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# DFT calculations for single-atom confinement effects of noble metals on monolayer g-C<sub>3</sub>N<sub>4</sub> for photocatalytic applications†

 Cheng Yang,<sup>ab</sup> Zong-Yan Zhao,<sup>\*c</sup> Hai-Tang Wei,<sup>a</sup> Xi-Yu Deng<sup>a</sup> and Qing-Ju Liu<sup>ID \*a</sup>

Graphitic carbon nitride, as a very promising two-dimensional structure host for single atom catalysts (SACs), has been studied extensively due to its significant confinement effects of single atoms for photocatalytic applications. In this work, a systematic investigation of g-C<sub>3</sub>N<sub>4</sub> confining noble metal single atoms (NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>) will be performed by using DFT calculations. The geometric structure calculations indicate that the most favorable anchored sites for the NM<sub>1</sub> is located in the six-fold cavity, and the deformed wrinkle space of g-C<sub>3</sub>N<sub>4</sub> helps the NM<sub>1</sub> to be stabilized in the six-fold cavity. The electronic structure calculations show that the conduction band of NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> moved down and crossed through the Fermi level, resulting in narrowing the band gap of the NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>. Moreover, the confined NM<sub>1</sub> provide a new channel of charge transport between adjacent heptazine units, resulting in a longer lifetime of photo-generated carriers except Ru, Rh, Os and Ir atoms. Furthermore, the d-band centres of NM<sub>1</sub> in NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> show that Rh<sub>1</sub>@, Pd<sub>1</sub>@, Ir<sub>1</sub>@ and Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs may have better photocatalytic performance than other NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs. Finally, Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs are considered to have higher photocatalytic activity than other NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs. These results demonstrate that the confinement effects of noble metals on monolayer g-C<sub>3</sub>N<sub>4</sub> not only makes the single atom more stable to be anchored on g-C<sub>3</sub>N<sub>4</sub>, but also enhances the photocatalytic activity of the system through the synergistic effect between the confined NM<sub>1</sub> and the monolayer g-C<sub>3</sub>N<sub>4</sub>. These detailed research may provide theoretical support for engineers to prepare photocatalysts with higher activity.

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## 1. Introduction

Environmental pollution and the energy crisis caused by excessive use of fossil fuels are the two major problems that have seriously affected the sustainable development of human being in the world today. Catalytic technologies play a critical role in solving two above-mentioned problems, which have been extensively used in many fields, such as chemical industry, production,<sup>1,2</sup> clean energy technologies<sup>3,4</sup> and environmental treatment.<sup>5,6</sup> Traditional supported metal catalysts, especially noble metals, including ruthenium (Ru), rhodium (Rh), palladium (Pd), silver (Ag), osmium (Os), iridium (Ir), platinum (Pt), gold (Au), have excellent catalytic performance. Therefore, they

are applied in a wide range of heterogeneous catalysis fields.<sup>7-10</sup> As is well-known, heterogeneous catalysts have the advantages of a stable structure and easy separation of products. Meanwhile, they also have some weakness, such as the low metal utilization rate and the low catalyst efficiency, which leads to the wasting of noble metal resources, the increase of production costs and the catalysts to be bulky and heavy. In contrast, homogeneous catalysts have a large number of homogeneous single active sites, which make the catalysts show high catalytic activity and selectivity. However, low stability and difficult separation of products is homogeneous catalysts' Achilles heel. Fortunately, single-atom catalysts (SACs) that were first put forward by Zhang's group in 2011 (ref. 11) are provided with both advantages of heterogeneous and homogeneous catalysts and become the bridge and tie to link both up.<sup>12-14</sup> For the past few years, SACs with the unique electronic structure and unsaturated coordination environment have drawn extensive attention around the world and can be used effectively in many catalytic reactions due to their low noble metal loadings and high utilization rates of noble metal atoms.<sup>15-17</sup> Unfortunately, the specific surface area of noble metal particles increases dramatically with the decrease of the size of noble metal particles to single atom, resulting in a sharp increase in the free energy of the noble metal surface.<sup>18</sup> That is, it is very easy for

