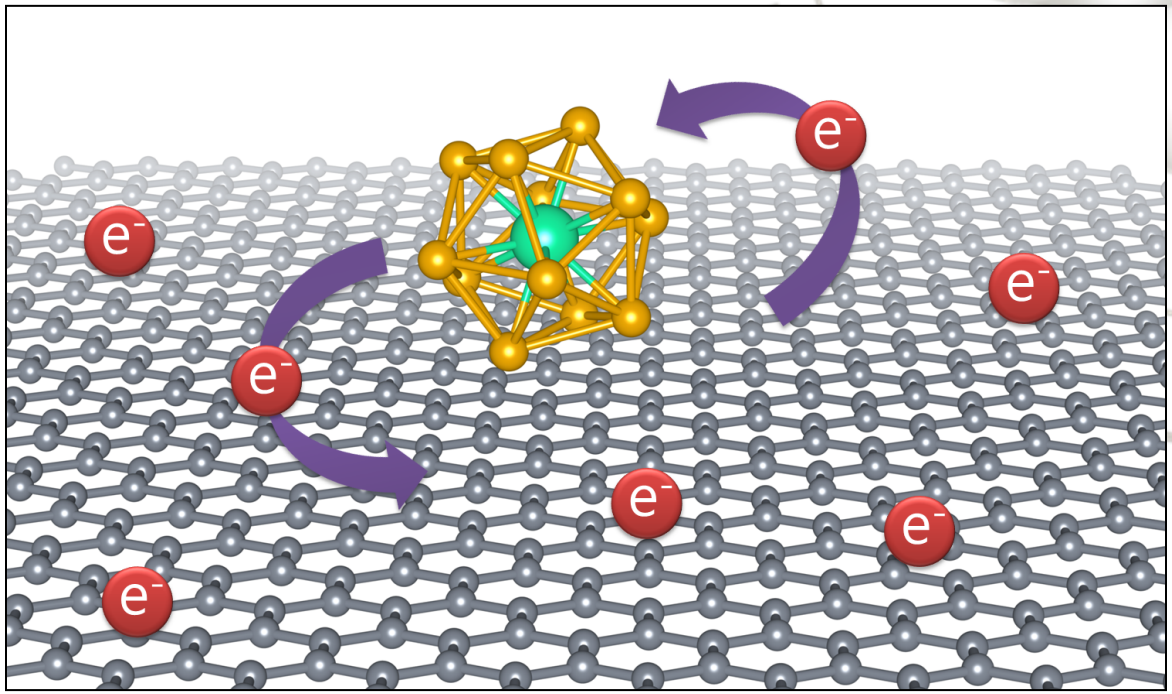
Magnetic Moment Tuning of Au Nanocluster and Its Application

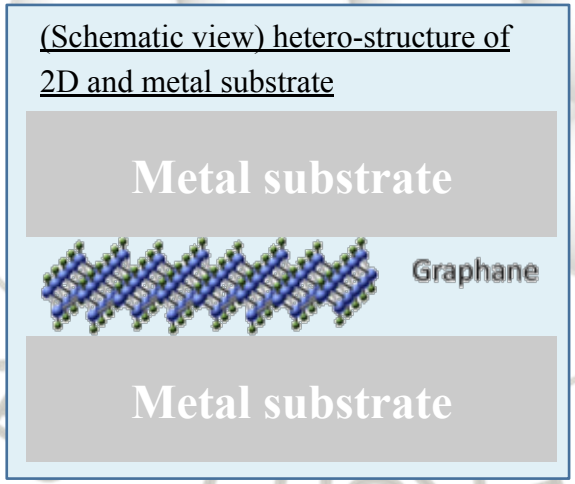


2014311544 Woosun Jang

2015. 06. 03

Intersection between magnetic materials and 2D

- What is the **intersection** between magnetic materials & 2D?
  - Magnetic materials
    - Mostly found in **metal** or **metal alloys**
    - Magnetic moment is a key property
  - 2D materials
    - Semiconducting surface, e.g. Si(111)
    - **2D materials**, e.g. TMDC, Phosphorene, Graphene

