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Efficient Electrocatalytic Semi-Hydrogenation of Alkynes by Interfacial Engineering of Atomically Precise Silver Nanoclusters

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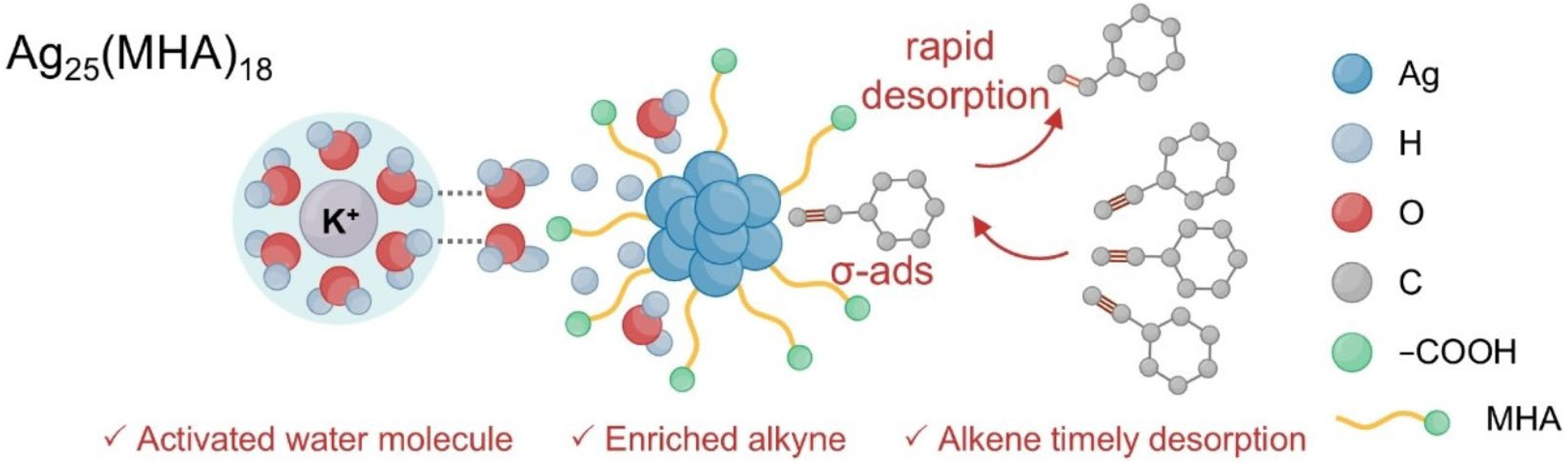
Paper presentation

Subrata Bag

31st May, 2025

Abstract



$Ag_{25}(MHA)_{18}$
K^+
rapid desorption
σ-ads
Ag
H
O
C
–COOH
MHA
✓ Activated water molecule
✓ Enriched alkyne
✓ Alkene timely desorption

Background

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Article | Published: 09 March 2023

Economically viable electroc
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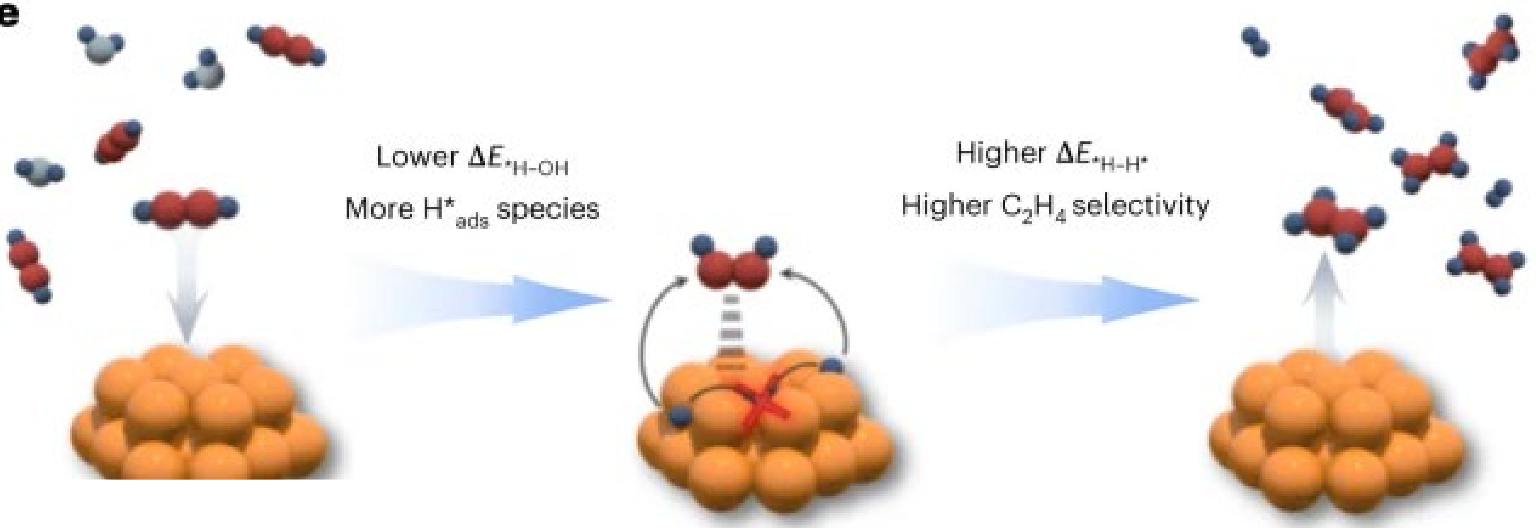

Effect of ligan
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Kaiyuan Zheng,[a] Xun Yuan

Background

J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Article

σ-Alkynyl Adsorption Enables Electrocatalytic Semihydrogenation of Terminal Alkynes with Easy-Reducible/Passivated Groups over Amorphous PdS_x Nanocapsules

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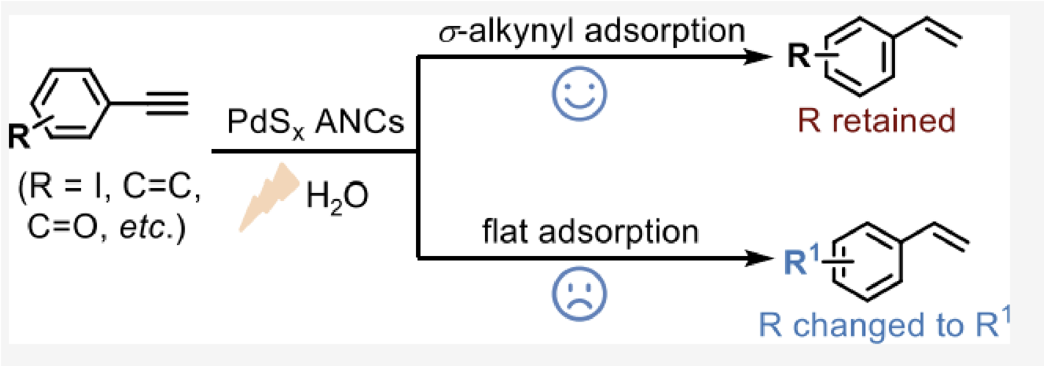
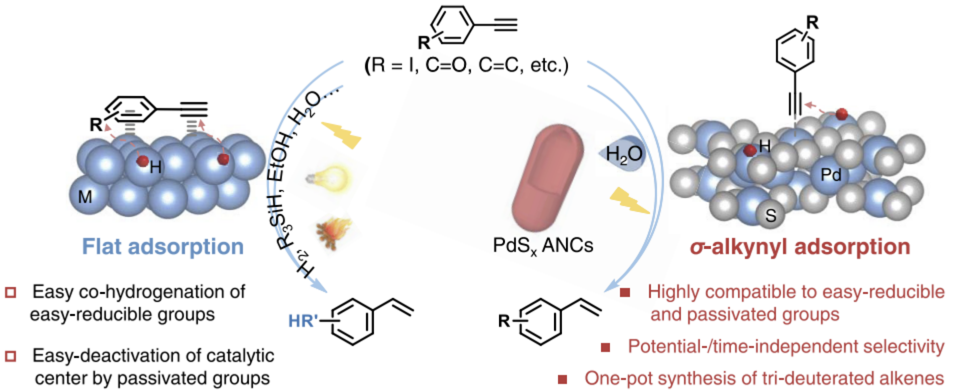




