X-TWICE 최종 발표 자료

전기화학적 수소 생성 반응에 효율적인 촉매 설계
(Designing Efficient Catalyst for Electrochemical Hydrogen Evolution Reaction)

Yoo group

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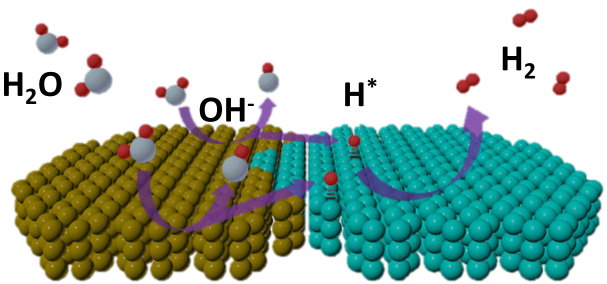
Background

- **Global hydrogen gas production**

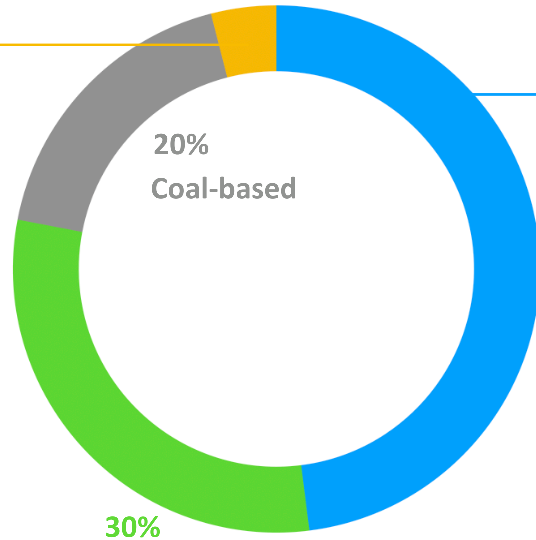
5%
Water electrolysis

Overall reaction

: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$



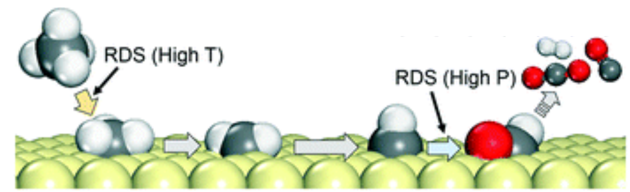
Nano-Micro Lett. 10, 2018, 75



45%
Natural gas reforming

Overall reaction

: $CH_4 + H_2O \rightarrow 3H_2 + CO$



React. Chem. Eng., 2020,5, 873-885

Advantage

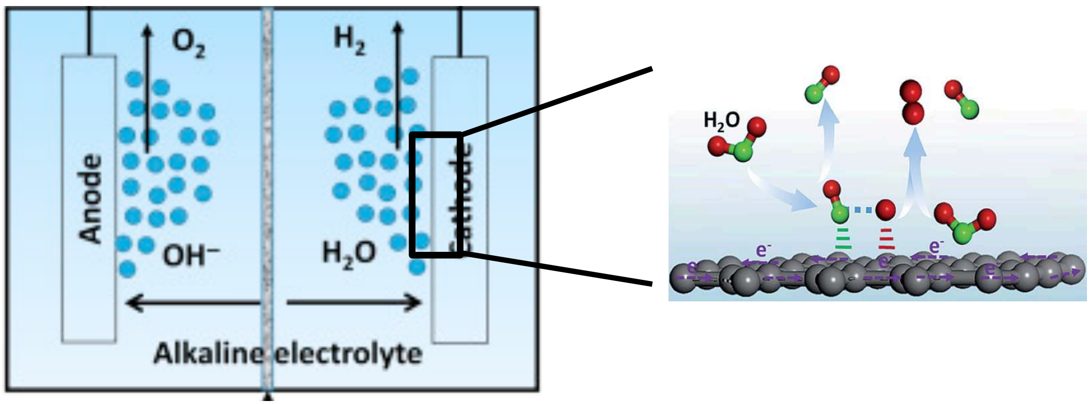
- Electricity supply by renewable energy
- No pollutant emission
- Plug-and-play mechanism

