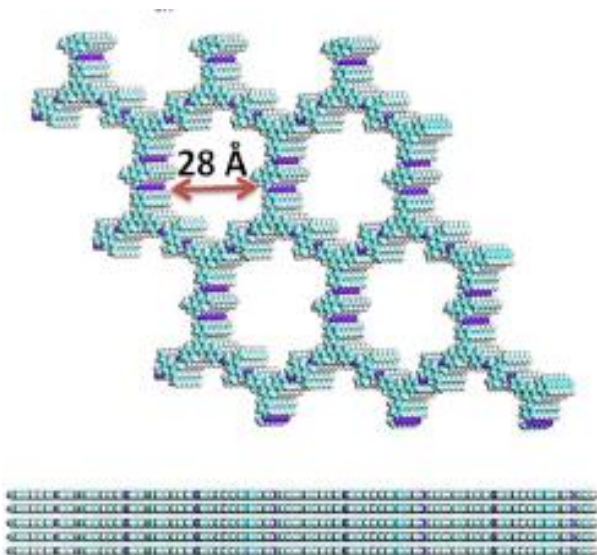


Fig 1: SEM image of COF-V

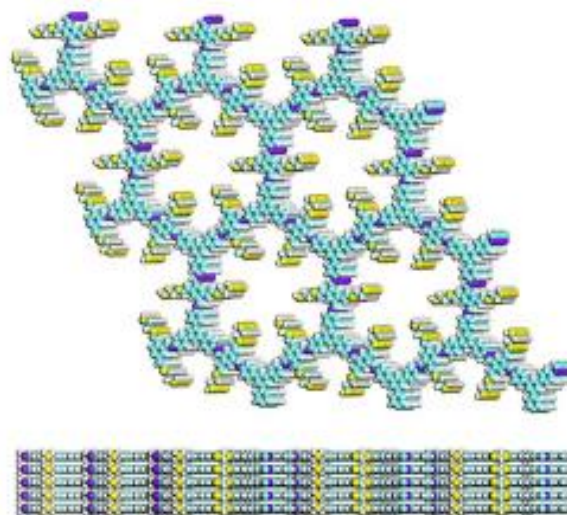
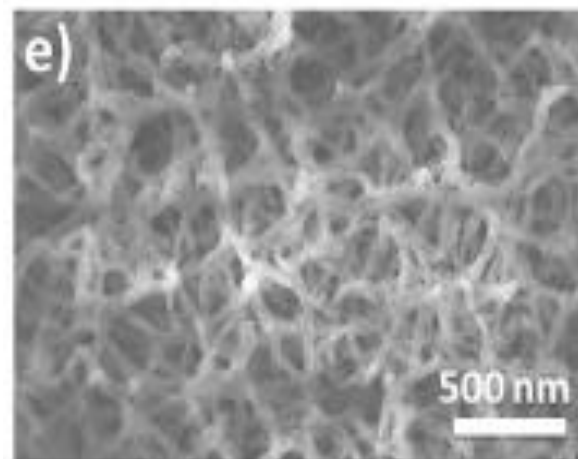


Fig 2: SEM image of COF-S-SH



Morphology

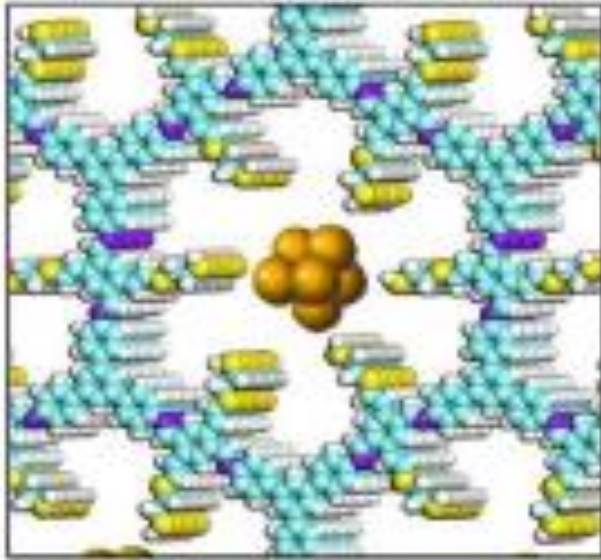


Fig 3: Structure of Au@COF.