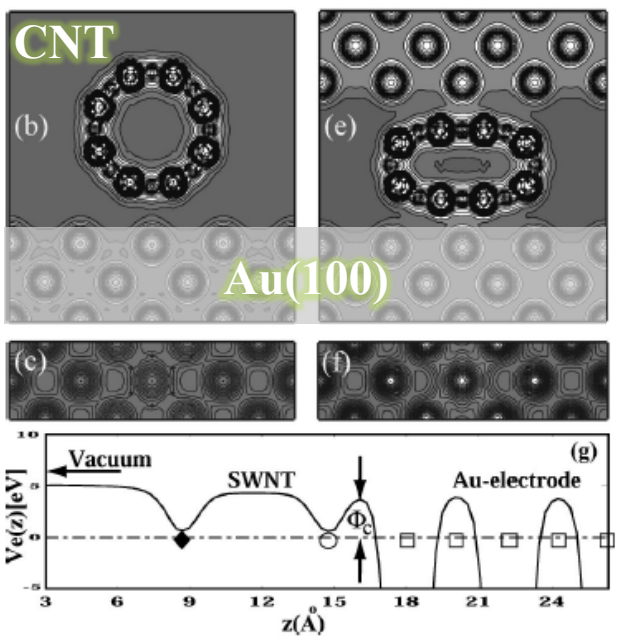


- How about joining metal alloys and 2D materials?
  - Think of following systems to tune the functionality of 2D and test the potential for applications
    - ✓2D material on metallic alloy surface support
    - ✓Intercalation of 2D material by inserting substrates between layers

Intersection between metal alloys and 2D material

- Criteria for selecting system
  - Interface between bimetallic system and 2D with one small and the other big system to satisfy the practical point of view
  - Tuning functionalities of the system by controlling composition and various dopants
  - Potential for possible applications

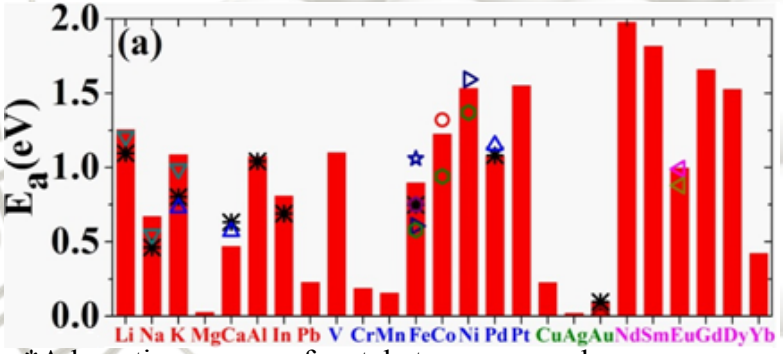
- Second idea group
  - Nanotube on metal substrate
    - ✓ But recently these systems are not so popular and already well investigated
  - Metal adsorption on 2D material
    - ✓ Overcrowded and not fresh



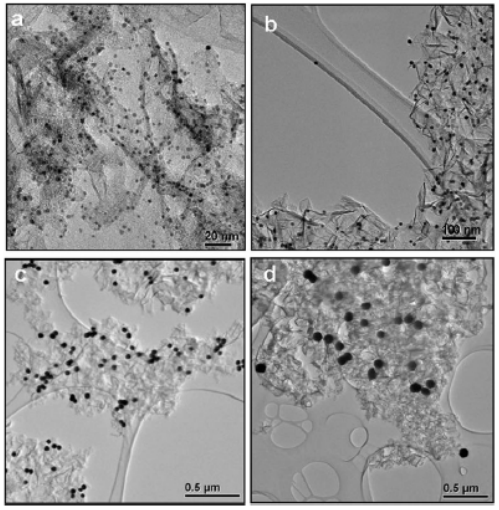
S. Dag *et al., Appl. Phys. Lett.*, **83**, 3180 (2003)

