Comparison of the Stability of 2H Nanosurfaces by the Adsorption of Small Molecules: A DFT Study

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ABSTRACT

Density functional theory (DFT) calculations were carried out to understand the structural stability of 2D nanosheets of gold and silver in hexagonal phase of 2H by the adsorption of small molecules. In this work, we have obtained the bonding and adsorption properties of such small molecules as H$_2$O, H$_2$O$_2$, and C$_2$H$_5$OH on 2H phase of gold and silver nanosurfaces, through DFT method using Quantum Expresso (QE) code. The high absorption energy values of (-2.45 eV, -2.46 eV, -2.41 eV) for H$_2$O, H$_2$O$_2$, and C$_2$H$_5$OH molecules on 2H-Au surfaces, respectively obtained than that of 2H-silver surfaces that the interaction between small molecules and both 2H nanosurfaces corresponds to physisorption. However, during the adsorption, the gold surface in the 2H phase (2H-Au) seems to preserve its atomic structure, while 2H-Ag surface changes from 2H to the fcc structure. Based on the analysis of electronic and physicochemical properties, the composite systems of 2H-gold/2H-silver-small molecules exhibit semiconductor behaviour. While 2H-Ag surfaces have short recovery time values for hydrogen peroxide (H$_2$O$_2$), this time is quite long for 2H-Au surfaces. Because of the long recovery time, Au-2H reported surfaces can be a candidate for possible applications of viral capture. Thus, the reported results are significant, and they would stimulate the experimental and further studies.

Keywords: 2H-Gold, 2H-Silver, nanosheets, Water, Ethanol, Hydrogen Peroxide, Anti-Viral 2D-Materials

I. INTRODUCTION

Recently, the great progress has been made in biomedical, biological, and chemical sciences; etc., owing to their size dependent properties [1], structural and electronic properties [2,3,4]. Also, a specific group of two-dimensional (2D) nanomaterials has drawn attention for physicochemical properties and extensive different applications [5,6,7]. Despite the increasing interest, there are still unknown areas.
Due to its tunable physical and chemical properties, humanity has long been interested in gold and silver for ages. Also, especially noble metals in nanomaterials [8,9] like gold (Au) and silver (Ag) the size affects the physical, chemical and mechanical properties of materials. Not only as enhancing the activity of drugs because of its antimicrobial properties but also surface plasmon resonance property makes it top materials as biosensor [1,10]. Additionally, the silver has biomedical potentials such as drug delivery, medical imaging, antibacterial agent [11,12] and molecular diagnostics [13]. Gold and silver nanoparticles have an antiviral activity against many types of bacteria [14] and fungi [15], and intracellular gene regulation [16].

Gold nanomaterials generally adopt thermodynamically stable face-centered cubic (fcc) phase [17,18]. Silver clusters smaller than 5 nm adopt icosahedral structure, while the clusters larger than 9 nm adopt face-centered cubic structure [19]. In its bulk form, the equilibrium crystal structure for silver is fcc but in nanosize other polytypes of silver have been observed [20].

2H phase nanomaterials are yet to be realized, so in this paper we study the behaviour of one of gold phase Au-2H [17] and one of the polytype of the silver Ag-2H [19] to explore their intriguing properties, the adsorption properties of small molecules on 2D nanosheet and other physicochemical properties with aim of the potential applications.

II. METHODS AND MATERIAL

All calculations we employed were performed using the Quantum-ESPRESSO suite of electronic structure codes, version 5.2.1 [21]. The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) [22] has been used for the exchange-correlation, and to deal with electron-ion core interactions the projected augmented wave method (PAW) has been employed; namely, Au.pbe-n-kjpaw_psl.1.0.0.UPF for gold, Ag.pbe-n-kjpaw_psl.1.0.0.UPF for silver, C.pbe-n-kjpaw_psl.1.0.0.UPF for carbon, O.pbe-n-kjpaw_psl.1.0.0.UPF for oxygen and H.pbe-kjpaw.UPF for hydrogen. These pseudopotentials are available from the Quantum ESPRESSO web site [21]. A cutoff energy of 45 Ry was selected for the plane waves used to expand the Kohn-Sham orbitals, and 350 Ry for the charge density. The Brillouin-zone was sampled with a $3 \times 3 \times 1$ Monkhorst-Pack grid. van der Waals corrections has been taken into account using the Grimme-D3 method [21].