Disadvantage

- Fossil fuel dependence
- Greenhouse gases emission(CO, CO_2, etc.)
- Storage and delivery problem

J. Mater. Chem. A, 2019, **7**, 14971–15005

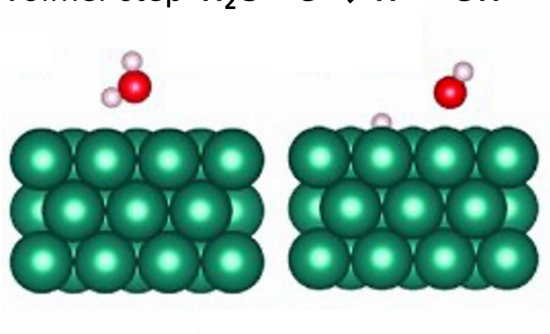
- **Hydrogen evolution reaction (HER) mechanism in alkaline medium**



Volmer step	$H_2O + e^- \rightarrow H^* + OH^-$
Heyrovsky step	$H_2O + H^* + e^- \rightarrow H_2 + OH^-$
Total reaction	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Rate determining step (RDS)

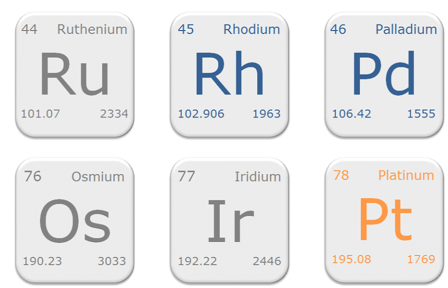
Volmer step $\mathbf{H_2O + e^- \rightarrow H^* + OH^-}$



H_2O dissociation step

Need high-activity Pt-group metal

Pt-group metal (PGM)



Rare-earth material

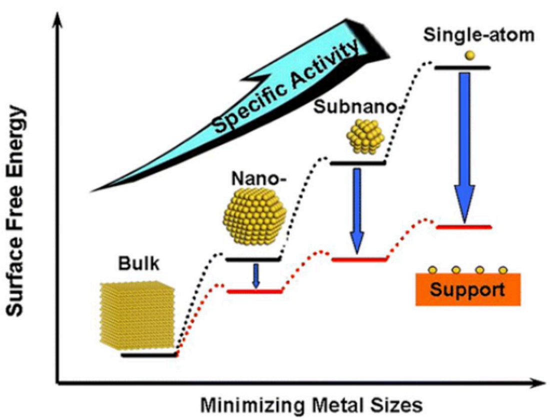
Scarce, high-price

Research summary

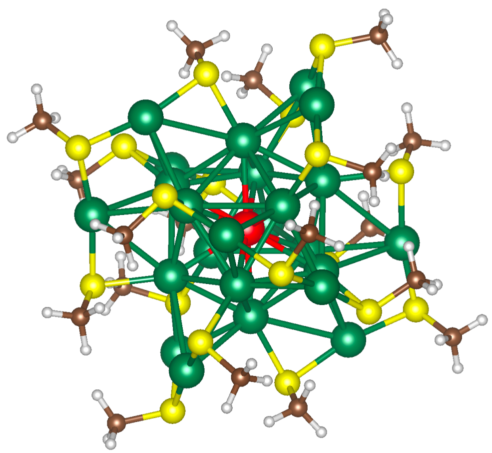
Catalyst design strategies

Computational approach

Nano sizing effect	Ligand-protected nanocluster	Predicting catalytic properties
Improving catalyst activity	Effect of active sulfur ligand	Hydrogen evolution reaction (HER) activity descriptor, ΔG_H
Increasing surface area per same volume	Substituting core atoms- bi/tri metallic nanocluster	Possible ligand removal potential