<sup>a</sup>School of Materials and Energy, National Center for International Research on Photoelectric and Energy Materials, Yunnan Key Laboratory for Micro/Nano Materials & Technology, Yunnan University, Kunming 650091, P. R. China. E-mail: qjliu@ynu.edu.cn; Fax: +86-871-65032713; Tel: +86-871-65032713

<sup>b</sup>School of Optoelectronic and Communication Engineering, Yunnan Open University, Kunming 650223, P. R. China

<sup>c</sup>Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, P. R. China. E-mail: zzy@kmust.edu.cn; Fax: +86-871-65107922; Tel: +86-871-65109952

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agglomeration to form large particles during the preparation of the catalysts and the catalytic reaction, resulting in deactivation of the catalysts. Therefore, it is very important for SACs to search the suitable confinement supports to effectively confine single atom.<sup>19–21</sup> As a matter of fact, confinement supports can effectively increase kinetic stabilization of a single atom to prevent the aggregation and create well-dispersed SACs by the strong metal–support interactions. Most importantly, confinement supports can also form new electronic structures and new coordination environment to affect the catalytic activity and selectivity.<sup>22</sup> This phenomenon is known as the confinement effects, which have already aroused enormous interest in catalytic research field. In recent years, many confinement supports for SACs have been widely researched, such as FeO<sub>x</sub>,<sup>23</sup> CeO<sub>2</sub>,<sup>24</sup> WO<sub>x</sub>,<sup>25</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>26</sup> MnO<sub>2</sub>,<sup>27</sup> SiO<sub>2</sub>,<sup>28</sup> ThO<sub>2</sub>,<sup>29</sup> TiC,<sup>30</sup> Mo<sub>2</sub>C,<sup>31</sup> metal–organic frameworks (MOFs),<sup>32</sup> and so on.

Two-dimensional (2D) materials have been extensively studied and used in a variety of applications.<sup>33,34</sup> Comparing with traditional three-dimensional (3D) materials, 2D materials are more suitable to confine noble metal single atoms to construct SACs due to their unique physical and chemical properties,<sup>35</sup> including (1) 2D materials have excellent mechanical strength, high chemical and thermal stability; (2) 2D materials can confine more noble metal single atoms to provide more active sites because of their large surface area; (3) 2D materials can regulate the electronic structure of noble metal single atoms to improve the catalytic performance through synergistic effect;<sup>36,37</sup> (4) the intrinsic catalytic activities of the pristine 2D materials can be triggered by the confined noble metal single atoms;<sup>38–40</sup> (5) the vacant structure on both sides of 2D materials is helpful for the adsorption, diffusion and dissociation of reactants and reaction products.

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), as an emerging kind of 2D material with layered structure, is a typical synthetic polymer semiconductor composed of sp<sup>2</sup> carbon (C) and sp<sup>2</sup> nitrogen (N) atoms forming  $\pi$ -conjugated system.<sup>41</sup> In fact, g-C<sub>3</sub>N<sub>4</sub> can be regarded as a special case of graphene *via* doping of N atoms. But, unlike N-doped graphene, g-C<sub>3</sub>N<sub>4</sub> has more N species and a lot of huge N-coordinating cavities available for confining single atoms. More interestingly, pristine g-C<sub>3</sub>N<sub>4</sub>, as a very promising photocatalyst in itself,<sup>42</sup> has been widely researched in the field of photocatalysis, including contaminant degradation,<sup>43</sup> hydrogen production<sup>44,45</sup> and carbon dioxide (CO<sub>2</sub>) reduction.<sup>46,47</sup> However, the photocatalytic property of pristine g-C<sub>3</sub>N<sub>4</sub> has been limited due to its serious recombination of photo-generated carriers and narrow light absorption range.<sup>42</sup> Thus, to promote the photocatalytic performance of pristine g-C<sub>3</sub>N<sub>4</sub>, some SACs photocatalysts *via* g-C<sub>3</sub>N<sub>4</sub> confining noble metal single atoms (NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>, NM = Ru, Rh, Pd, Ag, Os, Ir, Pt, Au) have been researched in recent years. For instance, Gao and co-workers demonstrated that the single atoms of Pd and Pt supported on g-C<sub>3</sub>N<sub>4</sub> as an efficient photocatalyst significantly increase catalysts' ability to absorb visible-light and effectively reduce the reaction barriers during CO<sub>2</sub> reduction.<sup>48</sup> Density functional theory (DFT) calculations showed that the preferred product is HCOOH and CH<sub>4</sub> on Pd@g-C<sub>3</sub>N<sub>4</sub> SACs and Pt@g-C<sub>3</sub>N<sub>4</sub> SACs from CO<sub>2</sub> reduction, respectively. Moreover, Xiong