![Figure 1](image_url)

Figure 1: Optimized structures of (a) Au$_{2H}$ and Ag$_{2H}$ (top and side view) and (b) H$_2$O, H$_2$O$_2$, and C$_2$H$_5$OH molecules, respectively. Gold, silver, carbon, oxygen and hydrogen atoms are represented by yellow, gray, brown, red and pink spheres, respectively.

Firstly, 2H phase of gold and silver nanosheets are created with the VESTA programme and isolated Au-2H and Ag-2H nanosheets and the other small molecules, H$_2$O, H$_2$O$_2$, C$_2$H$_5$OH, are optimized using Quantum-ESPRESSO. Then the small molecules are
placed the preferred position on the Au-2H and Ag-2H nanosheets. While the structure of Au-2H has 10 atoms, the structure of Ag-2H nanosheet contains 12 atoms. 2D Au-2H and 2D Ag-2H nanosheets, and small molecules, H₂O, H₂O₂, C₆H₅OH, are shown in Fig. 1.

Adsorption energies were computed as follows:

$$E_{ads} = E(\text{complex}) - E(\text{nanosheet}) - E(\text{molecule})$$

where $E(\text{nanosheet})$, $E(\text{molecule})$ and $E(\text{complex})$ are the total energies of nanosheet, molecule and complex system including nanosheet with the molecule. Before the optimization performed, the structures are shown in Fig. 2.

![Figure 2: Top views of structures for H₂O, H₂O₂, and C₆H₅OH molecules on (a) Au₂H and (b) Ag₂H nanosheet before the optimization, respectively.](image)

The electrical conductivity and sensitivity of a material can be determined as:

$$\sigma \propto \exp\left(-E_g/2k_BT\right)$$

where $E_g$ is the bandgap, $T$ is the temperature, $k_B$ is the Boltzmann constant and the sensitivity of a material as:

$$%S = \left|\frac{\sigma_{\text{nanosheet}} - \sigma_{\text{complex}}}{\sigma_{\text{nanosheet}}}\right| \times 100$$

where $\sigma_{\text{nanosheet}}$ is the conductivity of nanosheet, $\sigma_{\text{complex}}$ is the conductivity of complex system.

Band gap energy and the percentage change of energy gap can be expressed as:

$$E_g = E_L - E_H$$

$$%\Delta E_g = 100 \times \frac{(E_g(\text{complex}) - E_g(\text{nanosheet}))}{E_g(\text{nanosheet})}$$

where $E_L$ is lowest unoccupied molecular orbital (LUMO), $E_H$ is highest occupied molecular orbital (HOMO) and %$\Delta E_g$ is the percentage change of energy gap $E_g$ of complex after adsorption with respect to the bare nanosheet.

The main purpose of the density functional theory of chemical reactivity is that links of the chemical potential of DFT with the first derivative of the energy with respect to the number of electrons. Hence the negative of the electronegativity is the remark established by Parr, Donnelly, Levy and Palke, the negative of the electronegativity ($\chi$) [23,24];

$$\mu = \left(\frac{\partial E}{\partial N}\right)_V = -\chi$$

The parameters such as electronegativity ($\chi$), global hardness ($\eta$), chemical potential ($\mu$), global electrophilic index ($\omega$), spherical softness ($S$), nucleofugality $\Delta E_n$ and electrofugality $\Delta E_e$ and electronic charge ($\Delta N_{\text{max}}$) are related to HOMO and LUMO energies.