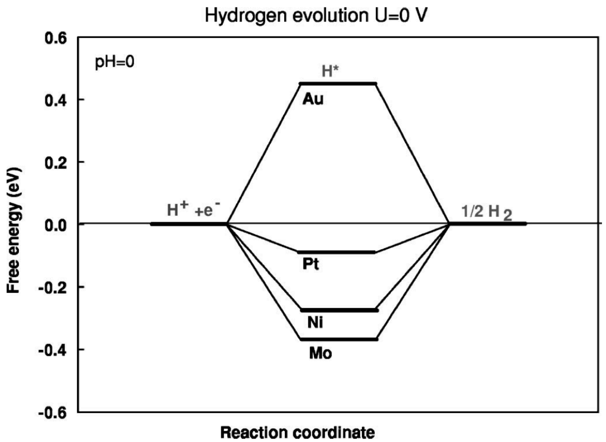


Acc. Chem. Res. 2013, 46, 8, 1740–1748



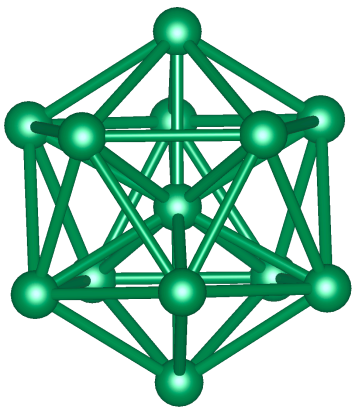
$MAg_{24}(SCH_3)_{18}$

- Ag
- C
- S
- H
- Core metal



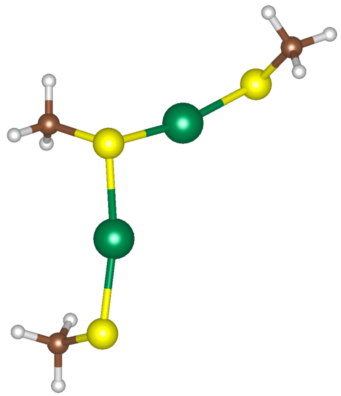
Journal of The Electrochemical Society, 152, 2005, 3 J23-J26

- **Ag nanocluster (Ag_{25})**



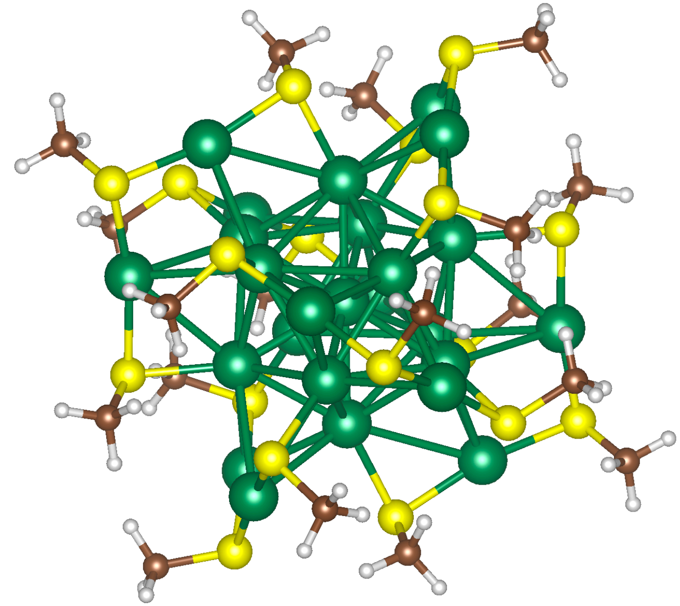
Ag_{13}

+



6 $Ag_2(SCH_3)_3$

➡



$Ag_{25}(SCH_3)_{18}$

Icosahedral nanoparticle core + **Shell network of Six ligand units** ➡ **Fully-ligand protected Ag_{25} nanocluster**

