RESEARCH ARTICLE

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In Situ Encapsulation of Atomically Precise Nanoclusters in Reticular Frameworks via Mechanochemical Synthesis

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Published: 30th October 2024

Swetashree Acharya
11.01.2025

Background

GDCh Research Articles Angewandte Chemie International Edition www.angewandte.org

How to cite: *Angew. Chem. Int. Ed.* **2024**, *63*, e202401443
doi.org/10.1002/anie.202401443

VIP **Hydrogen Production** *Very Important Paper*

Heteroatom-Doped Ag_{25} Nanoclusters Encapsulated in Metal–Organic Frameworks for Photocatalytic Hydrogen Production

He Wang, Xiyuan Zhang, Wei Zhang, Meng Zhou, and Hai-Long Jiang**

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Design and Remarkable Efficiency of the Robust Sandwich Cluster Composite Nanocatalysts ZIF-8@Au_{25}@ZIF-67

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Cite This: *J. Am. Chem. Soc.* 2020, 142, 4126–4130 Read Online

Motivation

The mechanochemical preparation of frameworks has been applied in various fields, such as nanoparticle immobilization, biomedical delivery and gas adsorption, notably for encapsulating enzymes and enhancing their catalytic activity.

Why this paper?

Talks about a universal method for fabricating diverse APNC@framework nanocomposites under mild conditions and in a short time- which is highly desirable but challenging.

Introduction

- The combination of atomically precise nanoclusters (APNCs) and reticular frameworks is promising for generating component-specific nanocomposites with emergent properties.

- Traditional liquid-phase synthesis often hampers this potential by damaging APNCs and limiting combination diversity.

- Here, mechanochemical synthesis to explore the encapsulation of diverse oil and water-soluble APNCs within various reticular frameworks is employed. establishing a database of 21 unique APNC−framework combinations, including metal−organic frameworks (MOFs), covalent−organic frameworks (COFs), hydrogen−bonded organic frameworks (HOFs), and multivariate MOFs.

- These framework coatings not only spatially immobilize APNCs but also secure their structures, preventing aggregation and degradation while enhancing stability and activity.

- The mechanochemical synthesis strategy facilitates tailored support screening, catering to specific needs, and shows promise for developing multifunctional systems, including enzyme−APNC@frameworks material for cascade reactions.