The recovery time ($\tau$) can be described as follows:

$$\tau = \frac{1}{\nu} \exp\left(-\frac{E_{ads}}{k_BT}\right)$$

where $\nu$ is the attempt frequency, $k$ is the Boltzmann constant and $T$ is temperature. Under UV vacuum light ($\nu \approx 3 \times 10^{12} \text{ sn}^{-1}$) at 298K and UV radiation ($\nu \approx 10^{16} \text{ sn}^{-1}$) at 398K is applied to recover of the molecule from the studied surfaces [25].
III. RESULTS AND DISCUSSION

Not only surface disinfection properties but also its anti-viral properties like hydrogen peroxide, ethanol is used in hospitals and medical practices. Furthermore, there are many articles that have been studied about the water’s antibacterial and antiviral effectiveness. Therefore, we wanted to compare and discuss the antiviral features of these molecules and focused on the adsorption of them on nanosheet.

After the optimization, the zigzag structure of the 2D nanosheet are not preserved and turned into more stable phase in all complexes represented in Fig. 3.

The optimized geometries of the complexes and the distances of gold and silver atoms on the nanosheets in all complex structures are shown in Fig. 4. After the interaction with \( \text{H}_2\text{O} \), \( \text{H}_2\text{O}_2 \), and \( \text{C}_2\text{H}_5\text{OH} \) molecules, the nanosheets turned into stable phase face-centered cubic structure and the distances for all complex structures change between 2.62-2.87 Å. The lattice constants for gold and silver are 4.0796 Å and 4.0855 Å in Inorganic Crystal Structure Database (ICSD). If the distances between atoms are calculated for fcc structure of gold and silver by ICSD data, the distances are 2.8847 Å and 2.8888 Å for gold and silver, respectively.

Figure 3: The examples of changing structure of (a) Au\(_{2\text{H}}\) and (b) Ag\(_{2\text{H}}\) nanosheets after the interaction with \( \text{H}_2\text{O} \), \( \text{H}_2\text{O}_2 \), and \( \text{C}_2\text{H}_5\text{OH} \), respectively.
After the optimization the calculated adsorption energy values in eV are shown in Tab. 1. 2D Au-2H nanosheet adsorbs molecules more than 2D-Ag-2H nanosheet. Negative adsorption energy suggests that the adsorption process is exothermic.

**Table 1** The calculated adsorption energy values (in eV) of H$_2$O, H$_2$O$_2$, C$_2$H$_5$OH on 2D Au$_{2H}$ and Ag$_{2H}$ nanosheets.

| Structure       | Energy values (eV) |
|-----------------|--------------------|
|                 | E$_{ads}$(H$_2$O)$_{Au2H}$ | -2.44635 |
|                 | E$_{ads}$(H$_2$O)$_2$$_{Au2H}$ | -2.46071 |
|                 | E$_{ads}$(C$_2$H$_5$OH)$_{Au2H}$ | -2.40893 |
|                 | E$_{ads}$(H$_2$O)$_{Ag2H}$ | -0.73425 |
|                 | E$_{ads}$(H$_2$O)$_2$$_{Ag2H}$ | -0.71338 |
|                 | E$_{ads}$(C$_2$H$_5$OH)$_{Ag2H}$ | -0.77370 |

While 2D Au-2H nanosheet adsorbs the most hydrogen peroxide while 2D Ag-2H adsorbs it the least. The same goes for ethanol molecule that the ethanol molecule is adsorbed the most by the 2D Ag-2H but the least by 2D Au-2H.

To calculate the electronic properties and physicochemical properties, the energy values of HOMO and LUMO are measured, presented in Tab. 2. The sign of $\Delta E_g$ shows the increase or decrease in $E_g$, so we employed the $|\Delta E_g|$ absolute value.

**Table 2** HOMO (E$_H$), LUMO (E$_L$) and Fermi (E$_F$) energy values (in eV) of H$_2$O, H$_2$O$_2$, and C$_2$H$_5$OH on 2D Au$_{2H}$ and 2D Ag$_{2H}$ nanosheets.

| Structure | E$_H$ (eV) | E$_L$ (eV) | E$_F$ (eV) |
|-----------|------------|------------|------------|
| Au$_{2H}$ | -3.7717    | -3.1882    | -3.4799    |
| Ag$_{2H}$ | -3.2647    | -2.4462    | -2.8554    |
| H$_2$O     | -3.5807    | -2.3489    | -2.9648    |
| H$_2$O$_2$ | -3.4959    | -2.3883    | -2.9421    |
| C$_2$H$_5$OH | -4.1865 | -3.1613    | -3.6739    |
|           | -3.1030    | -3.0004    | -3.0517    |
|           | -3.2254    | -1.9761    | -2.6007    |
|           | -2.9421    | -1.9842    | -2.7488    |
|           | -111.1054  | 114.4045   | 86.8418    |
|           | 35.3207    | 75.6984    | -87.4649   |
|           | 75.6984    | 114.4045   | 86.8418    |
|           | 111.1054   | -87.4649   | 86.8418    |