Intersection between metal alloys and 2D material

- Tuning functionality using metal adsorption on 2D
  - Interactions between metals and graphene
    - ✓ STRONG: rare earth, 3d-transtion metals, Pd, Pt
    - ✓ INTERMEDIATE: group I–IV metals
    - ✓ WEAK: **Au**, Mg (physisorption)
- How about Au nanocluster which have many applications when adsorbed on 2D nanosheets?
  - A lot of experimental results came out
    - ✓ Application) Interestingly these system can be applied into the medical area
    - ✓ Question) How atoms are not bound well but cluster can be bound?
  - Also only a few DFT results exists



*Adsorption energy of metal atoms on graphene



*TEM of Au nanoparticle on folded and overlapping graphene

X. Liu *et al., Crystals* ***3,*** 79 (2013)

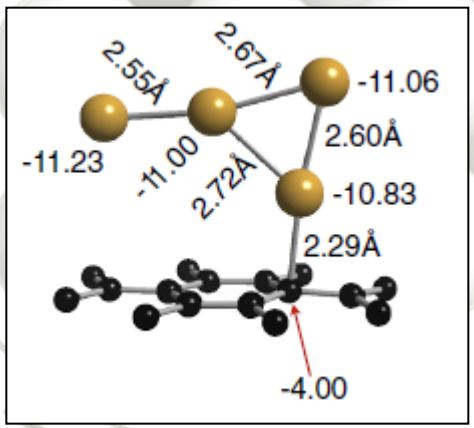
S. Dag *et al., Appl. Phys. Lett.,* **83**, 3180 (2003)

K. Jeon and Z. Lee, *Chem. Commun.,* **47**, 3610 (2011)

M. Amft *et al., J. Phys.: Condens. Matter* **23**, 205301 (2011)

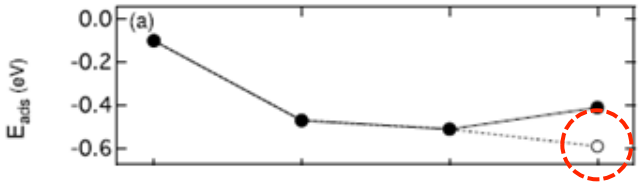
Intersection between metal alloys and 2D material

- Literature review & mapping stage
  - Contrast to ad-atoms on graphene, Au^{Y}_{4} has the highest E_{ads} of −0.59 eV (red dotted circle)
  - Density-of-states explained hybridization of Au s–d_{z2} cluster states with p_z states of carbon, which implies strong interaction between Au cluster and graphene

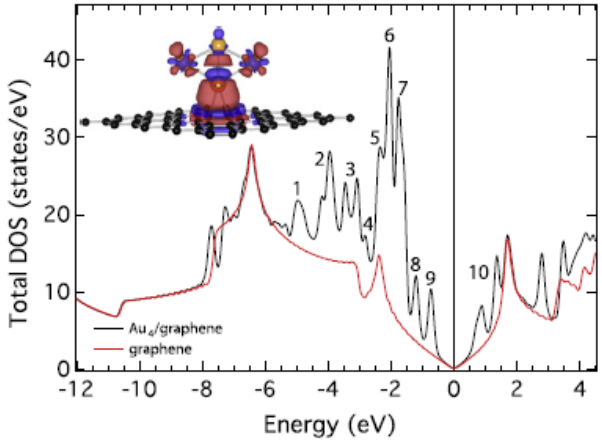


*Schematic view of Au^{Y}_{4}

- **Stability(binding energy) of heterostructure is confirmed**



Au clusters on 2D

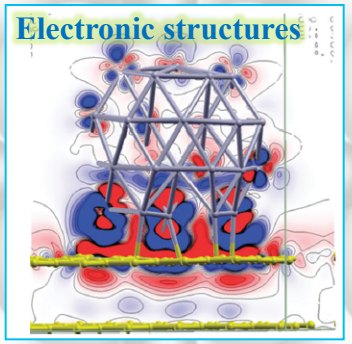


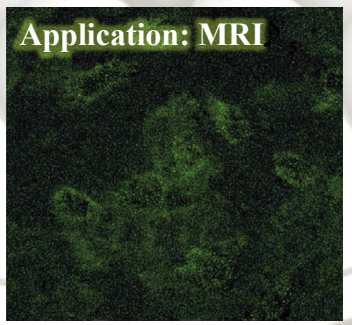
- Then how does the magnetic moment of Au nanocluster affected by 2D substrate?