Motivation

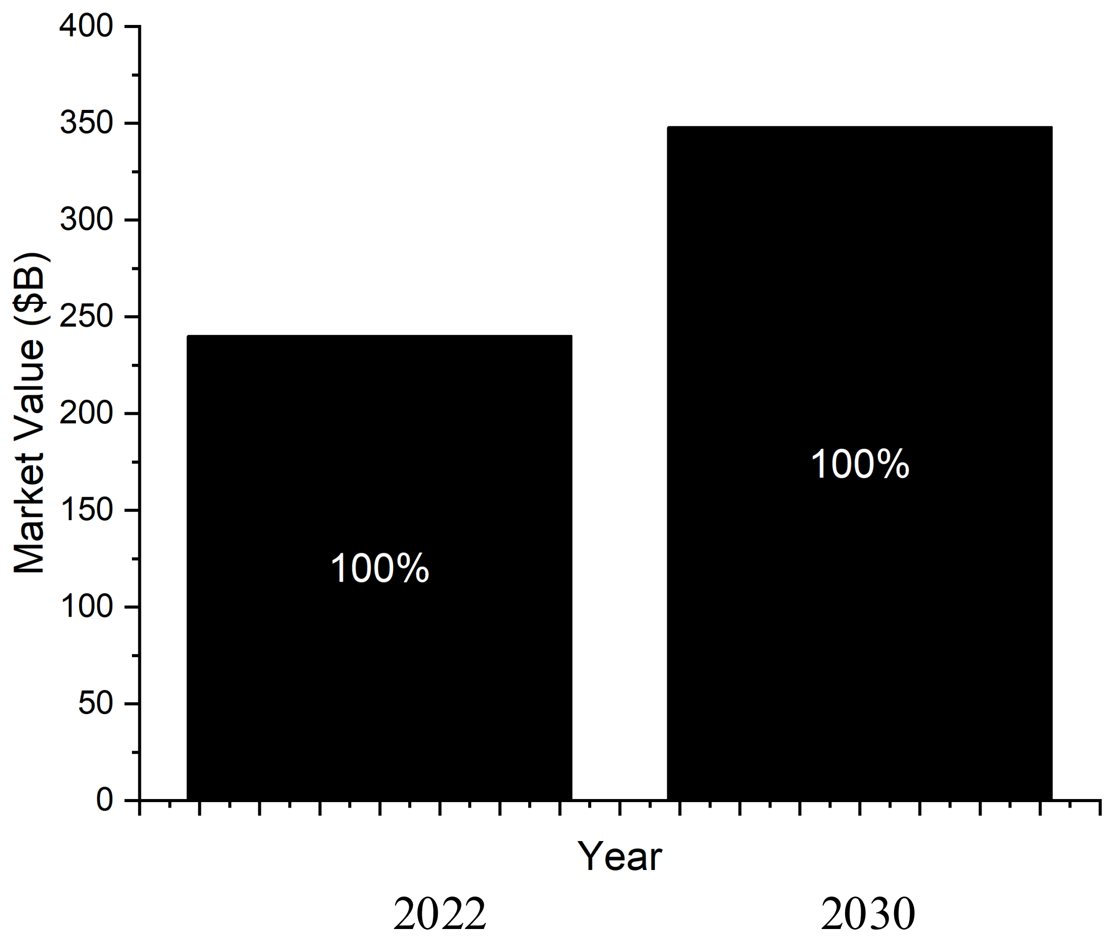
- Alkene is used in various industries as a starting material in synthesis of alcohols, plastics, lacquers, detergents, and fuels.
- Electrocatalysis using atomically precise NC is very inspiring to the nanocluster researcher.

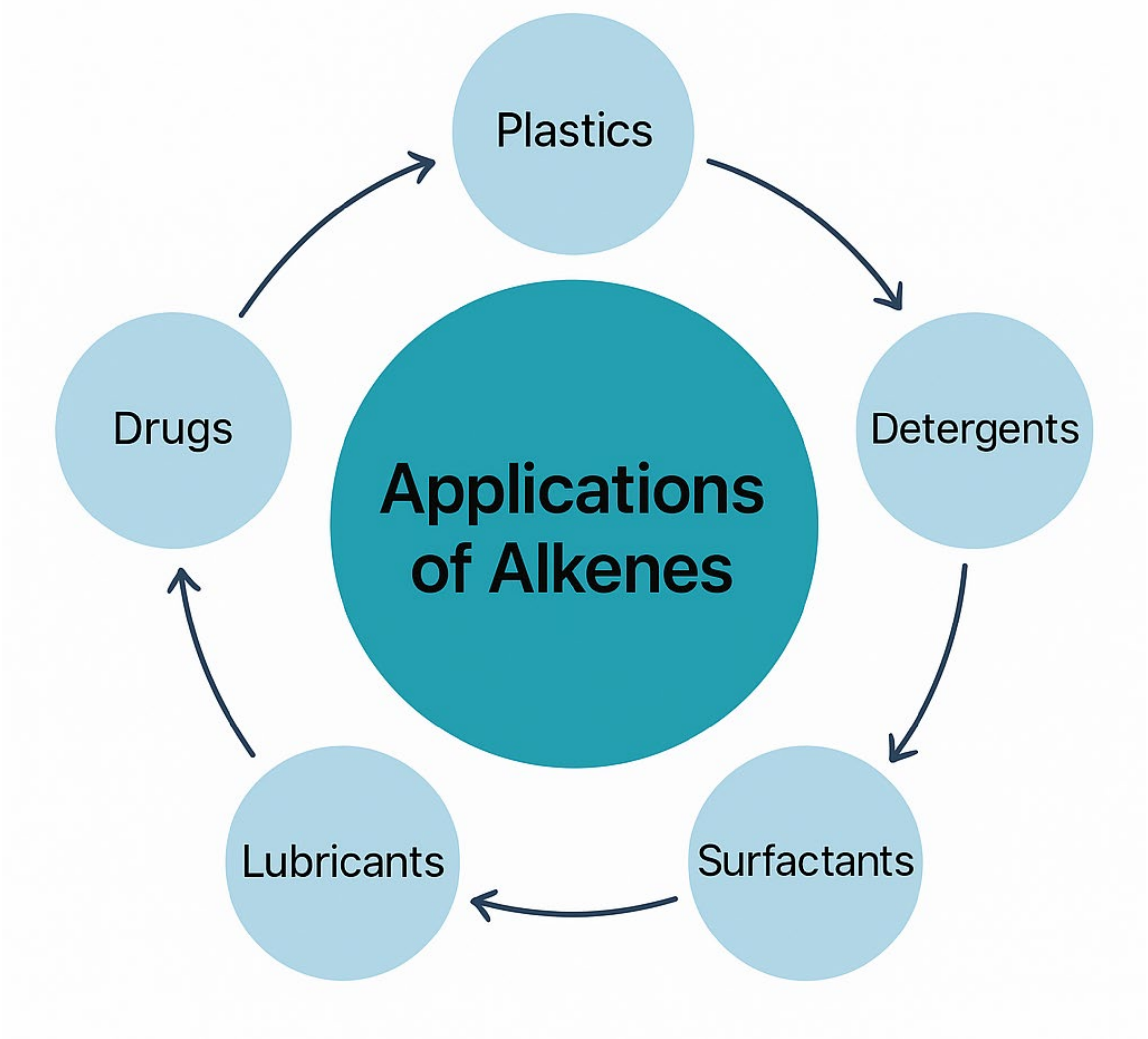
Why this paper?

- This piece of research article give an elaborative idea how an interfacial engineering can create activated H from water by applying voltage which is conducive for reduction.
- It is also reported that how enzyme like pocket of NC enhance the selectivity.
- This article widen the window of catalysis using nanocluster which enhance the relevance of nanocluster.