Results and discussion

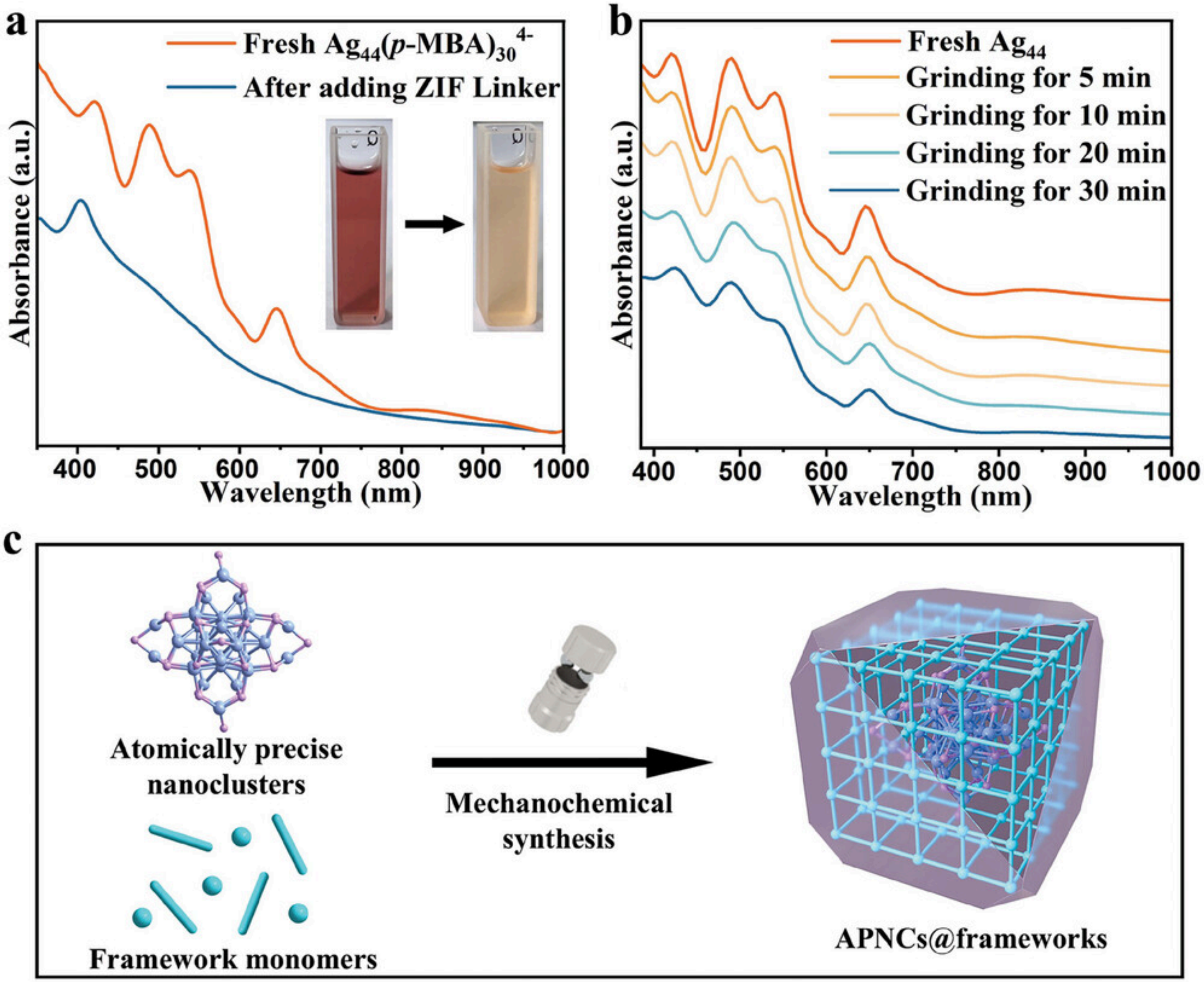


Figure 1. Ag_{44} compatibility studies and APNCs@frameworks synthesis. a) UV–vis spectra of fresh Ag_{44} and a mixture of Ag_{44} and the MOF linker. b) UV–vis spectrum of Ag_{44} after grinding at 480 rpm. c) Synthesis of APNCs@frameworks.