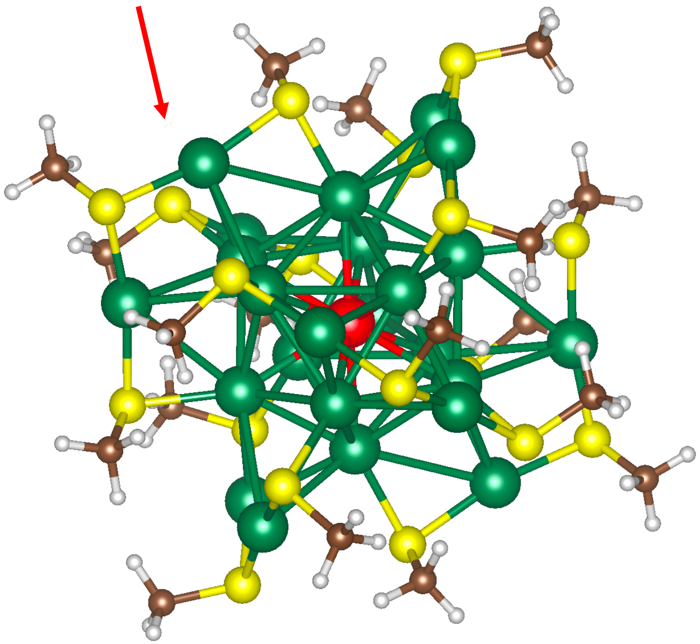
Ag S

C H

Methods

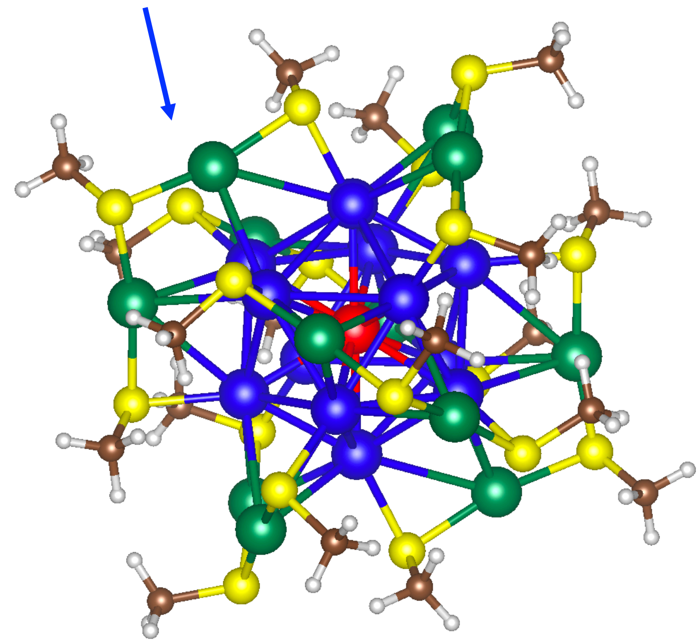
- **Bimetallic Ag nanocluster (MAg_{24})**