Introduction

Market value of alkene industry

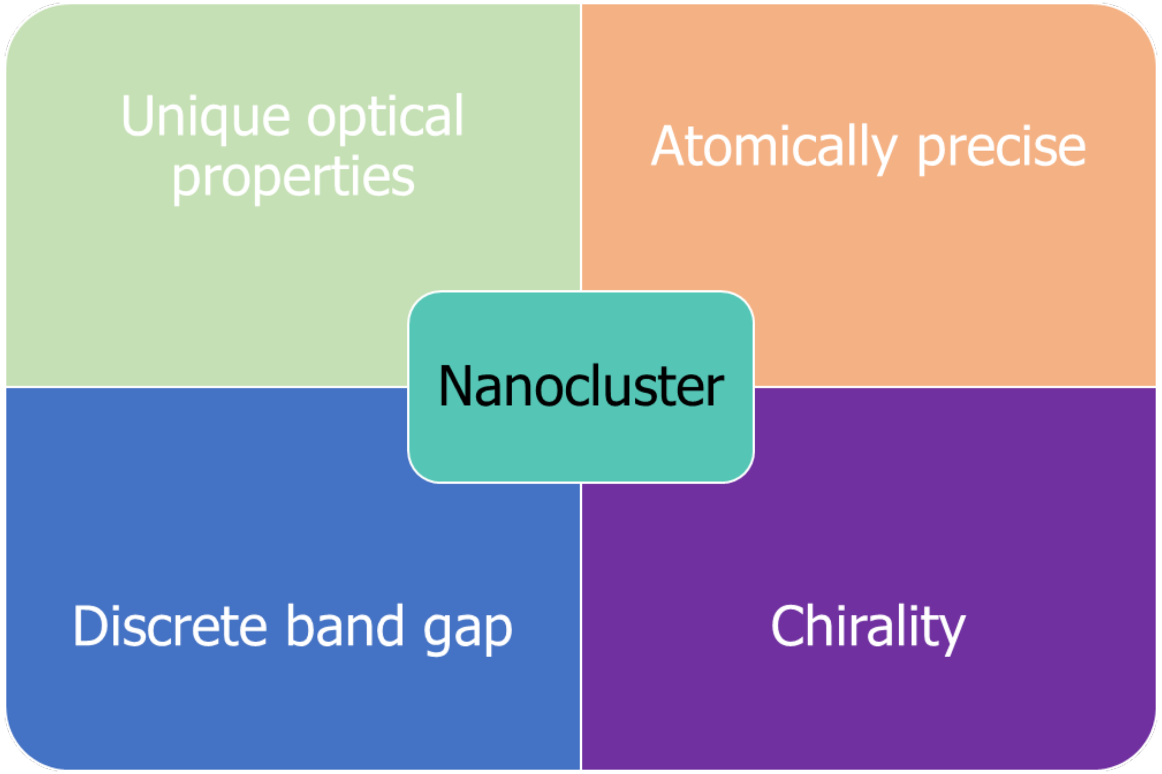


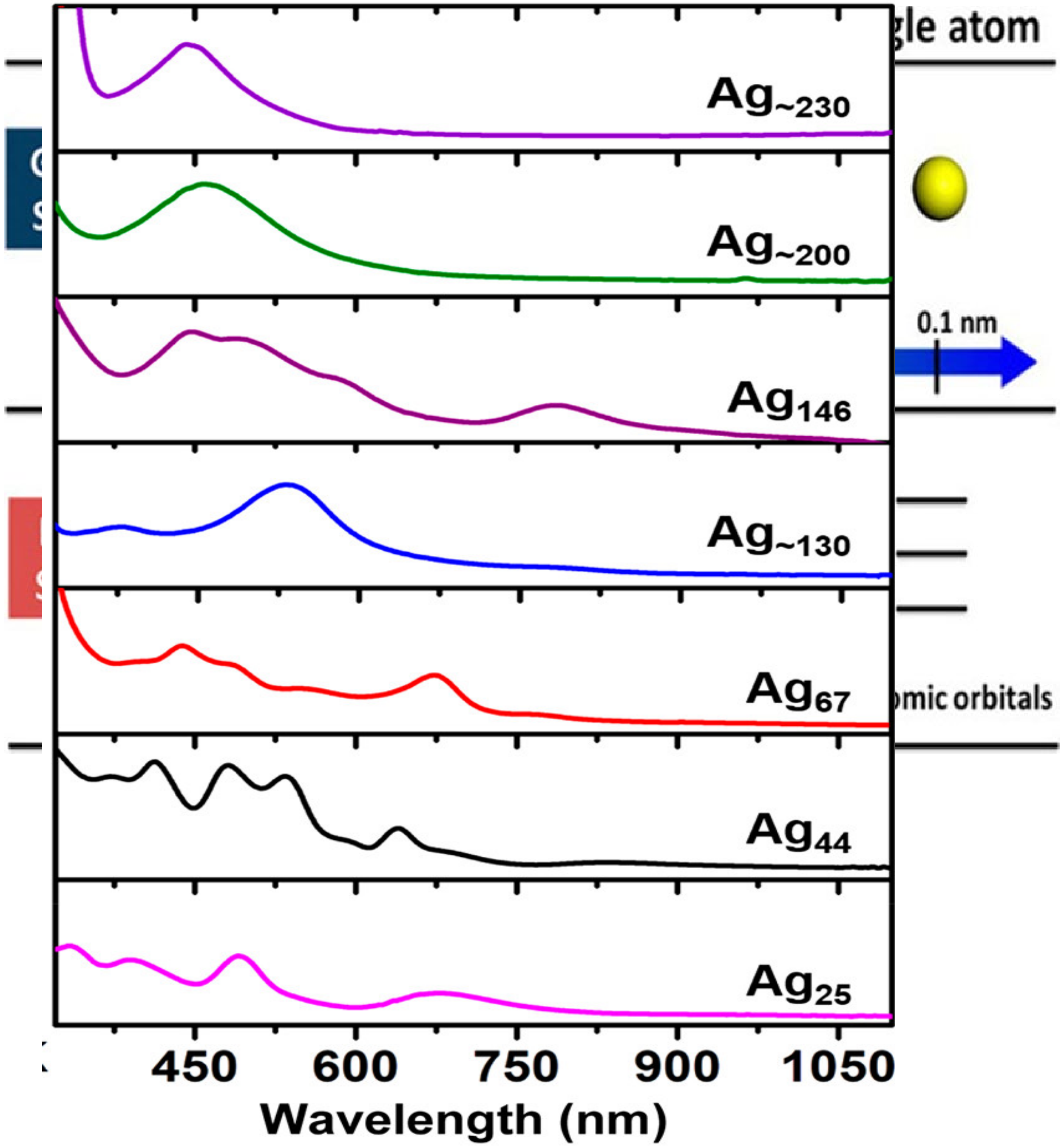


Introduction

What is Nanocluster?

Nanoclusters are atomically precise, crystalline materials most often existing on the 0-2 nanometer scale





Introduction

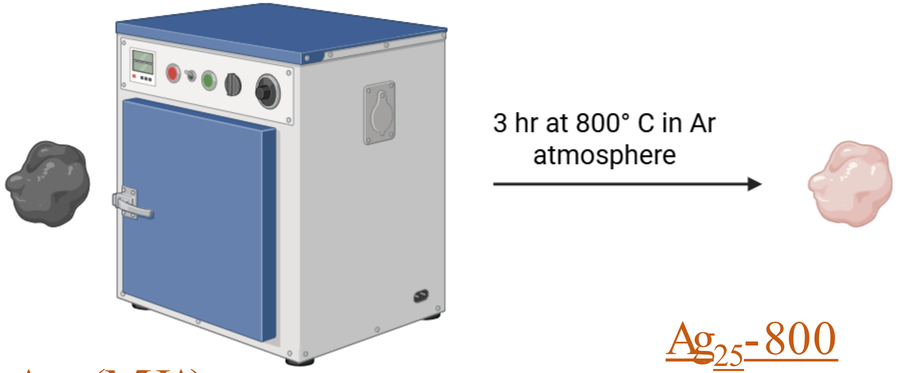
- The traditional thermocatalytic semi-hydrogenation process has seen significant advancements over the past decades. However, it typically requires high temperatures, elevated pressures, and the use of flammable and strong hydrogen donors—such as hydrogen gas (H_2), alcohols, amines, silanes, and metal hydrides—which introduces safety and cost-related challenges in storage and transportation. Moreover, the process often suffers from low selectivity and versatility due to over-hydrogenation and poor tolerance toward functional groups.
- Although electrochemical hydrogenation offers gentle, safe, and efficient advantages, its large-scale application is limited by low Faradaic efficiency (FE) and poor selectivity, primarily due to competing hydrogen evolution reactions (HER) and over-hydrogenation side reactions.
- So any electrocatalyst which can enhance the FE and selectivity at the same time would be the most desired catalyst.
- Here NC comes in our mind whose tunable properties and enzyme like pocket structure can fulfill our need.