*et al.* demonstrated that the charge transfer between confined Pt single atoms and ligand g-C<sub>3</sub>N<sub>4</sub> has great effect on photocatalytic reactions. Compared with pristine g-C<sub>3</sub>N<sub>4</sub>, Pt<sup>2+</sup> single atoms confined in g-C<sub>3</sub>N<sub>4</sub> as catalyst showed higher photocatalytic activity due to its novel electronic structure.<sup>49</sup> Further, Su and co-workers reported that high-valence Pt<sup>II</sup> single atoms confined in g-C<sub>3</sub>N<sub>4</sub> can modulate the valence band structure and lower the valence band maximum level of the semiconductor catalyst to tune photocatalytic water splitting performance of pristine g-C<sub>3</sub>N<sub>4</sub>.<sup>50</sup> This work proposed a new way for preparing high efficient photocatalysts by modifying the valence band structure of that. In brief, noble metal single atoms confined in g-C<sub>3</sub>N<sub>4</sub> are a very practical and effective way to improve the photocatalytic performance.

Although the above reports have greatly enhanced our understanding on monolayer g-C<sub>3</sub>N<sub>4</sub> as the structure hosts for NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs, a comprehensive understanding of confinement effects on NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs for photocatalysis is still missing. In this work, based on DFT calculations, a systematic study on NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs will be conducted for the first time to reveal the single-atom confinement effects of noble metals on g-C<sub>3</sub>N<sub>4</sub> for photocatalysis. The results will help in obtaining a better understanding of confinement effects of NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs and a new clue of designing many novel photocatalysts with high catalytic activity, stability and selectivity.

## 2. Computational methods

In this work, all calculations were conducted with Cambridge serial total energy package (CASTEP) module based on DFT.<sup>51</sup> The interaction between valence electrons and the ionic core was described by using the ultra-soft pseudo-potential.<sup>52</sup> The form of the Perdew–Burke–Ernzerhof (PBE) functional at the generalized gradient approximation (GGA) level was employed as the exchange–correlation functional.<sup>53</sup> A plane wave basis set were used to describe electron wave functions with the cut-off energy of 500 eV. The empirical correction method (DFT-D) from the scheme of Tkatchenko and Scheffler (TS) was employed to describe the van der Waals interactions.<sup>54</sup> The irreducible Brillouin zone was sampled by Monkhorst–Pack *k*-point meshes of 3 × 3 × 1 and 5 × 5 × 1 during geometry optimization and electronic properties calculations in the reciprocal space, respectively. The lattice parameters and the positions of atoms were relaxed until the maximum force, the maximum stress, the maximum displacement, maximal energy change and the self-consistent field tolerance were less than 0.03 eV Å<sup>-1</sup>, 0.05 GPa, 1 × 10<sup>-3</sup> Å, 1 × 10<sup>-5</sup> eV per atom and 1 × 10<sup>-6</sup> eV per atom, respectively. In this paper, the calculated band gap value of pristine monolayer g-C<sub>3</sub>N<sub>4</sub> (1.16 eV) was far less than the experimental result reported previously (2.70 eV) by Wang and his co-worker,<sup>42</sup> due to the well-known limitations of the GGA method in describing the electronic structures of the materials. Furthermore, since g-C<sub>3</sub>N<sub>4</sub> is a covalent system, the band gap correction of g-C<sub>3</sub>N<sub>4</sub> is failed using the GGA + *U* method. However, the hybrid approach which can give the correct band gap is not suitable to describe widely the electronic

structure of  $g\text{-C}_3\text{N}_4$  system due to its huge time cost.<sup>55</sup> In this work, although the band gap value of the system is underestimated, the calculated results can still be used to accurately describe the photocatalytic performance of the system.