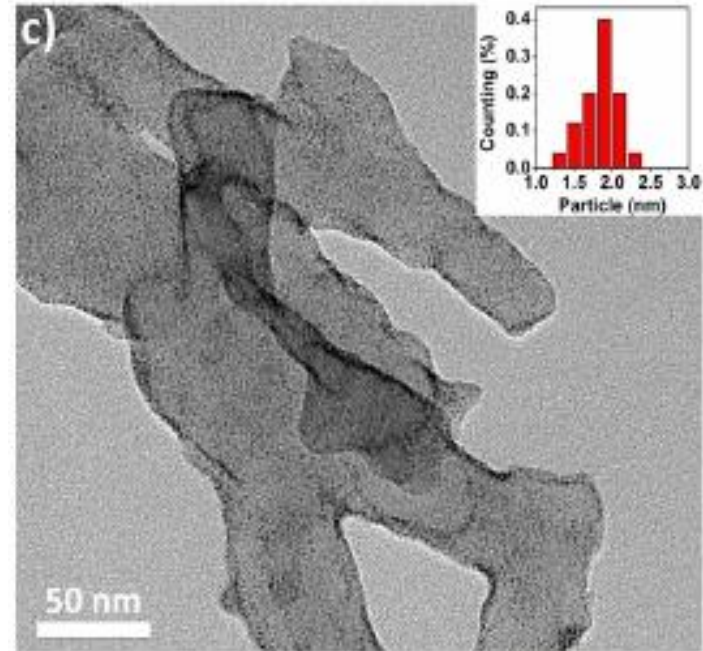


Fig 4: TEM image of Au@COF.

- The ultra small Au NCs were uniformly distributed on COF support
- The Au NCs possessed an average diameter of (1.8 ± 0.2) nm

Photostability

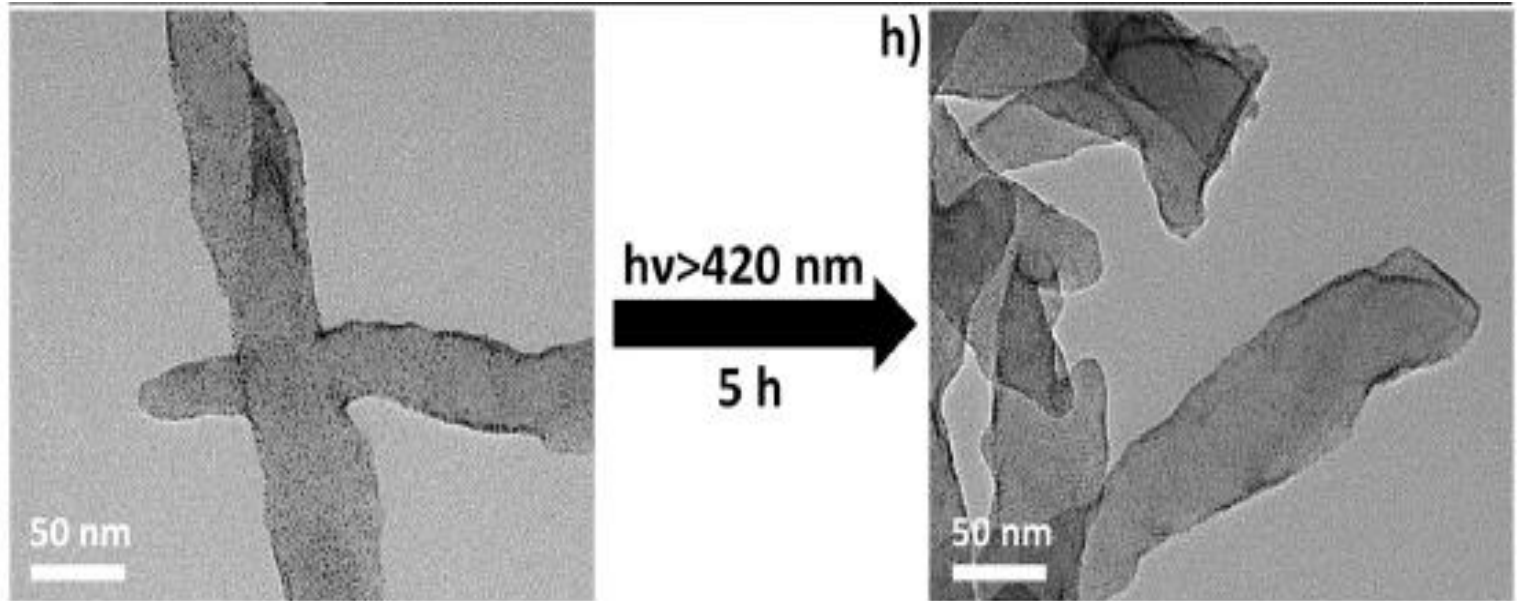


Fig 5: TEM images of Au@COF before irradiation and after irradiation with a 300W Xe arc lamp for 5 h