Results and discussion

Synthesis and characterization of $Ag_{25}(MHA)_{18}$

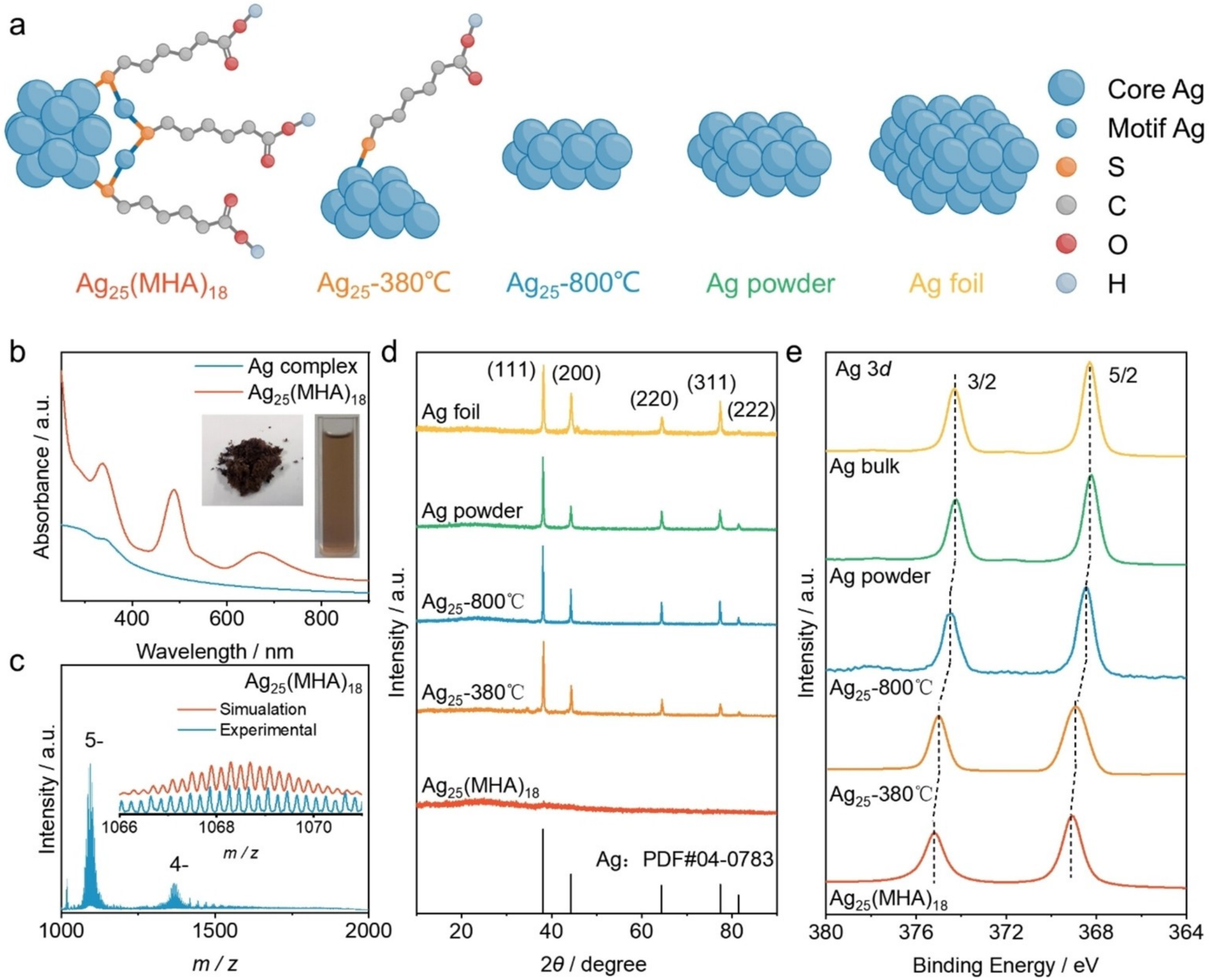
Ag_{25}-380

$Ag_{25}(MHA)_{18}$ loaded on CB



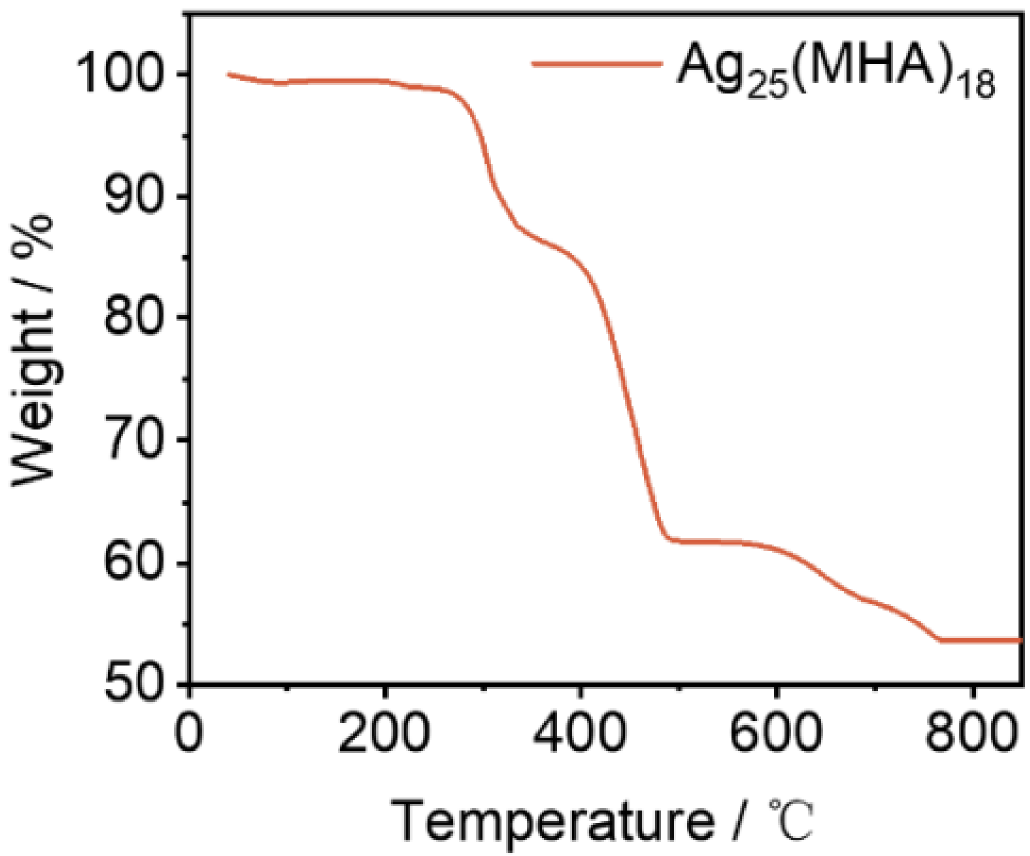
Ag_{25}-800

$Ag_{25}(MHA)_{18}$ loaded on CB



Results and discussion

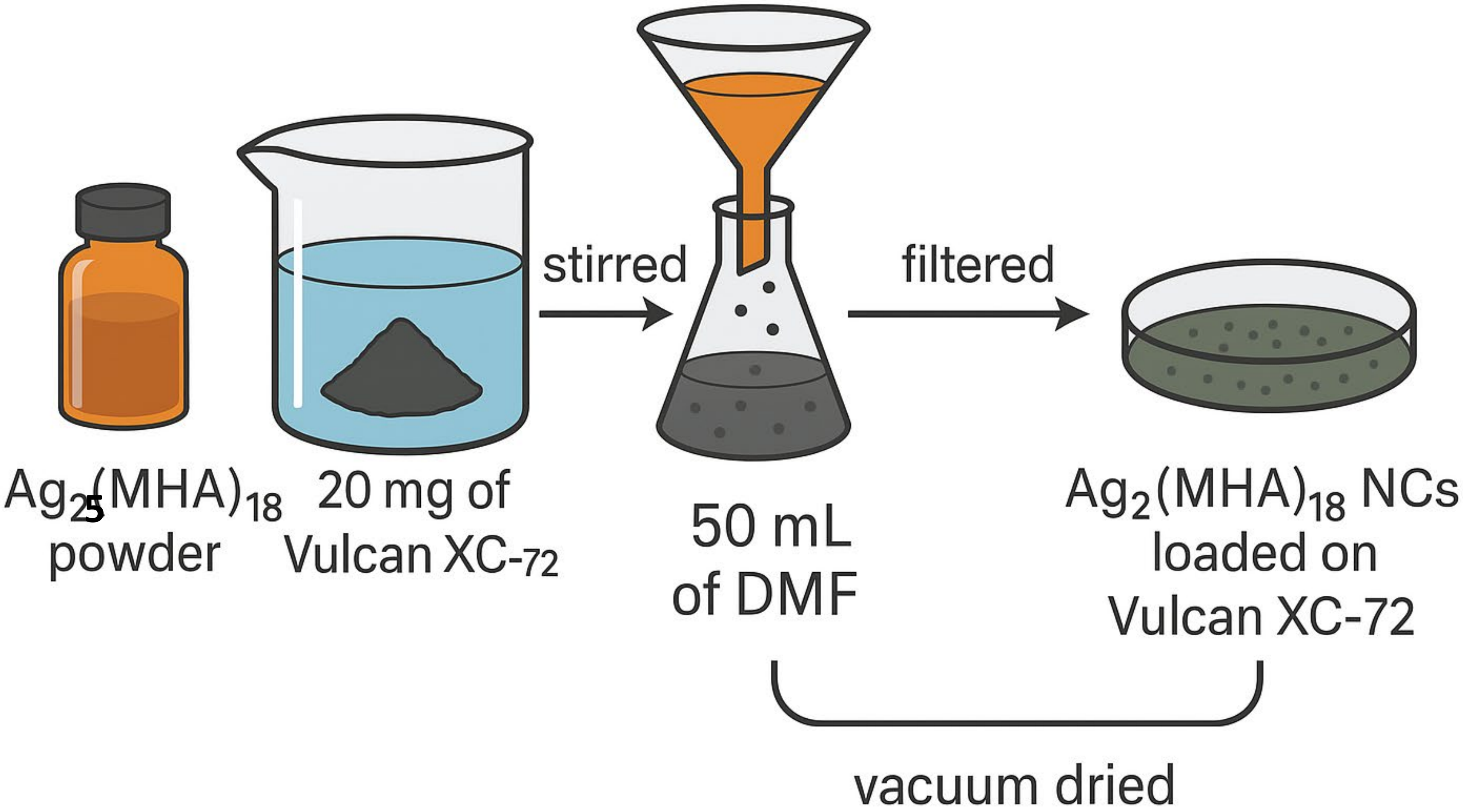
TGA analysis