M. Amft *et al., J. Phys.: Condens. Matter* **23**, 205301 (2011)

Magnetic moment in Au nanocluster

	Au	Gd@Au
Phosphorene	Semiconductor Metallic	Semiconductor **Magnetic moment tuning** Band gap tuning
Graphene	Metallic	Metallic system **Magnetic moment tuning**





- We investigated interface structures between Au based nanoclusters and 2D mat erials, which shows different electronic structure (metallic and semiconducting)
- By placing Gd/Au cluster on 2D nanosheets, we can try to tune magnetic mome nt and also HOMO-LUMO states
- We are interested in following properties: Charge transferring between composit es, Electronic structures and Magnetic moments

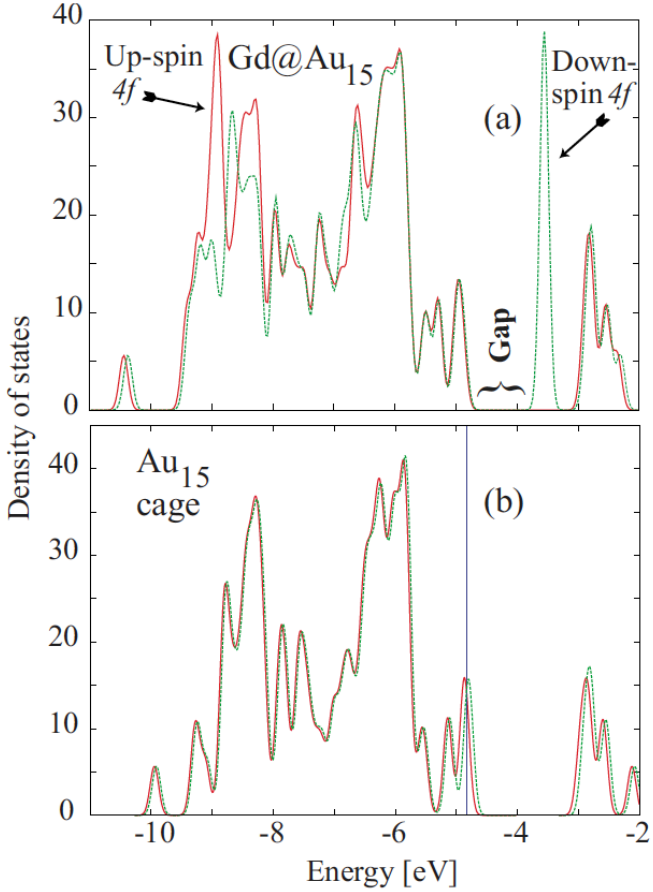
  (e.g. $\Delta\rho$, density of states, HOMO-LUMO gap),

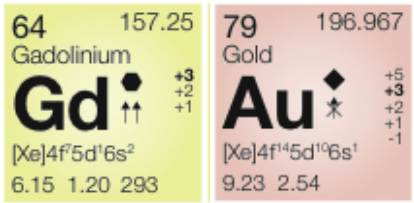
Angew. Chem. Int. Ed. 2011, 50, 11644; *Phys. Chem. Chem. Phys.*, 2013, **15**, 11950

Gd@Au nanocluster research examples

Example 1 : HOMO – LUMO gap tuning

- By doping Gd in Au_{15} cage structure, tuning of HOMO-LUMO gap was done
- Because of electrons in Gd 4f orbital, magnetic moment of $Gd@Au_{15}$ was strongly increased
- Also, hybridization of occupied Gd 4f and Au 5d stabilized whole nanocluster
- Unoccupied holes near HOMO level was filled by trivalent Gd, finally to stabilize