- Au NCs supported on COF-S-SH maintained ultrafine and high dispersion after continuous light irradiation
- The result suggests that the ultra small pore structure of the COF and the strong S–Au binding energy provide extra stability of Au NCs under light

Photo-catalytic studies

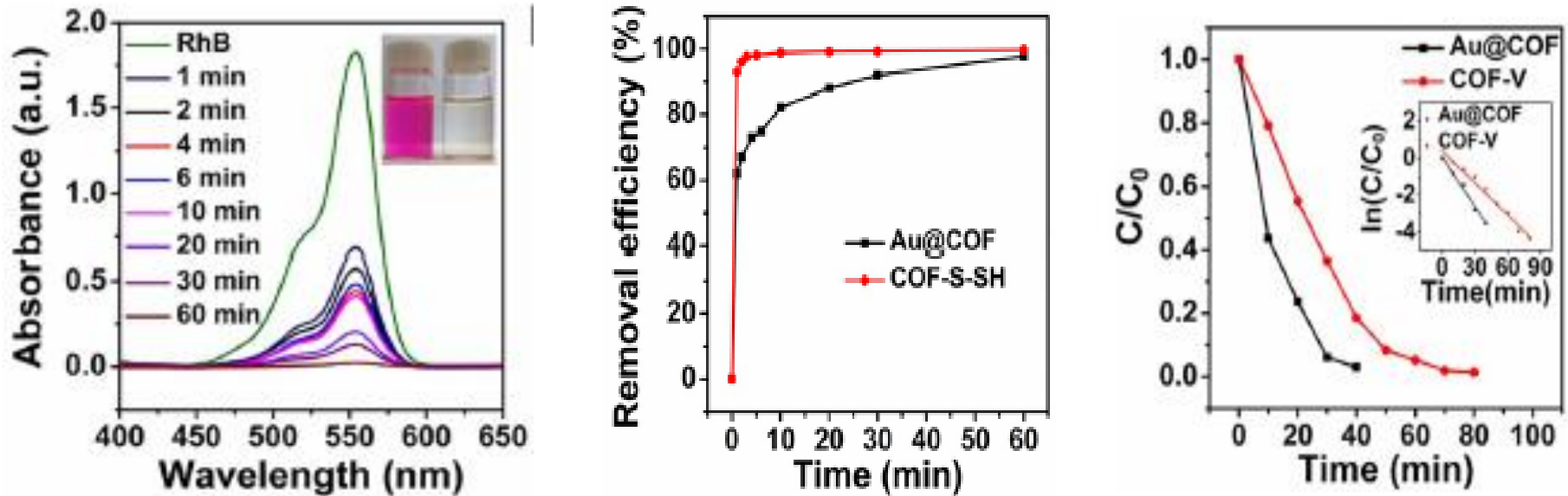


Fig 6: a) UV/Vis spectra of RhB at different times after the addition of Au@COF b) Efficiency of the removal of RhB over Au@COF and COF-V c) Efficiency of the degradation of RhB over COF-V and Au@COF.

- RhB dye used as a model to evaluate the controllable photocatalytic performance of Au@COF
- This was mainly attributed to blocking of the porous structure of COF by Au NCs