Component	Molecular Weight (g/ mol)	Weight %
Ag25 (metal)	2696.7	50.26
18 MHA ligands	2668.14	49.74
Total	5364.84	100

Results and discussion

Preparation of electrocatalyst



Results and discussion

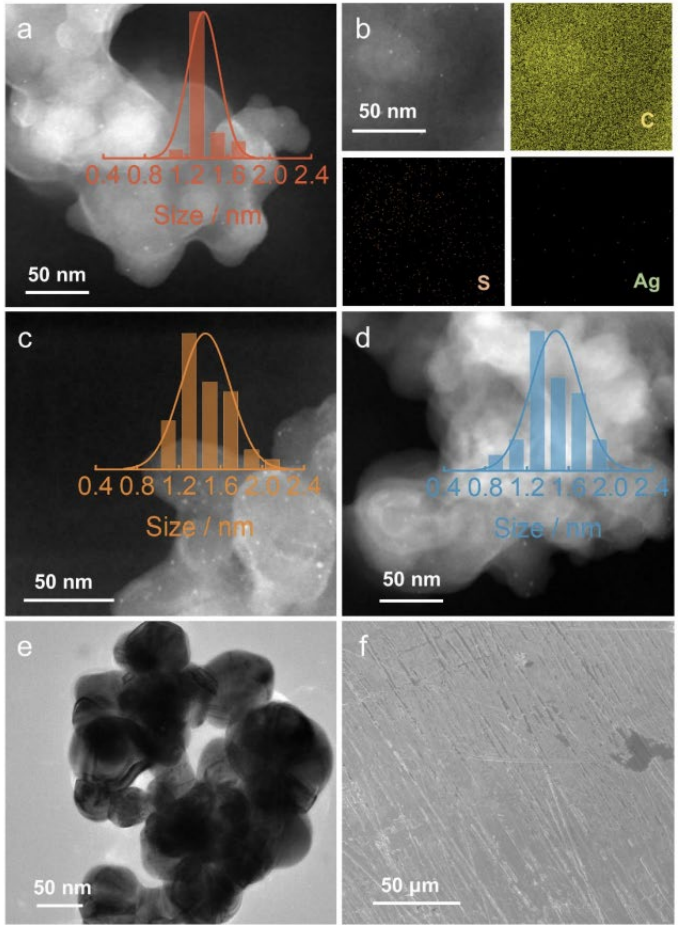
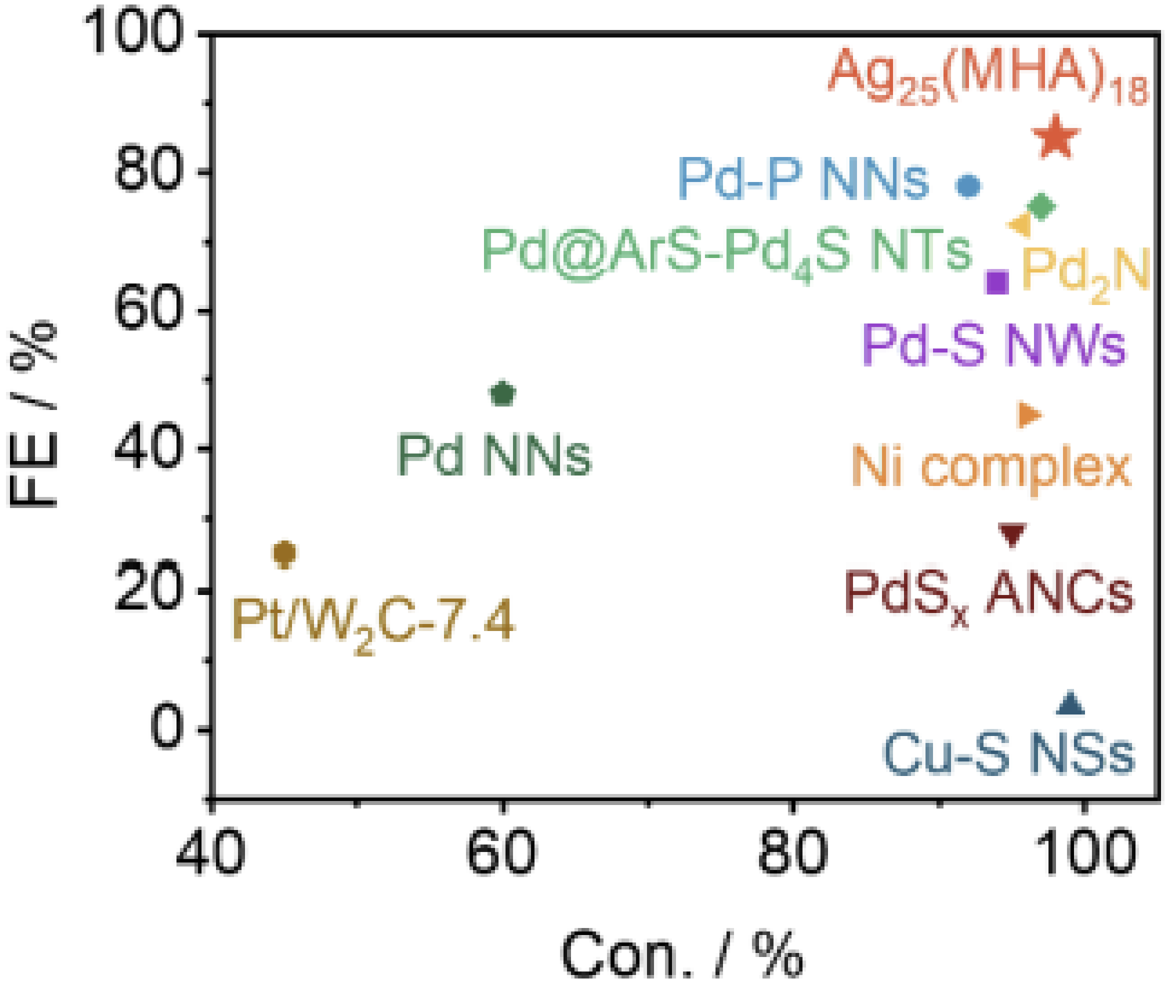
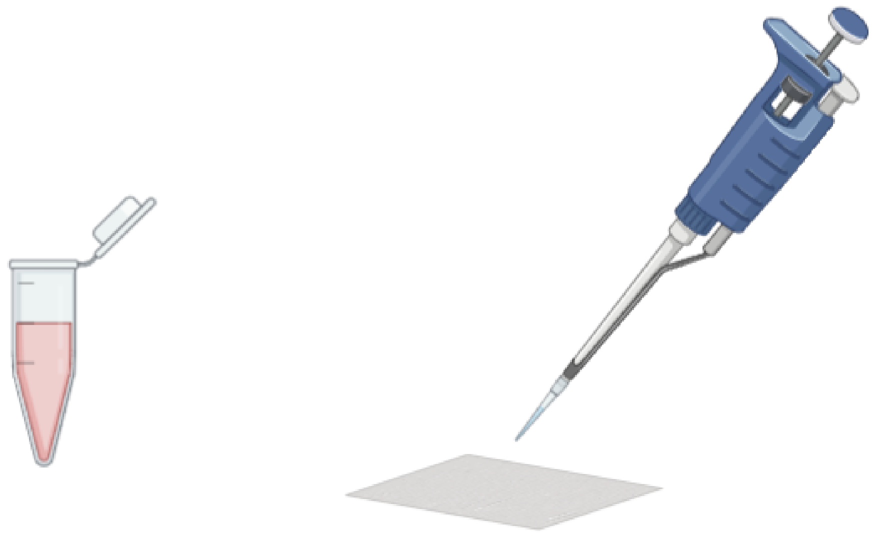