Characterization of the Ag$_{44}$@ZIF-8 composite

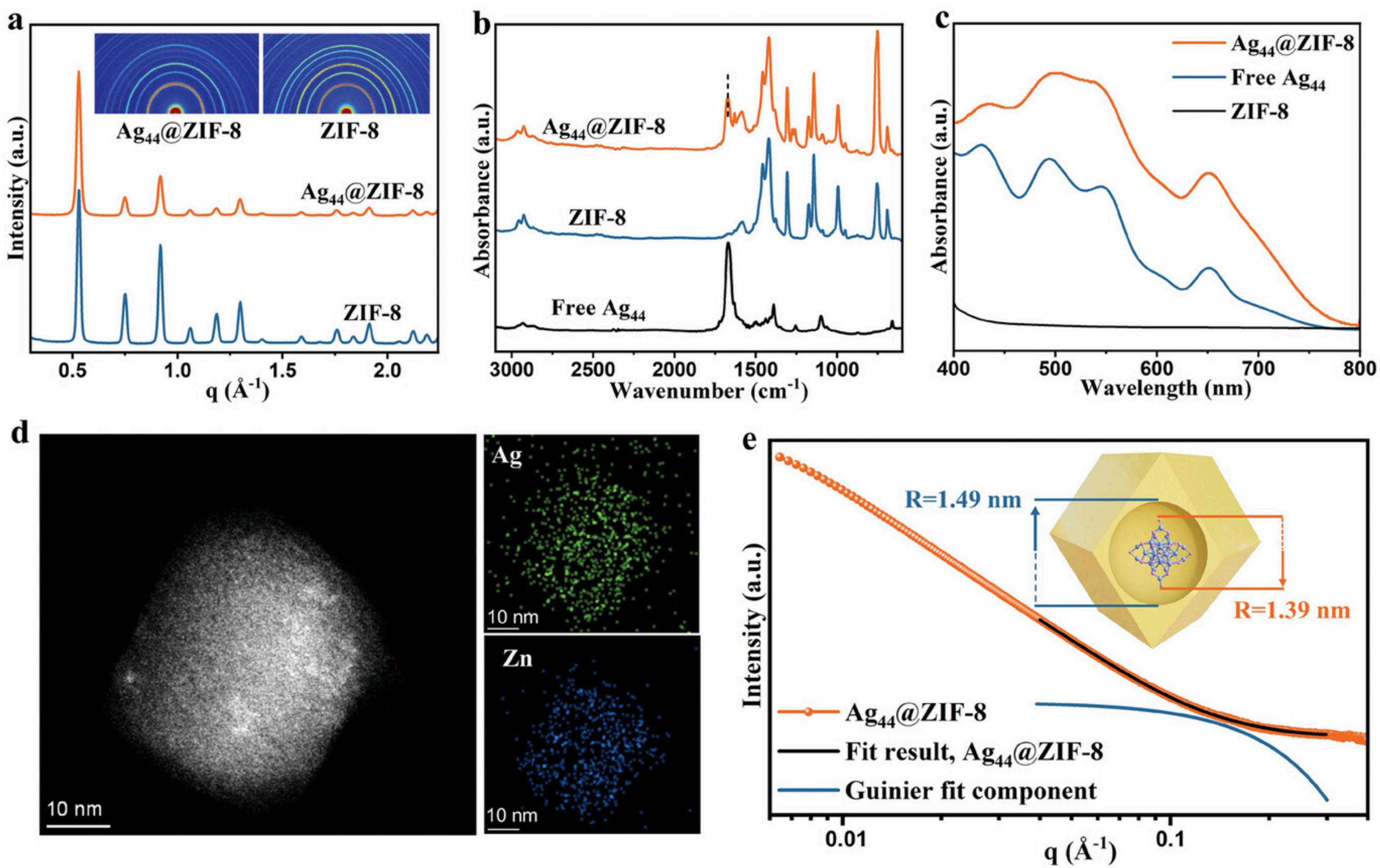


Figure 2. Characterization of the Ag$_{44}$@ZIF-8 composite. a) WAXS patterns of ZIF-8 and Ag$_{44}$@ZIF-8. b) FTIR data of ZIF-8, Ag$_{44}$, and Ag$_{44}$@ZIF-8. c) UV–vis spectra of ZIF-8, Ag$_{44}$, and Ag$_{44}$@ZIF-8. d) HAADF-STEM image of Ag$_{44}$@ZIF-8 and the corresponding elemental mappings of Ag and Zn. e) Fitted SAXS patterns and single-component fits (power law and Guinier fits) of Ag$_{44}$@ZIF-8. The inset shows the radius (arrows) of Ag$_{44}$ and the observed mesopores in Ag$_{44}$@ZIF-8.