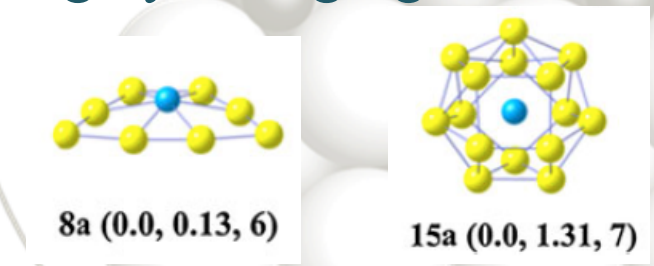


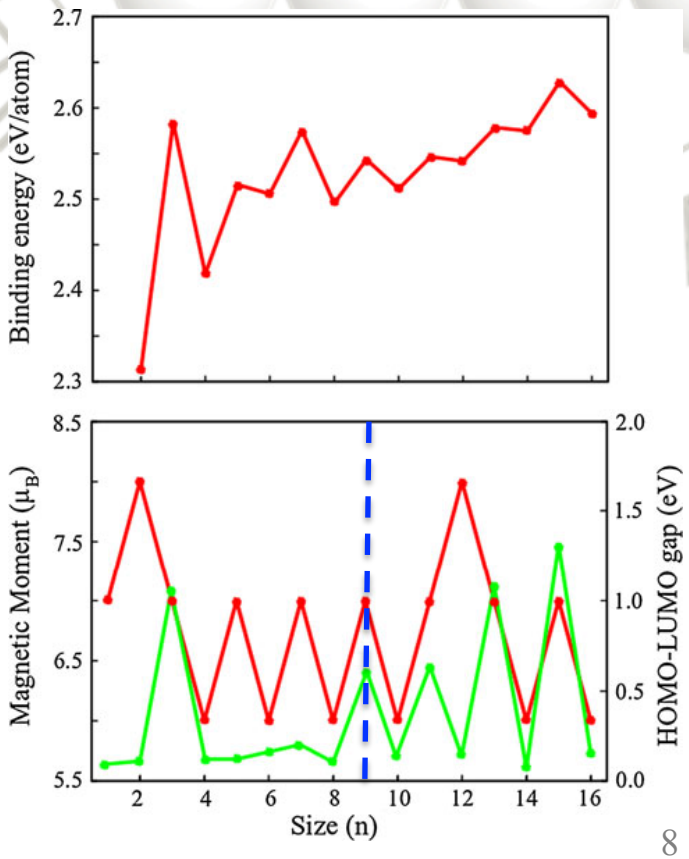
B. D. Yadav and V. Kumar, *Appl. Phys. Lett.*, **97**, 133701 (2010)

Gd@Au nanocluster research examples

Example 2 : Gap and magnetic moment tuning by changing # of Au

- Changing the number of Au atom consisting nanocluster made different structure, leading to change in magnetic moment and HOMO-LUMO gap
- By doping Gd in Au nanocluster, binding energy was greatly increased, implying that the Gd dopant stabilizes the structure
- Atoms under 9 formed plannar cluster, while the others formed distorted polyhedron cluster
- Magnetic moment was affected by electrons at Gd 4*f* orbital, while the binding energy effected by electrons at 5*d* and 6*s* orbital to fill out unfilled holes near HOMO level