Photo-catalytic studies

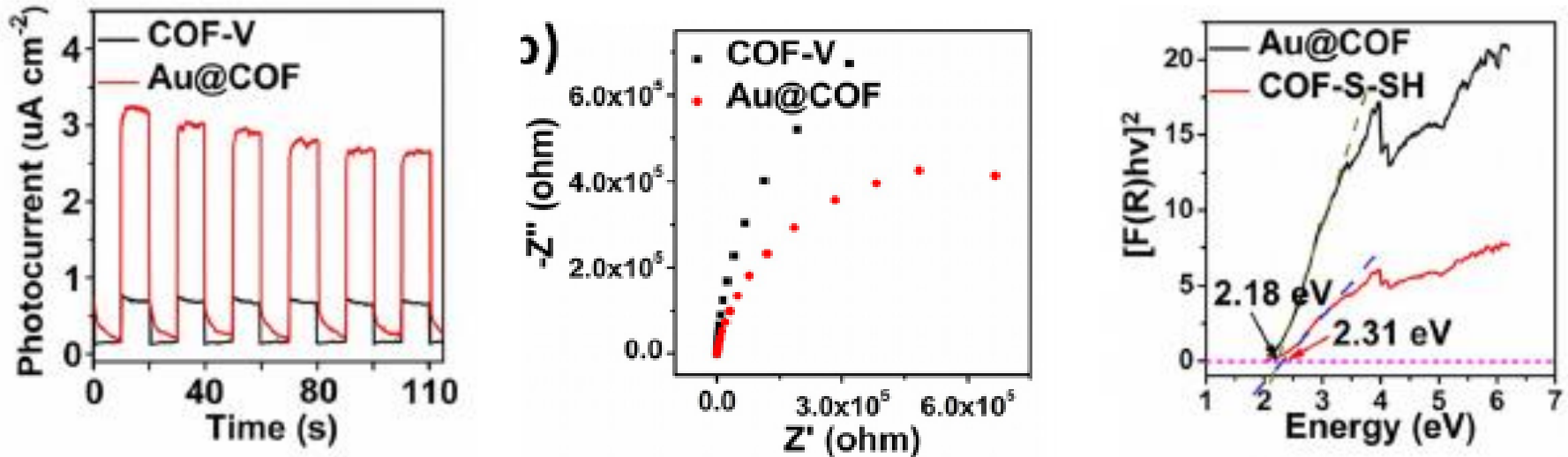


Fig 7: a) Transient photocurrent densities of COF-V and Au@COF under irradiation with light b) EIS Nyquist plots of COF-V and Au@COF. c) Time-resolved photoluminescence emission decay spectra of COF-V and Au@COF.

- The dispersed Au NCs on the COF support successfully promote the generation of more photoexcited charges
- Indicates the higher photogenerated carrier separation efficiency