Pt, Pd, Au doping into core-center site



- **Trimetallic Ag nanocluster ($PtAu_xAg_{24-x}$)**

Au partial doping into core-surface sites



Core-center (M) Ag S C H

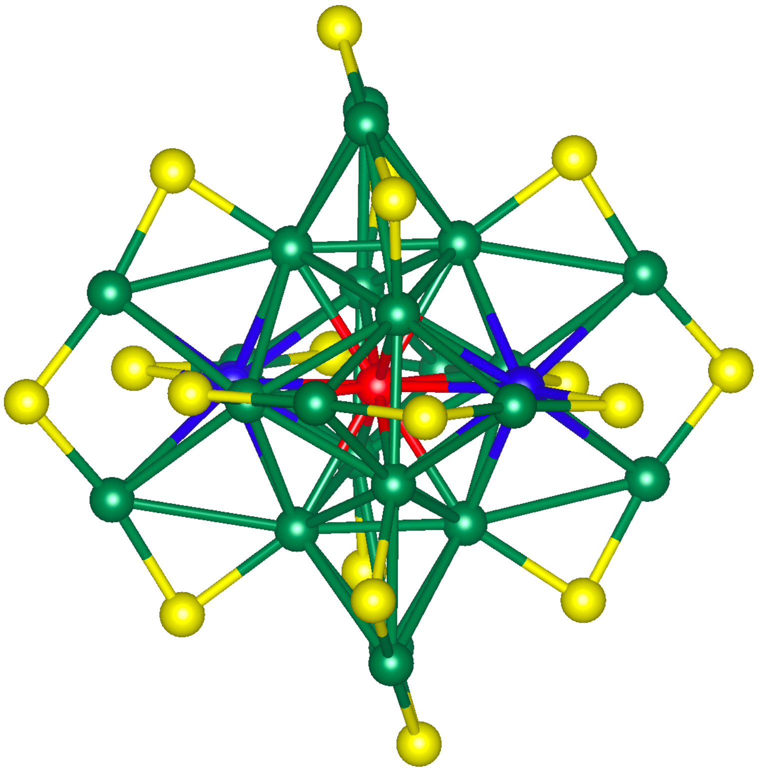
Core-center (Pt) Core-surface Staple Ag

- **Core-center** atom can be replaced with other atoms (Au, Pd, and Pt).
- Au atoms are partially substituted (x=2 or 8) into the **core-surface** sites on $PtAg_{24}$.