Figure 4: After the optimization the distances between (a) gold atoms on Au2H nanosheet and (b) silver atoms on Ag2H nanosheet.
Although the minimal adsorption of ethanol by 2D Au-2H nanosheet, it caused the largest enhancer band gap to change on Au$_{2H}$-C$_2$H$_5$OH. The band gap of complex Ag$_{2H}$-H$_2$O$_2$ decreased after the adsorption changed the band gap in a negative way. The band gap of Ag$_{2H}$-C$_2$H$_5$OH is less than the isolated 2H Ag nanosheet’s.  

In order to use the 2D nanosheets as a means in biomedical applications, it is crucial to ensure that the molecule can be captured and retained by the surface for a very long time.

| Structure | Ag$_{2H}$ | Au$_{2H}$-H$_2$O | Ag$_{2H}$-H$_2$O | Au$_{2H}$-H$_2$O$_2$ | Au$_{2H}$-C$_2$H$_5$OH | Ag$_{2H}$-C$_2$H$_5$OH |
|-----------|-----------|------------------|------------------|----------------------|-----------------------|-----------------------|
| μ         | -3.47995  | -2.8554          | -2.96480         | -3.67390             | -3.0517               | -2.60075              |
| S         | 1.71380   | 1.22175          | 0.81182          | 0.97542              | 9.7466               | 0.80045               |
| η         | 0.29175   | 0.40925          | 0.61590          | 0.51260              | 0.0513               | 0.62465               |
| ω         | 20.75416  | 9.96163          | 7.13593          | 13.16576             | 90.7687              | 5.41415               |
| ΔE$_n$    | 24.37998  | 13.02170         | 10.40868         | 17.09596             | 93.8470              | 8.32722               |
| ΔE$_s$    | 17.42008  | 7.3108           | 4.47908          | 9.74816              | 87.7427              | 3.12573               |
| ΔN$_{max}$| 11.92785  | 6.9773           | 4.81377          | 7.16719              | 59.4873              | 4.16353               |

The calculated recovery time are too small to desorb H$_2$O, H$_2$O$_2$, C$_2$H$_5$OH from Ag-2H nanosheet. Nonetheless, the recovery times for Au-2H nanosheet is too long (~10$^{21}$ years).

| Structure | τ$_{UV}$ vacuum light | τ$_{UV}$ radiation |
|-----------|-----------------------|--------------------|
| Au-2H-H$_2$O | 7.8539 x 10$^{28}$ | 2.1942 x 10$^{25}$ |
| Ag-2H-H$_2$O | 0.8716 | 0.0002 |
| Au-2H-H$_2$O$_2$ | 1.3735 x 10$^{29}$ | 2.9608 x 10$^{24}$ |
| Ag-2H-H$_2$O$_2$ | 0.3867 | 9.6642 x 10$^{5}$ |
| Au-2H-C$_2$H$_5$OH | 1.8290 x 10$^{28}$ | 1.2593 x 10$^{25}$ |
| Ag-2H-C$_2$H$_5$OH | 4.0505 | 0.0010 |

IV. CONCLUSION

In this study, DFT calculations are performed to determine the electronic structure properties and the dynamics of H$_2$O, H$_2$O$_2$ and C$_2$H$_5$OH placed on the top of the 2D Au-2H and 2D Ag-2H nanosheets. The nanosheets with molecules after the optimization show us that the structure of 2H nanosheets turn into the more stable face-centered cubic structure. 2D Au-
2H hcp structure doesn’t seem to change because the (111)$_{fcc}$ correspond with (0001)$_{hcp}$ surface. Negative adsorption energy suggests that the adsorption process of small molecules is exothermic. Also, the band gap of all complexes except Ag$_2$H$_2$O$_2$ increased. Au-2H nanosheet can be a candidate for possible applications for viral capture.