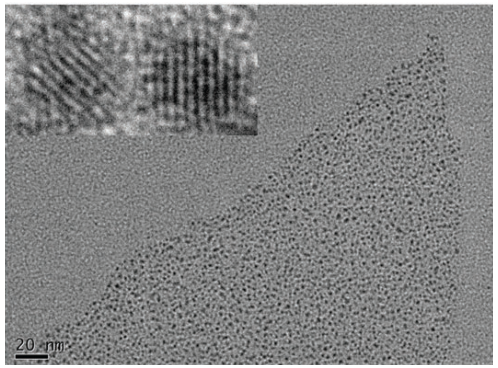


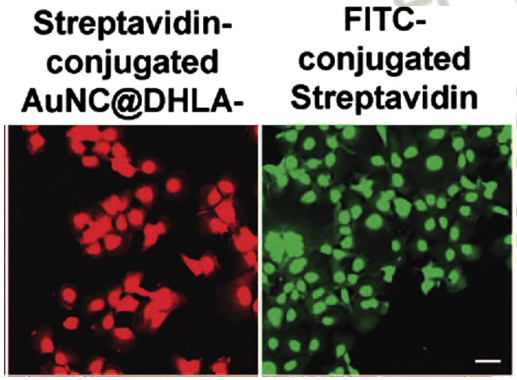
P. P. Shinde, B. D. Yadav and V. Kumar, *J. Mater. Sci.*, **47**, 7642 (2012)

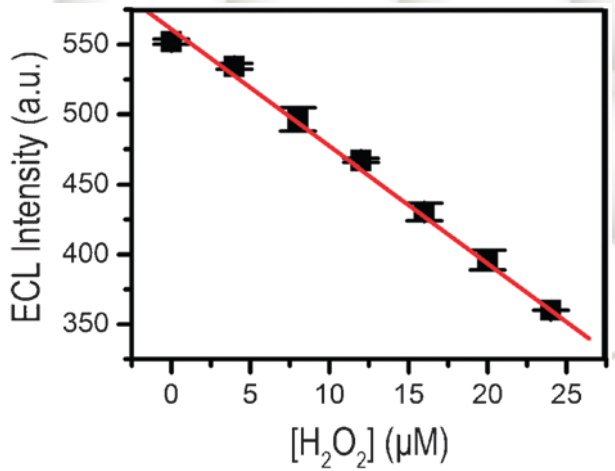
Au nanocluster on 2D

Application : Au nanocluster on graphene – Sensors

- Experimentally, there was a successful case of Au nanocluster deposited on graphene

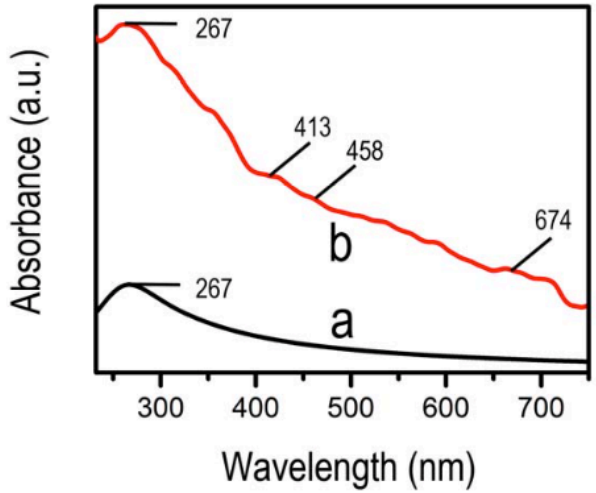






- These Au nanoclusters on graphene was able to detect H_2O_2 and shows luminescence

- Even for absorbance for UV to visible light range, Au nanocluster greatly increased its rate, showing the possibility for utilizing as photosensor