Enhanced stability of Ag_{44}@ZIF-8

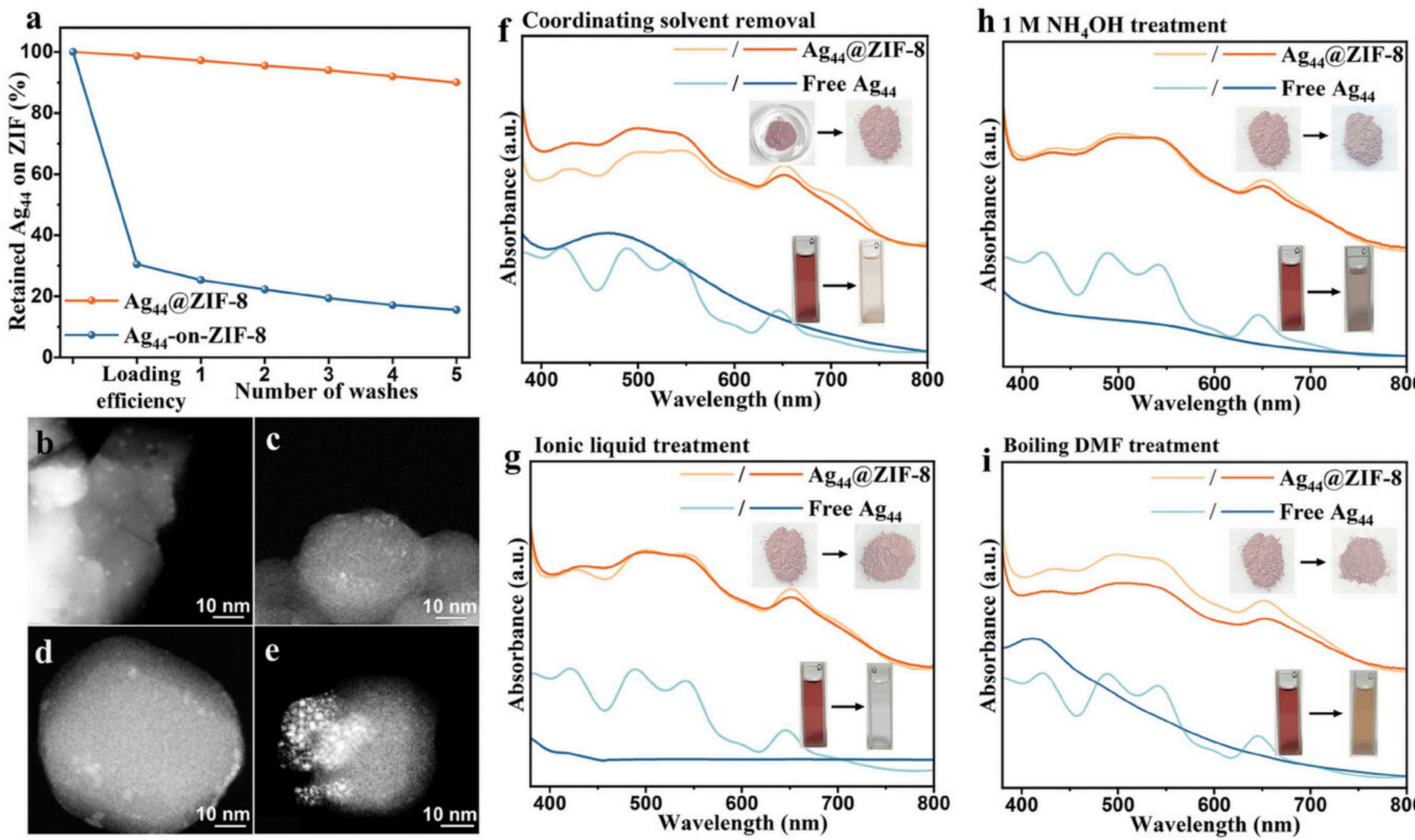


Figure 3. Enhanced stability of Ag_{44}@ZIF-8. a) Calculated loading efficiency and the wash experiments of Ag_{44}@ZIF-8 and Ag_{44}-on-ZIF-8. HAADF-STEM images of Ag_{44}@ZIF-8 b) before and c) after thermal treatment, and Ag_{44}-on-ZIF-8 d) before and e) after thermal treatment. UV–vis spectra and digital images of free Ag_{44} and Ag_{44}@ZIF-8 before (light blue and pale yellow) and after (dark blue and orange) f) coordinating solvent removal, g) ionic liquid treatment, h) 1 m NH4OH treatment, and i) boiling DMF treatment.