V. REFERENCES

[1]. Sonika Dawadi, Saurav Katuwal, Aakash Gupta, Uttam Lamichhane, Ranjita Thapa, Shankar Jaisi, Ganesh Kamichhane, Deval Prasad Bhattarai, and Niranjan Parajuli. 2021. Current Research on Silver Nanoparticles: Synthesis, Characterization, and Applications, Journal of Nanomaterials. (Feb 2021)

[2]. Angel Humanez Tobar, Jean F. Murillo G, Cesar Ortega Lopez, Jairo Arbey Rodriguez Martinez, and Miguel J. Espitia R. 2020. Study of structural and electronic properties of three- and two-dimensional transition-metal dioxides using first-principles calculations, Computational Condensed Matter, 25

[3]. Christian a. Celaya, Mourad Bounjah, Miguel Reina, Jesus Muniz, and Luis Enrique Sansores. 2021. Theoretical study of Au$_{20}$/WS$_2$ composite material as a potential candidate for the capture of XO (X=C, N, S) gases, Computational Condensed Matter, 28

[4]. Pooja Kapoor, Munish Sharma, A. Kumar, S. K. Chandel, and P. K. Ahluwalia. 2017. Structural, electronic and mechanical properties of alloyed Au-Cu monolayer, AIP Conference Proceedings 1832

[5]. Ye Chen, Zhanxi Fan, Zhicheng Zhang, Wenxin Niu, Cuiling Li, Nailing Yang, Bo Chan and Hua Zhang. 2018. Two-Dimensional Metal Nanomaterials: Synthesis, Properties, and Applications, Chemical Reviews, 118, 13, 6409-6455

[6]. Chaoliang Tan, Xiehong Cao, Xue-Jun Wu, Qiyuan He, Jian Yang, Xiao Zhang, Junze Chen, Wei Zhao, Shikui Han, Gwang-Hyeon Nam, Melinda Sindoro, and Hua Zhang. 2017. Recent Advances in Ultrathin Two-Dimensional Nanomaterials, Chemical Reviews, 117, 9, 6225-6331

[7]. Hua Zhang. 2015. Ultrathin Two-Dimensional Nanomaterials, ACS Nano, 9, 10, 9451–9469

[8]. Pooja Kapoor, Jagdish Kumar, Arun Kumar, Ashok Kumar, and P. K. Ahluwalia. 2017. Electronic, Mechanical, and Dielectric Properties of Two-Dimensional Atomic Layers of Noble Metals, Journal of Electronic Materials, 46

[9]. Pooja Kapoor, Arun Kumar, Munish Sharma, Jagdish Kumar, Ashok Kumar, and P. K. Ahluwalia. 2018. Alloyed monolayers of Cu, Ag, au and Pt in hexagonal phase: A comprehensive first principles study, Materials Science and Engineering: B, 228, 84-90

[10]. Shao Su, Qian Sun, Xiaodan Gu, Yongqiang Xu, Jianlei Shen, Dan Zhu, Jie Chao, Chunhai Fan, and Lianhui Wang. 2019. Two-dimensional nanomaterials for biosensing applications, TRAC Trends in Analytical Chemistry, (Oct 2019)

[11]. Svitlana Chernousova, Matthias Epple. 2013. Silver as antibacterial agent: ion, nanoparticle, and metal, Angewandte International Edition Chemie, 52, 1636-1653

[12]. Wen-Ru Li, Xiao-Bao Xie, Qing-Shan Shi, Hai-Yan Zeng, You-Sheng Ou- Yang, Yi-Ben Chen.2010. Antibacterial activity and mechanism of silver nanoparticles on Escherichia coli, Appl. Microbiol Biotechnology, 85, 1115-1122