Figure S2. SEM and TEM images of Ag-based catalysts. (a) HAADF-STEM image of $Ag_{25}(MHA)_{18}$; inset: size diagram of $Ag_{25}(MHA)_{18}$. (b) Corresponding element maps of $Ag_{25}(MHA)_{18}$ show distributions of C (yellow), S (orange), and Ag (green), respectively. (c) HAADF-STEM image of Ag_{25}-380℃; inset: size diagram of Ag_{25}-380℃. (d) HAADF-STEM image of Ag_{25}-800℃; inset: size diagram of Ag_{25}-800℃. (e) HAADF-STEM image of Ag powder. (f) SEM image of Ag foil.



Results and discussion

Working electrode preparation



2 mg of Ag_{18}(MHA)+0.98 mL DMF and 20 µL 5% Nafion

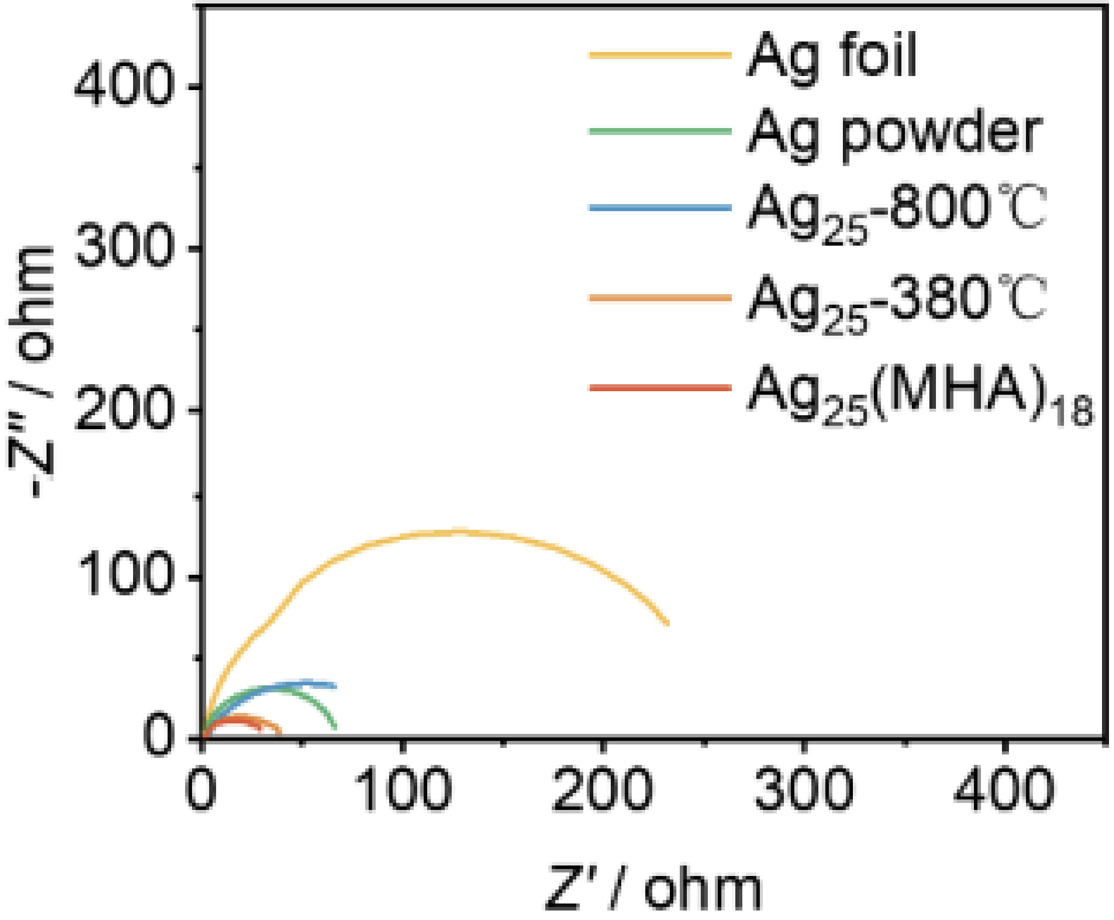
Electrochemical set up

1.0 M KOH/ H_2O
0.1mmol alkyne dissolved in 1.0 mL Diox

0.5 M K_2CO_3/ D_2O(6mL)

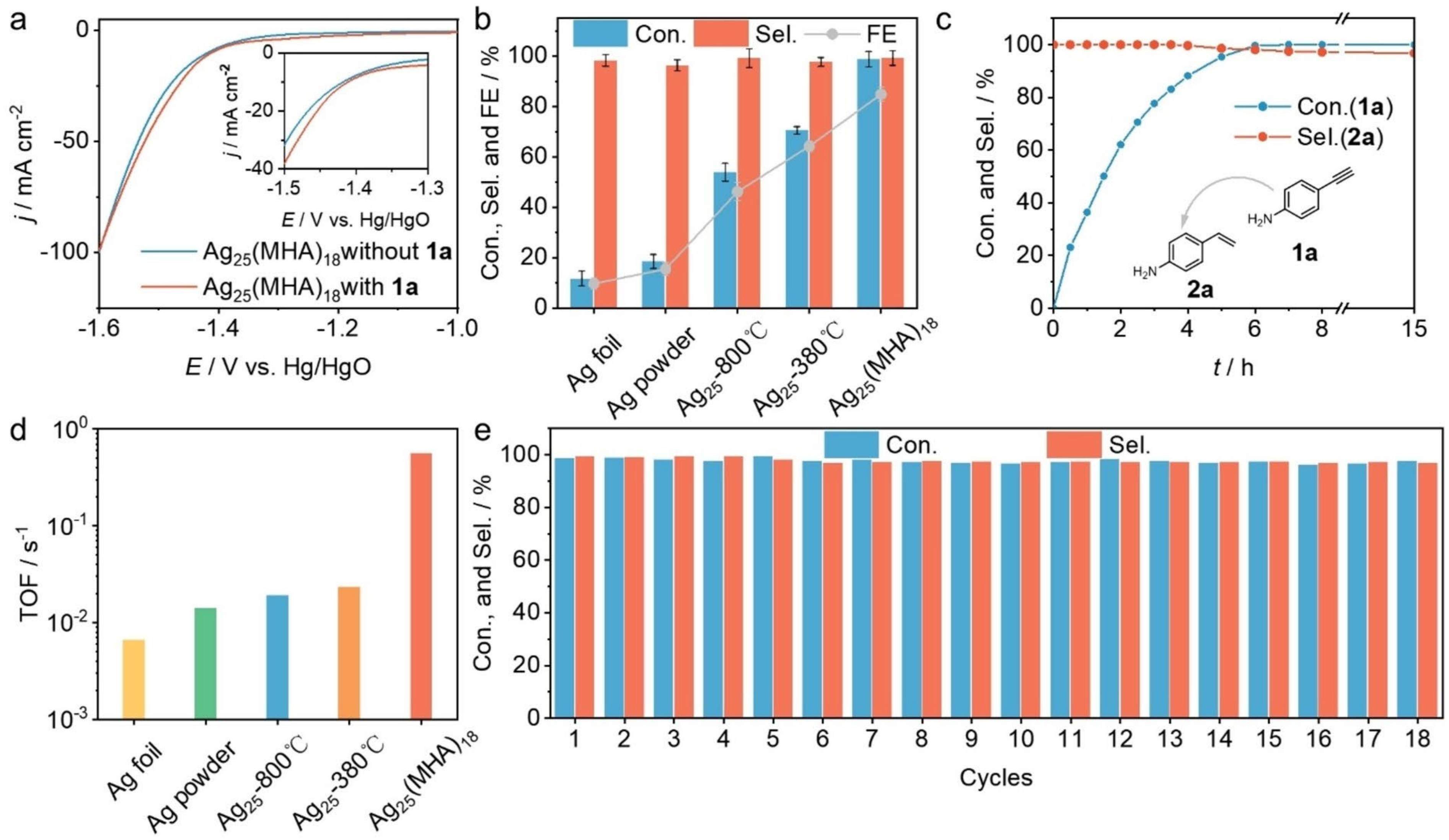
Results and discussion

Nyquist plot



Results and discussion

Catalytic performance study



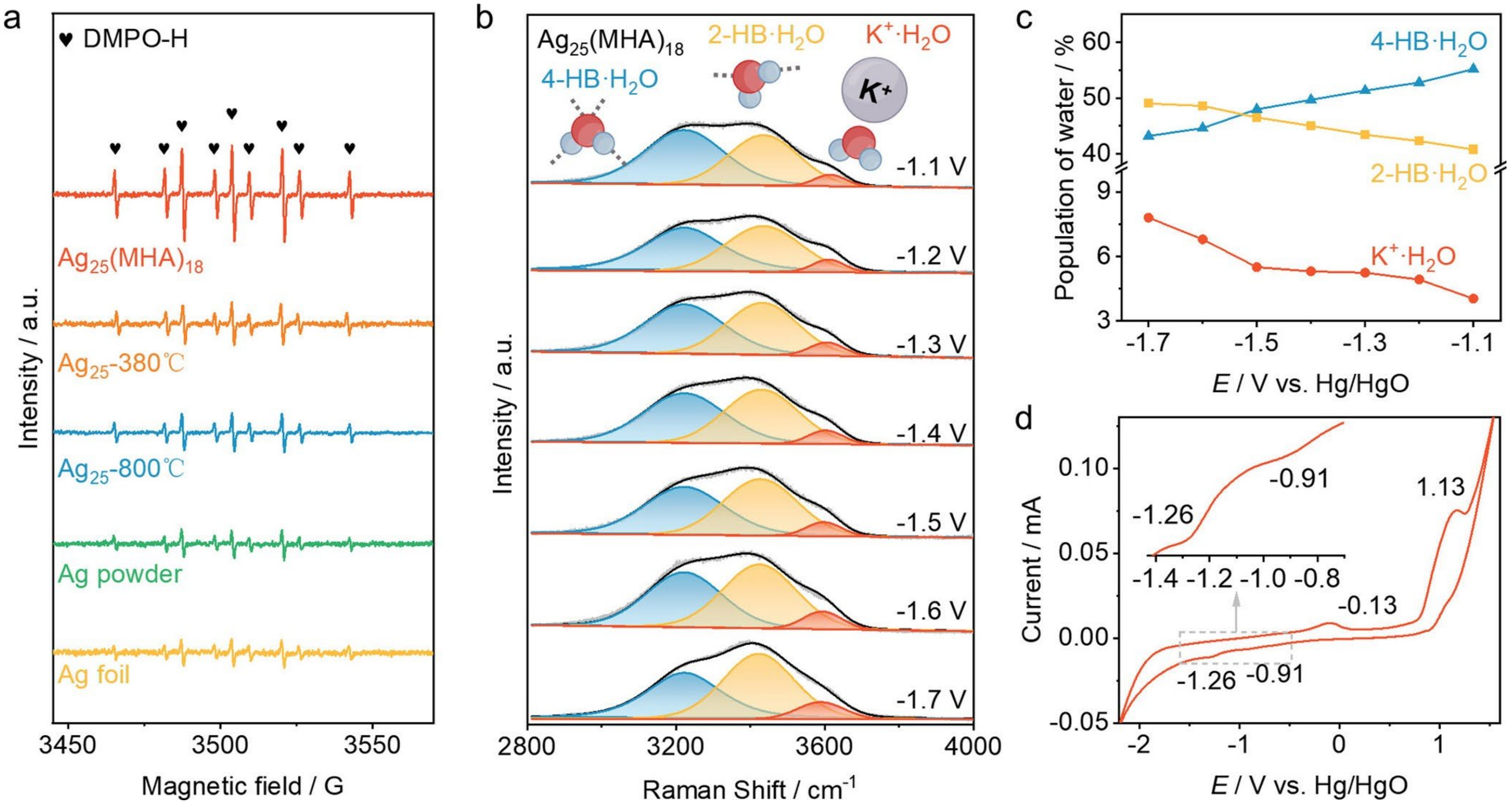
Results and discussion

Mechanism of electrocatalysis by parts

I. *Facilitated interfacial water molecule activation by $Ag_{25}(MHA)_{18}$*
II. *Enrichment of alkynes and their preferential σ-bonding-mode adsorption*
III. *Semi-hydrogenation mechanism of terminal alkynes catalyzed by $Ag_{25}(MHA)_{18}$*