APNC extensions

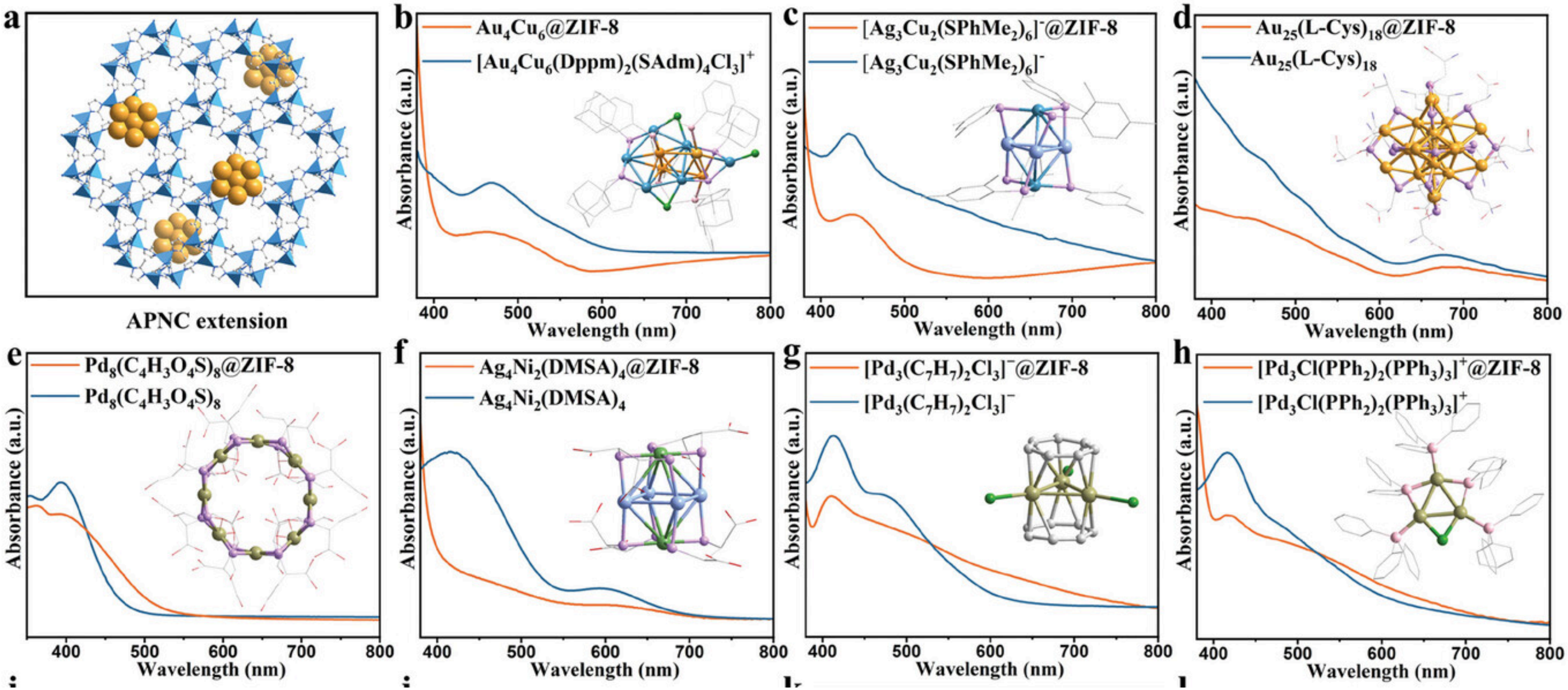


Figure 4. APNC extensions. a–h) UV–vis spectra of the composites of ZIF-8 with $[Au_4Cu_6(Dppm)_2(SAdm)_4Cl_3]^+$ (b), $[Ag_3Cu_2(SPhMe_2)_6]^-$ (c), Au_{25}(L-Cys)$_{18}$ (d), $Pd_8(C_4H_3O_4S)_8$ (e), $Ag_4Ni_2(DMSA)_4$ (f), $[Pd_3(C_7H_7)_2Cl_3]^-$ (g), and $[Pd_3Cl(PPh_2)_2(PPh_3)_3]^+$ (h).