[13]. Yin IX, Zhang J., Zhao IS, Mei ML, Li Q, Chu CH. 2020. The antibacterial Mechanism of Silver Nanoparticles and Its Application in Dentistry, International Journal of Nanomedicine, 15, 2555-2562
[14]. Jose Ruben Morones, Jose Luis Elechiguerra, Alejandra Camacho, Katherine Holt, Jun B Kouri, Jose Tapia Ramirez, and Miguel Jose Yacaman. 2005. The bactericidal effect of silver nanoparticles, Nanotechnology, 16, 2346–2353

[15]. Monali Gajbhiye, Jayendra Kesharwani, Avinash Ingle, Aniket Gade, Mahendra Rai. 2009. Fungus-mediated synthesis of silver nanoparticles and their activity against pathogenic fungi in combination with fluconazole, Nanomedicine, 5, 382-6

[16]. Nathaniel L Rosi, David A Gilijohann, C Shad Thaxton, Abigail K R Lytton-Jean, Min Su Han, and Chad A Mirkin. 2006. Oligonucleotide-modified gold nanoparticles for intracellular gene regulation, Science, 312, 1027–30

[17]. Zhanxi Fan, Michel Bosman, Zhiqi Huang, Ye Chen, Chongyi Ling, Lin Wu, Yuriy A. Akimov, Robert Laskowski, Bo Chen, Peter Ercius, Jian Hua Zhang. 2015. Ultrathin Two-Dimensional Nanomaterials, ACS Nano, 9, 10, 9451-9469

[18]. Pooja Kapoor, Jagdish Kumar, Arun Kumar, Ashok Kumar, and P. K. Ahluwalia. 2017. Electronic, Mechanical, and Dielectric Properties of Two-Dimensional Atomic Layers of Noble Metals, Journal of Electronic Materials, 46

[19]. Pooja Kapoor, Arun Kumar, Munish Sharma, Jagdish Kumar, Ashok Kumar, and P. K. Ahluwalia. 2018. Alloyed monolayers of Cu, Ag, au and Pt in hexagonal phase: A comprehensive first principles study, Materials Science and Engineering: B, 228, 84-90

[20]. Shao Su, Qian Sun, Xiaodian Gu, Yongqiang Xu, Jianlei Shen, Dan Zhu, Jie Chao, Chunhai Fan, and Lianhui Wang. 2019. Two-dimensional nanomaterials for biosensing applications, TRAC Trends in Analytical Chemistry, (Oct 2019)

[21]. Svitlana Chernousova, Matthias Eppe. 2013. Silver as antibacterial agent: ion, nanoparticle, and metal, Angewandte International Edition Chemie, 52, 1636-1653

[22]. Wen-Ru Li, Xiao-Bao Xie, Qing-Shan Shi, Hai-Yan Zeng, You-Sheng Ou- Yang, Yi-Ben Chen. 2010. Antibacterial activity and mechanism of silver nanoparticles on Escherichia coli, Appl. Microbiol Biotechnology, 85, 1115-1122

[23]. Yin IX, Zhang J., Zhao IS, Mei ML, Li Q, Chu CH. 2020. The antibacterial Mechanism of Silver Nanoparticles and Its Application in Dentistry, International Journal of Nanomedicine, 15, 2555-2562

[24]. Jose Ruben Morones, Jose Luis Elechiguerra, Alejandra Camacho, Katherine Holt, Jun B Kouri, Jose Tapia Ramirez, and Miguel Jose Yacaman. 2005. The bactericidal effect of silver nanoparticles, Nanotechnology, 16, 2346–2353

[25]. Monali Gajbhiye, Jayendra Kesharwani, Avinash Ingle, Aniket Gade, Mahendra Rai. 2009. Fungus-mediated synthesis of silver nanoparticles and their activity against pathogenic fungi in combination with fluconazole, Nanomedicine, 5, 382-6

[26]. Nathaniel L Rosi, David A Gilijohann, C Shad Thaxton, Abigail K R Lytton-Jean, Min Su Han, and Chad A Mirkin. 2006. Oligonucleotide-modified gold nanoparticles for intracellular gene regulation, Science, 312, 1027–30

[27]. Zhanxi Fan, Michel Bosman, Zhiqi Huang, Ye Chen, Chongyi Ling, Lin Wu, Yuriy A. Akimov, Robert Laskowski, Bo Chen, Peter Ercius, Jian

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