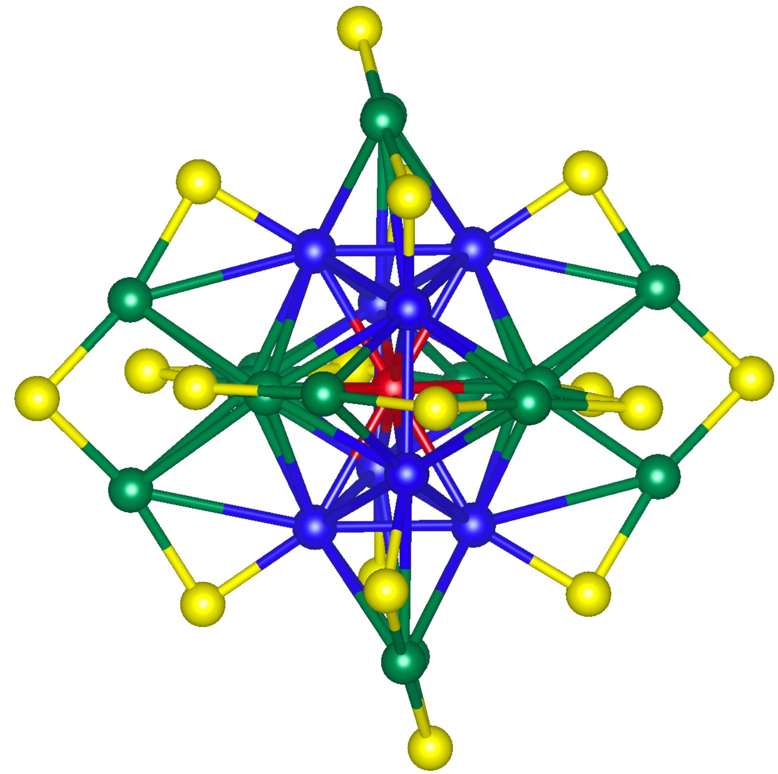
Methods

- **Scheme of trimetallic nanocluster structures**

Core-center (Pt) Doped Au Ag S



$PtAu_2Ag_{22}$



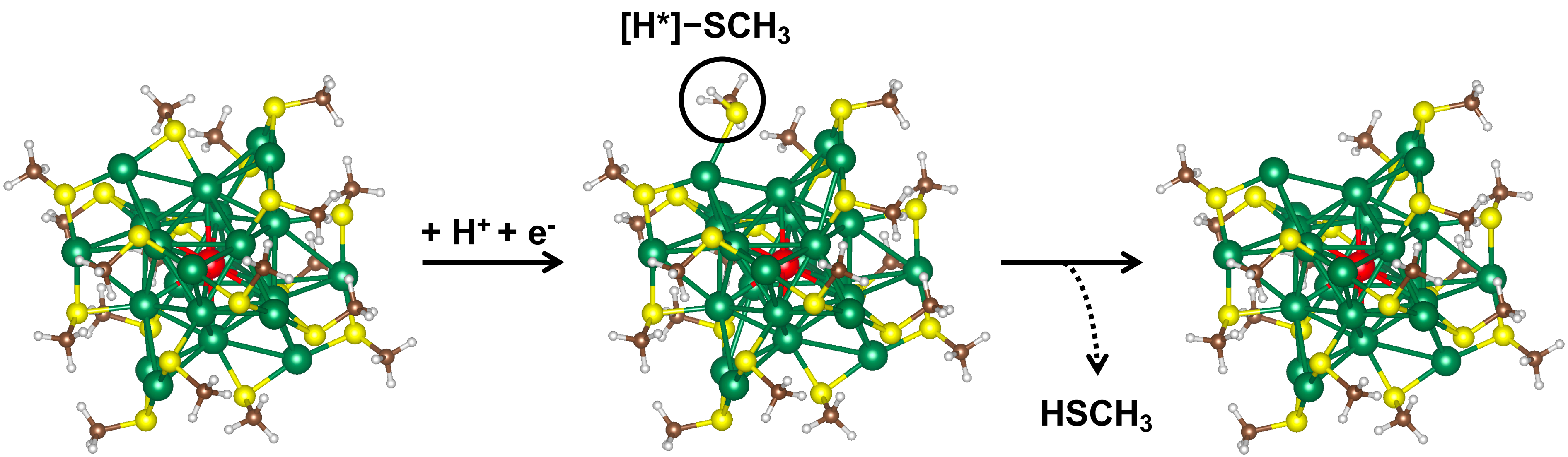
$PtAu_8Ag_{16}$

- Most stable Au doping sites among core-surface atoms were determined by calculations.

  ($-CH_3$ were omitted for a clarity.)

Ligand removal

- **Scheme mechanism for ligand removal**



Intact surface (Surface 1)

Dethiolated surface (Surface 2)

- Under the reducing condition, the thiolate ligands can be removed.
- Thiolate ligand removed site can be served as a new active site.

Ligand removal

- **Pre-electrolysis condition (Exp.)**
  - Alkaline condition (pH = 14) : - 0.6 V vs. RHE **(-1.4 V vs. NHE)**

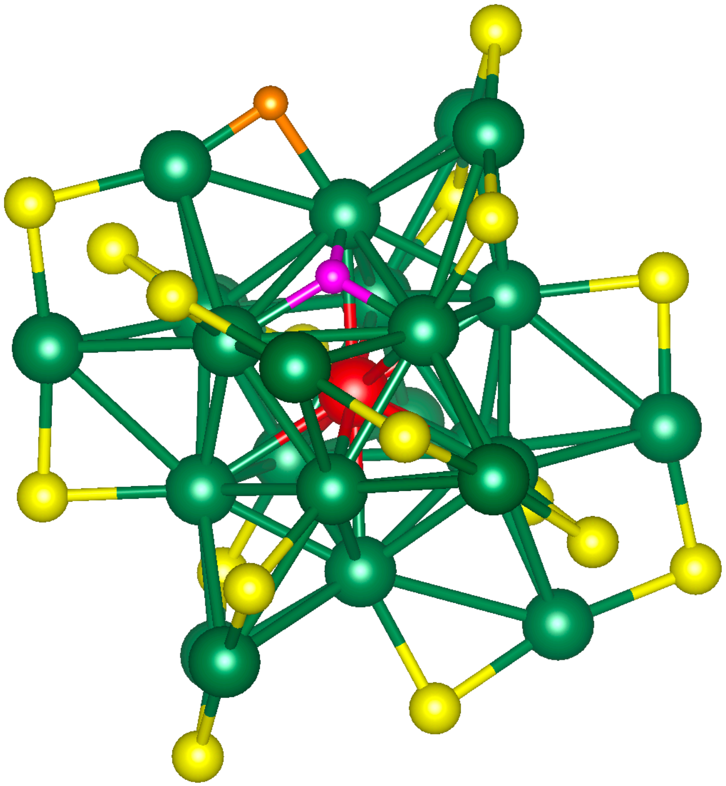
- **Calculated potentials for 1-ligand removal**