Mechanism

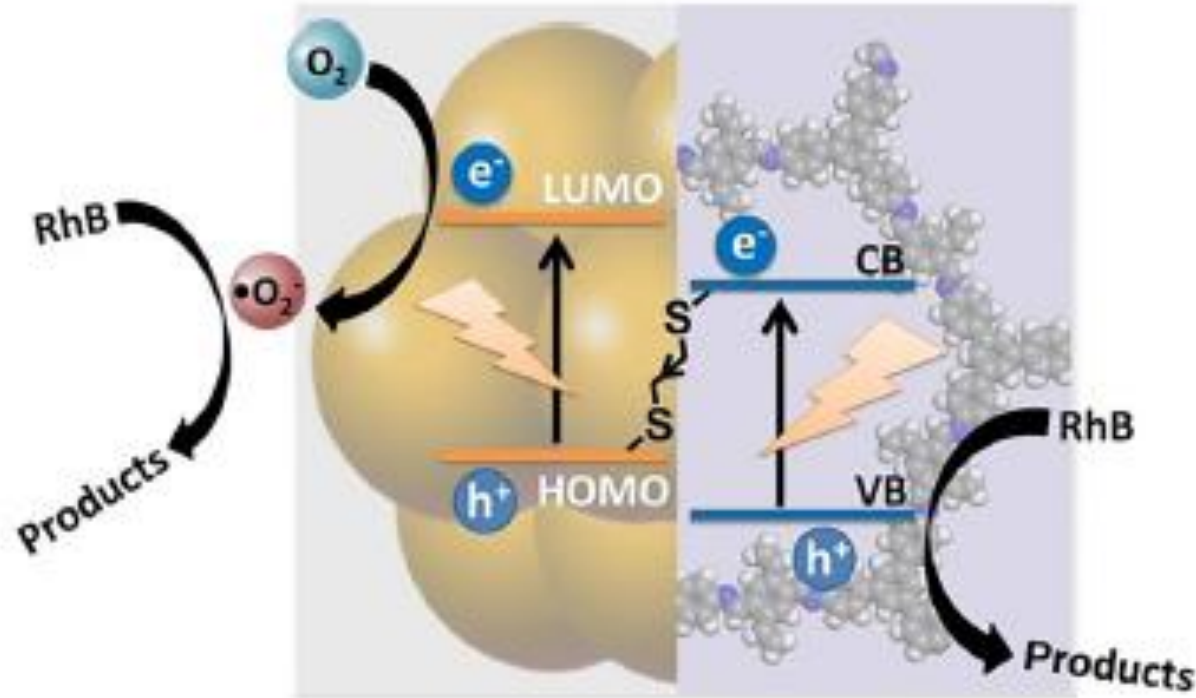


Fig 8: Principles of photogenerated electron transport between Au NCs and the COF support (electron @ in LUMO and h^+ in HOMO represent a photogenerated electron and hole of Au NCs, respectively; electron @ in CB and h^+ in VB represent a photogenerated electron and hole of COF-V, respectively).

Applications

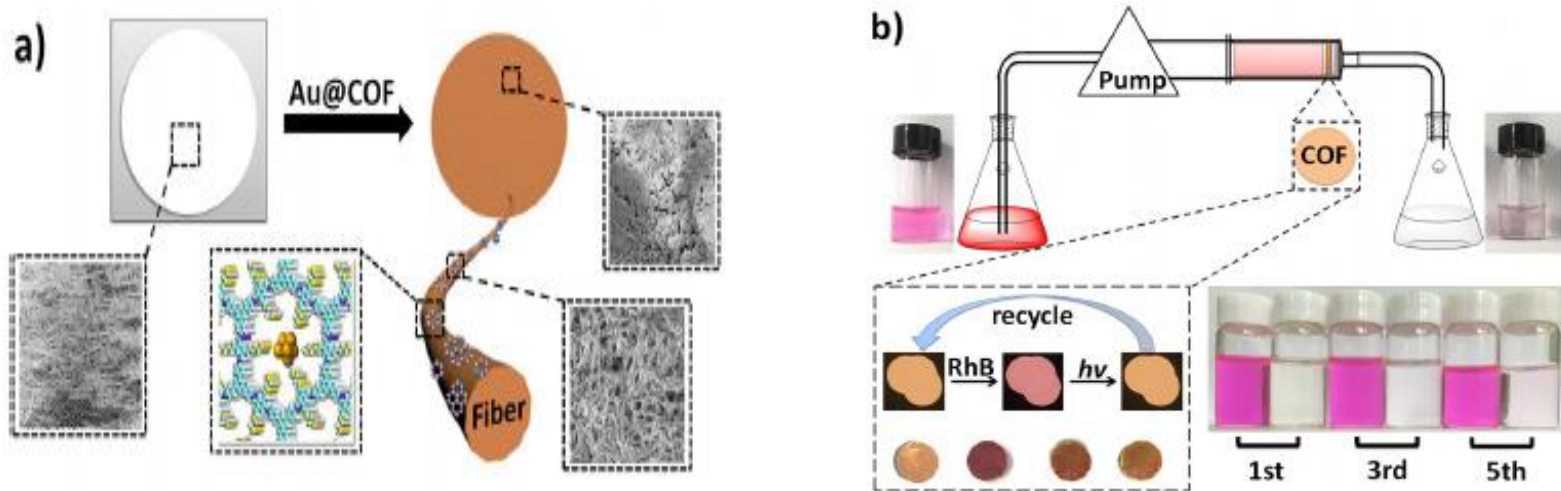


Fig 9: Diagrams of a) the filter paper model and b) the filter device.

- Au@COF shows efficient adsorption and degradation abilities, and could be industrially valuable for the purification of flowing waste water.
- The device functioned well at room temperature.
- The color of filter paper changed from red to yellow after irradiation for 30 min

Applications

- Bisphenol (BPA), a typical endocrine disruptive compound (EDC), is extremely harmful to the normal function of the liver and kidney
- They investigated the ability of Au@-COF to degrade BPA in water.
- Almost 98.44% of BPA was captured in the dark after 30 min.
- The high degradation efficiency of BPA over Au@COF was retained after 5 cycles

Conclusion

- A facile strategy to form bridges between ultrasmall Au NCs and a covalent organic framework has been developed for enhanced photostability and photocatalytic performance
- A novel composite material with Au NCs loaded on a thiol-modified COF was prepared
- The ultrasmall pores of the COF support and strong S–Au binding energy provided extra photostability of Au NCs
- Photocatalytic system was constructed by the formation of COF–S–Au bonding bridges, which effectively promote charge separation to enhance photocatalytic performance