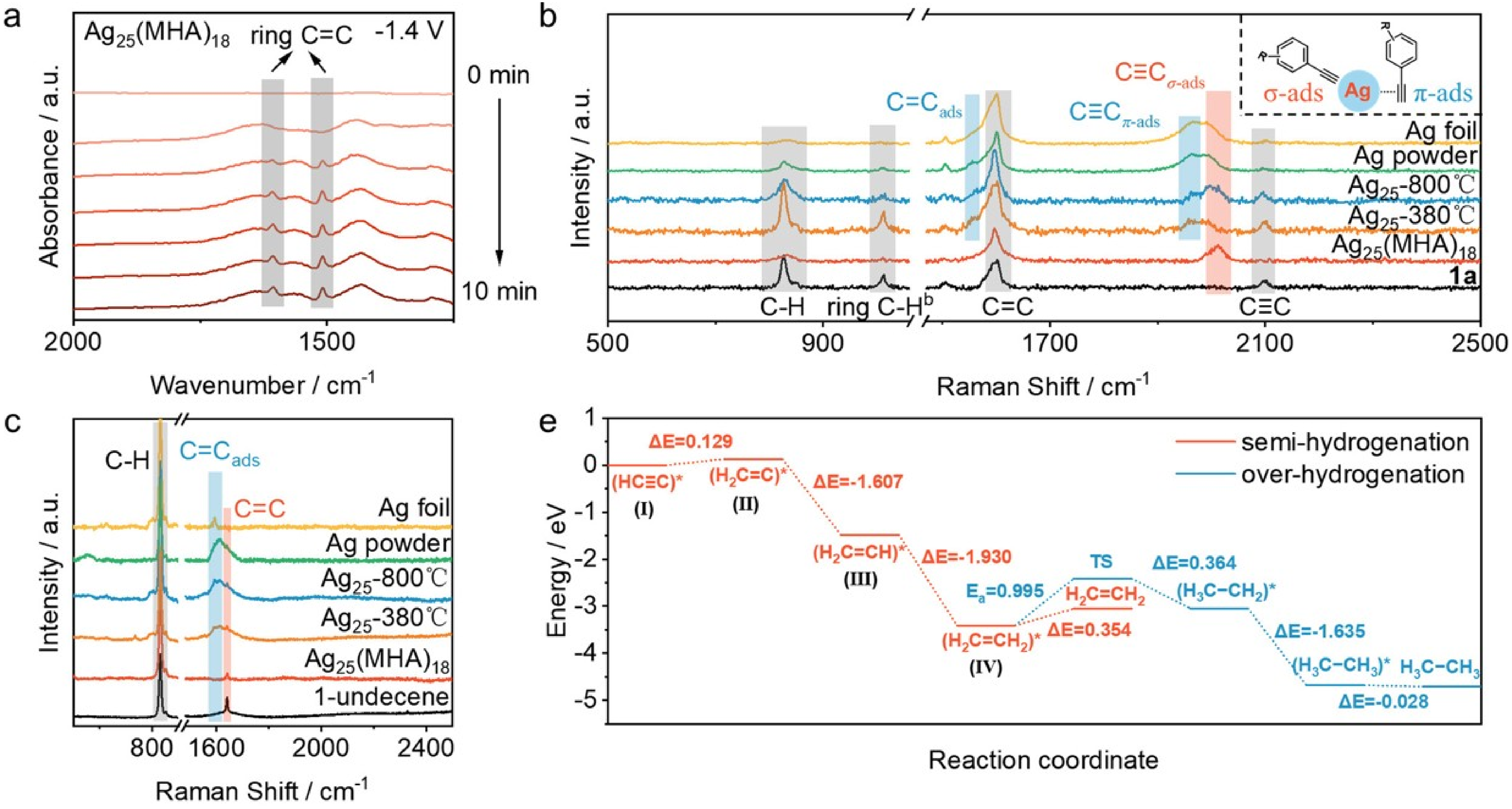
Results and discussion

Facilitated interfacial water molecule activation by $Ag_{25}(MHA)_{18}$



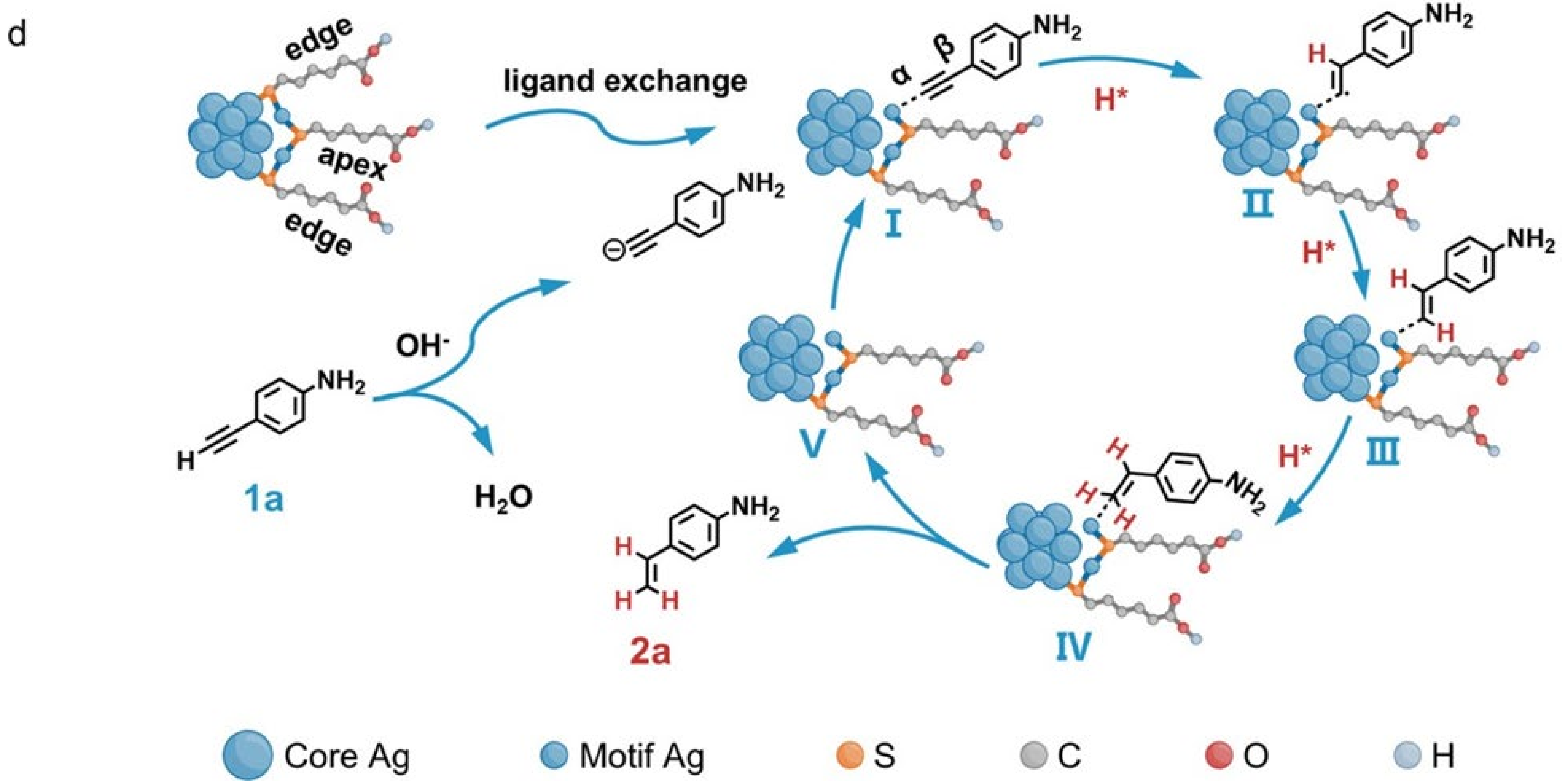
Results and discussion

Enrichment of alkynes and their preferential σ-bonding-mode adsorption



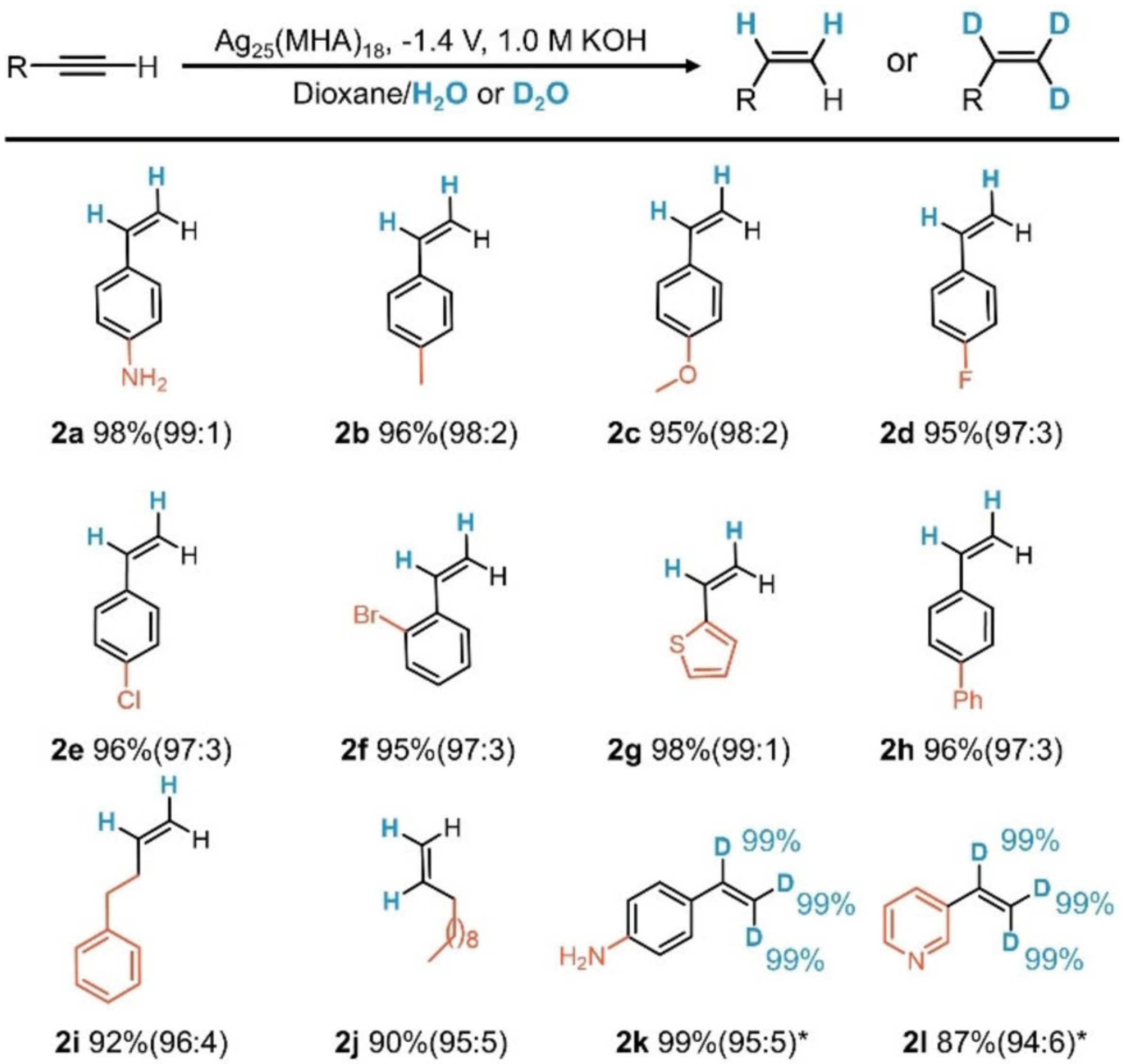
Results and discussion

Semi-hydrogenation mechanism of terminal alkynes catalyzed by $Ag_{25}(MHA)_{18}$



Results and discussion

Substrate scope



Conclusion

- This article provides an idea how hydrophobic ligand creates active hydrogen from water on applying voltage.
- Enzyme like pockets in NC enhance the selectivity.
- σ-bonding adsorption of alkynes and rapid desorption of product from surface of cluster increase the selectivity.
- A suitable mechanism has been proposed and validated by various experiments.