Surface	U (V vs. CHE)	Surface	U (V vs. CHE)
Ag_{25}	-0.33	$PtAu_2Ag_{22}$	-0.62
$AuAg_{24}$	-0.35	$PtAu_8Ag_{16}$	-0.65
$PdAg_{24}$	-0.48	Au_{25}	-0.81
$PtAg_{24}$	-0.40	$PtAu_{24}$	-0.92

- For all surfaces, a thiolate ligand can be removed at the experiment.
- We designed 1 ligand removed surface for a simplicity.

Active sites

- **Active sites on dethiolated surfaces**

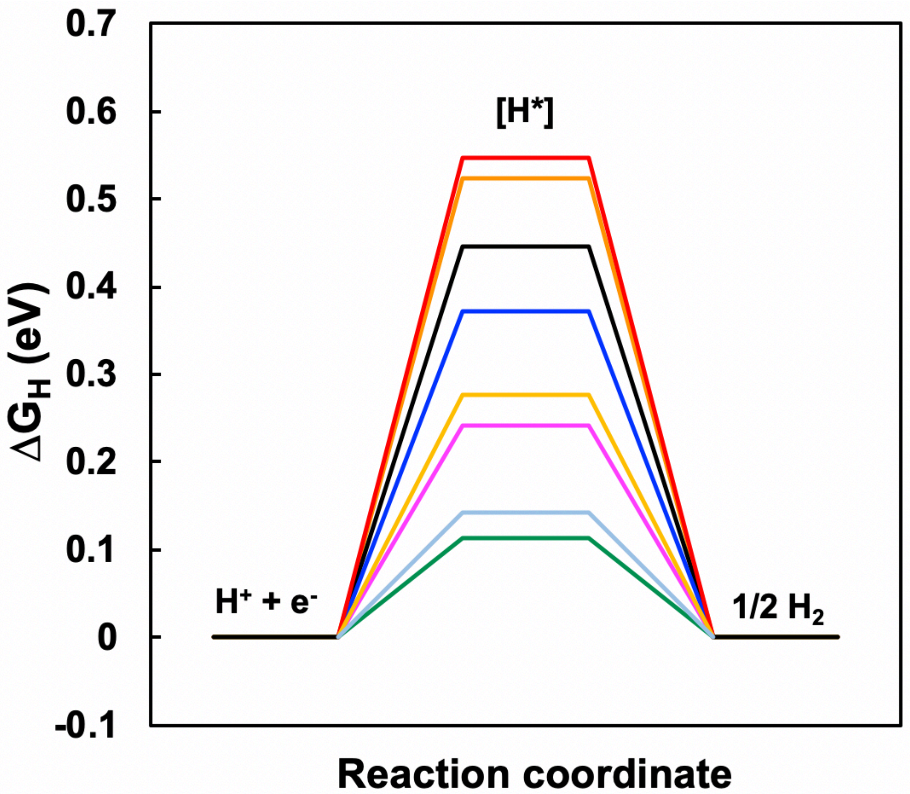


Color code	orange	magenta
Active site name	Bridge	3-fold

- When a ligand is removed, a new active site (bridge) is exposed.
- 3-fold site usually serves as active site on intact surface, while bridge site can be more active on dethiolated surface.