Y. Chen *et al., Chem. Commun.*, **47**, 11733 (2011)

Idea proposal: Expected output

Gd@Au nanocluster on 2D material

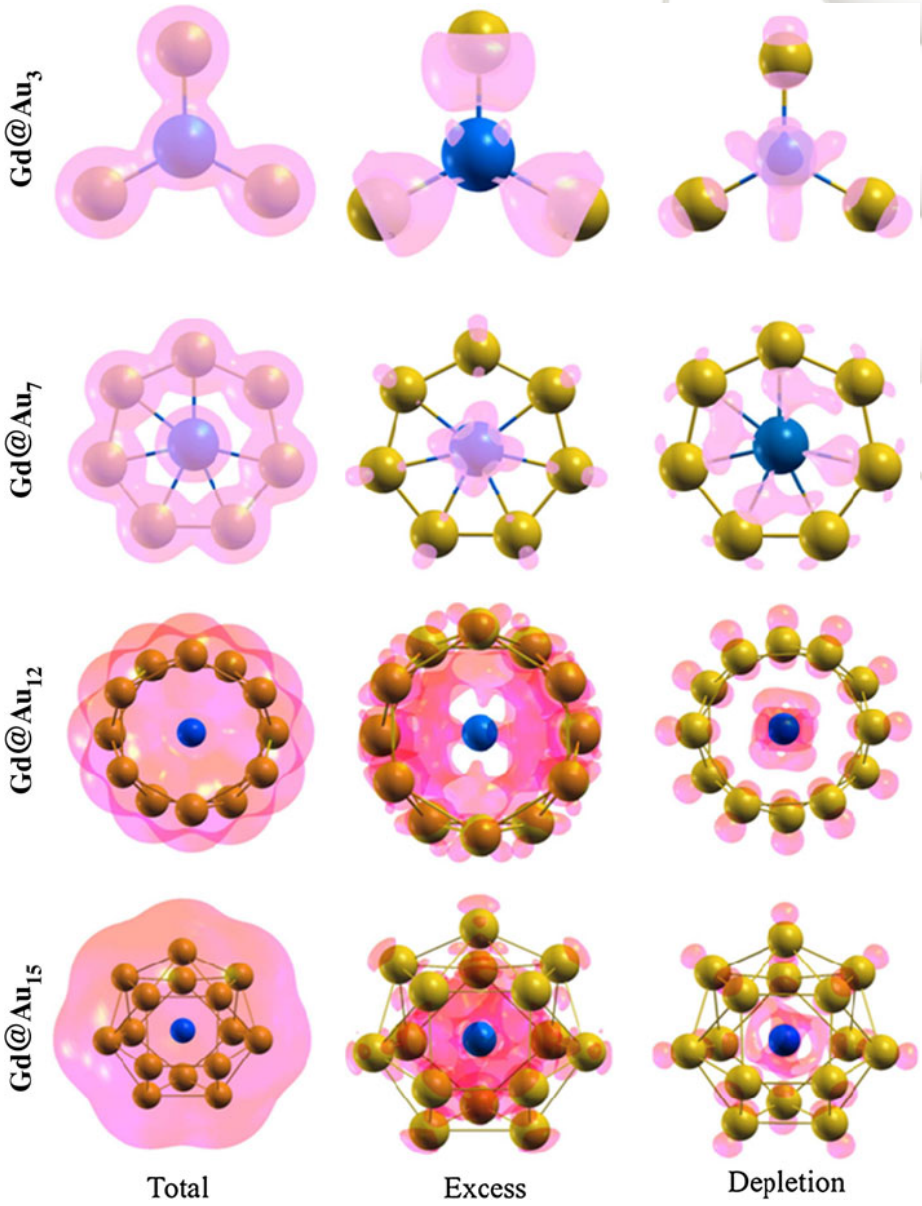
- By reviewing previous works, we concluded that various properties including magnetic moments and HOMO-LUMO gap of Au nanocluster can be tuned
- This change of magnetic moment and HOMO-LUMO gap expected to increase the efficiency of sensors and imaging medium
- To successfully achieve required properties, we first try to find appropriate shape of nanocluster by changing the number of Au atom consisting nanocluster
- Finally, by doping Au nanocluster, we greatly increase the efficiency of currently used Au nanocluster
- Even by changing 2D substrate instead of graphene, we think that it will help Gd@Au nanocluster successfully achieve required standards

Summary

- We investigated interface structures of Au based nanoclusters on two 2D materials showing different electronic structure
- Regarding to literature review, we are interested in following properties which is required for real applications like biosensor and photosensor: Charge transfer, HOMO-LUMO gap, Magnetic moments
- With this backgrounds, we proposed new ideas with expected outputs
  - By changing the number of Au atoms forming nanocluster, we try to improve properties mentioned above
  - Doping Gd in Au nanocluster deposited on 2D sheets, we try to tune magnetic moments and HOMO-LUMO gap
  - Finally by substituting the 2D substrate from graphene, we expect to greatly improve the efficiency of applications


Thank You!

Charge transferring between Gd and Au cluster



Charge transferring between Gd and Au cluster