Reticular framework extensions

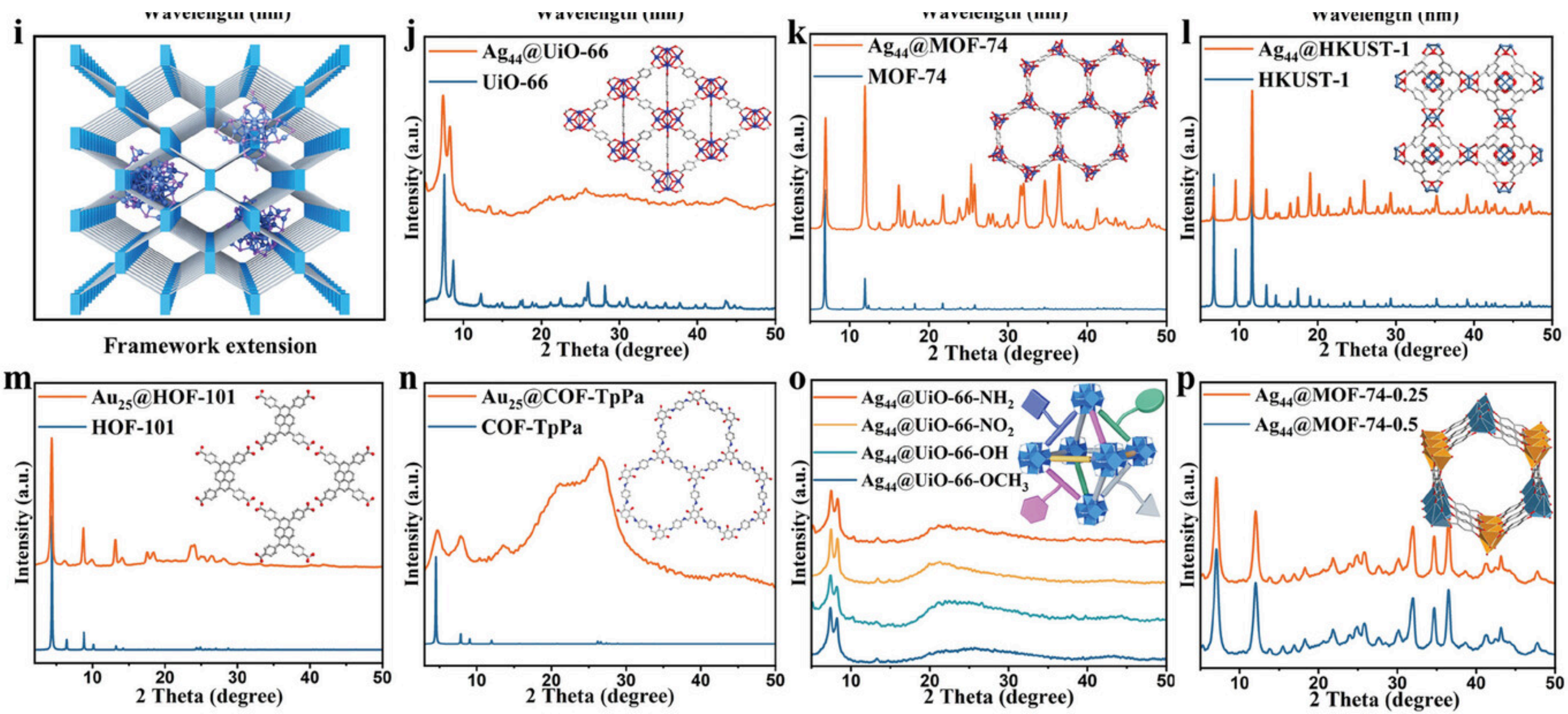
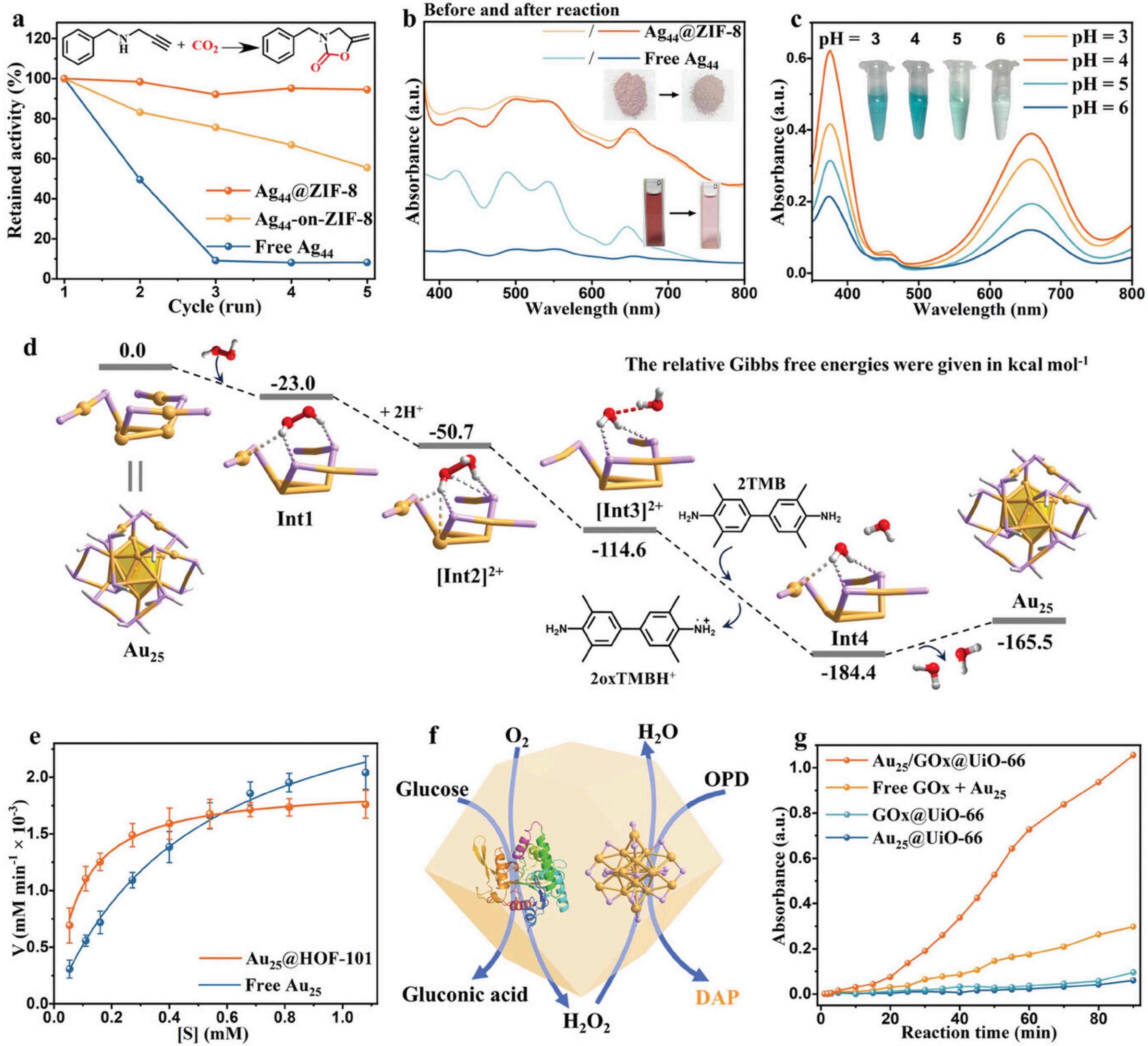


Figure 4. Reticular framework extensions. i–p) PXRD patterns of the composites of APNCs with UiO-66 (j), MOF-74 (k), HKUST-1 (l), HOF-101 (m), COF-TpPa (n), UiO-66-R (R = NH_2, NO_2, OH, OCH_3, o), and MOF-74-X (X = 0.25 and 0.5, p).

Catalytic performance of selected materials



Conclusion

- 21 APNCs@frameworks were successfully synthesized by using mechanochemical synthesis.

- This solid-state and room-temperature approach, overcomes compatibility issues associated with framework synthesis conditions, thereby preserving the structural integrity of APNCs during encapsulation.

- The resulting nanocomposites exhibit significantly improved stability and demonstrate a 315-fold increase in reactivity compared to free APNCs.

- This method expands the diversity of both APNCs and reticular frameworks, enabling the design of customized nanocomposites and multifunctional systems for specific applications.

- This diversity allows for the creation of tailormade nanocomposites capable of targeting precise functions such as HRP-mimicking catalysis and facilitates the construction of biocatalytic cascades with multiple catalytic components.