HER activity of nanoclusters

- Hydrogen adsorption free energy diagram and active sites



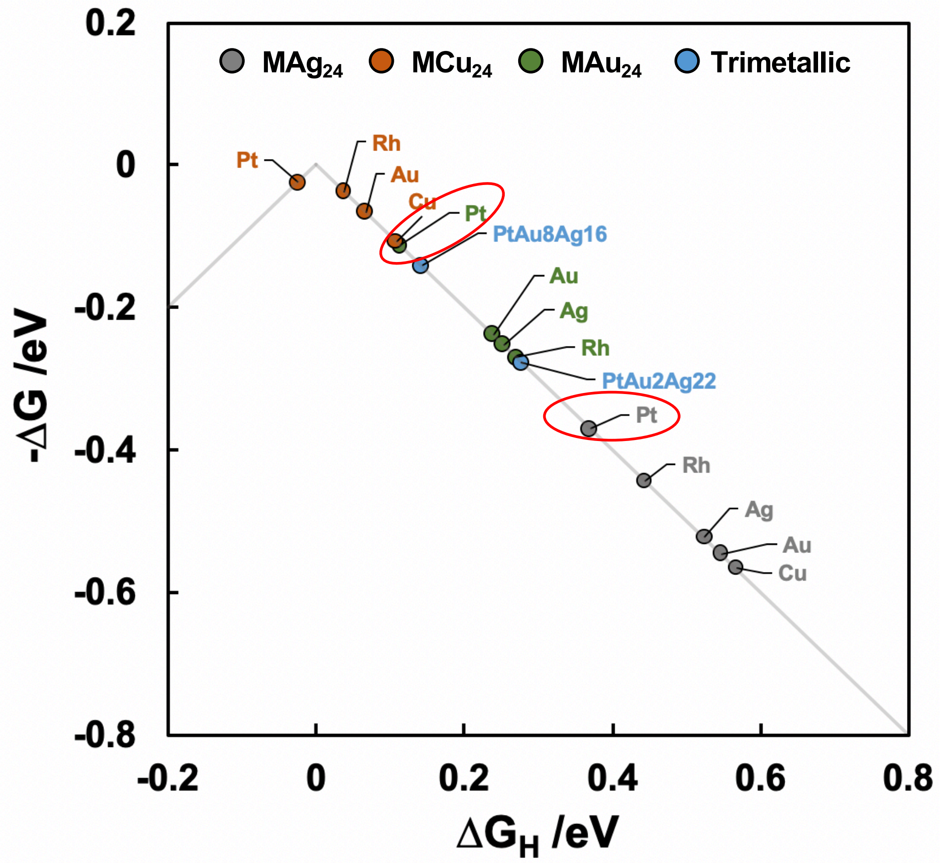
Surface	ΔG_H (eV)	Active site
$PtAu_{24}$	0.11	Bridge
$PtAu_8Ag_{16}$	0.14	Bridge
Au_{25}	0.24	Bridge
$PtAu_2Ag_{22}$	0.28	3-fold
$PtAg_{24}$	0.37	3-fold
$Pd(H)Ag_{24}$	0.45	Bridge
Ag_{25}	0.52	Bridge
$AuAg_{24}$	0.55	Bridge

$PtAu_{24}$ ~ $PtAu_8Ag_{16}$ > $PtAu_2Ag_{22}$ > $PtAg_{24}$ > $Pd(H)Ag_{24}$ > $AuAg_{24}$ ~ Ag_{25}

- Calculated ΔG_H values show that has $PtAu_8Ag_{16}$ as high HER activity as $PtAu_{24}$.

Volcano plot of HER

- **Volcano plot of HER on nanoclusters (1-ligand dethiolated surfaces)**



- As Au atoms are added into $PtAg_{24}$, ΔG_H moves toward top of volcano which means the optimum value. ($\Delta G_H=0$)
- Like pure TM catalysts, shell alloying can be a strategy for controlling catalytic activity.

Conclusions

- HER activity improves on $\mathbf{PtAg_{24}}$ compared to $\mathbf{Ag_{25}}$, but it has still much lower activity than $\mathbf{PtAu_{24}}$.
- HER activity of $\mathbf{PtAu_8Ag_{16}}$ is as high as that of $\mathbf{PtAu_{24}}$ even though it contains only a certain amount of Au atoms.
- Alloying, an important strategy for controlling catalytic activity in TM catalysts, can also be applied to nanoclusters.
- Using the volcano plot, we can design new shell alloying nanocluster catalysts in the future works.

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