To study the stability of NM atoms confined in  $g\text{-C}_3\text{N}_4$ , the binding energy was computed by the following formula.

$$E_b = E_{\text{NM}_1@g\text{-C}_3\text{N}_4} - E_{g\text{-C}_3\text{N}_4} - E_{\text{NM}_1} \quad (1)$$

where NM is the single atom of Ru, Rh, Pd, Ag, Os, Ir, Pt or Au;  $E_{\text{NM}_1@g\text{-C}_3\text{N}_4}$ ,  $E_{g\text{-C}_3\text{N}_4}$  and  $E_{\text{NM}_1}$  represent the total energies of the slab  $\text{NM}_1@g\text{-C}_3\text{N}_4$ , slab  $g\text{-C}_3\text{N}_4$  and a single NM atom, respectively.

## 3. Results and discussion

### 3.1. Optimized structure of pristine monolayer $g\text{-C}_3\text{N}_4$

The tri-*s*-triazine-based (heptazine)  $g\text{-C}_3\text{N}_4$  with perfect layered structures was chosen due to its excellent thermal stability among all the allotropes of  $g\text{-C}_3\text{N}_4$ .<sup>56</sup> The bulk crystal structure of  $g\text{-C}_3\text{N}_4$  was optimized based on the calculation parameters provided in Section 2. The calculation results are as follows:  $a = b = 7.127 \text{ \AA}$ ,  $c = 6.289 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$  and  $\gamma = 120.001^\circ$ , which are very consistent with previous calculation results,<sup>57,58</sup> and indicates that the computational methods are effective and reliable in this paper.

Further, the monolayer  $g\text{-C}_3\text{N}_4$  was constructed by cutting the bulk crystal structure of  $g\text{-C}_3\text{N}_4$  along the (001) plane. The  $2 \times 2 \times 1$   $g\text{-C}_3\text{N}_4$  supercell consisting of 32 N atoms and 24 C atoms were used in this study. Meanwhile, the vacuum space was built to be  $15 \text{ \AA}$  along  $z$  direction, which was enough to avoid periodic interactions between repeated slabs. Based on the computational methods provided in Section 2, the slab model of the monolayer  $g\text{-C}_3\text{N}_4$  was optimized. The optimized structure of  $2 \times 2 \times 1$   $g\text{-C}_3\text{N}_4$  supercell, whose calculated lattice constant was  $7.13 \text{ \AA}$ , as shown in Fig. 1(a). The calculated results were in good agreement with the previous theoretical<sup>59,60</sup> and experimental<sup>61</sup> results. As can be seen in Fig. 1(a), the  $2 \times 2 \times 1$   $g\text{-C}_3\text{N}_4$  supercell consists of four heptazine structural motifs ( $\text{C}_6\text{N}_7$ ) that are connected to each other by bridge N atoms

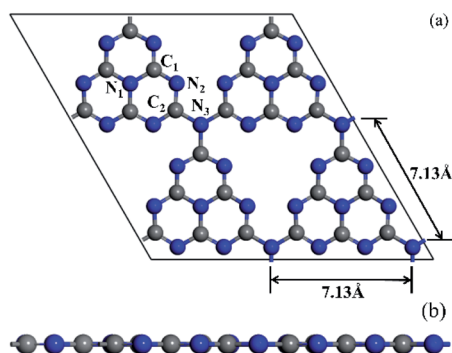


Fig. 1 Top view (a) and side view (b) of optimized structure for  $2 \times 2 \times 1$   $g\text{-C}_3\text{N}_4$  supercell. The balls in gray and blue represent the C and N atoms, respectively. Roman numbers labeled on the C and N atoms represent different sites, respectively.

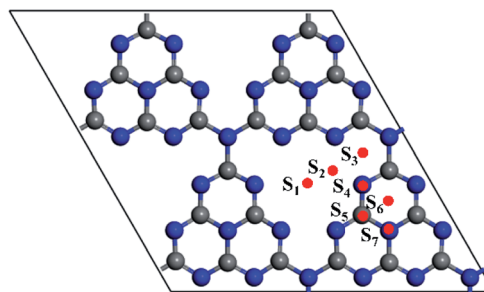


Fig. 2 The possible deposition sites for NM atoms. Position:  $S_1$ , centre of the six-fold cavity;  $S_2$ , corner of the six-fold cavity;  $S_3$ , top of the five-membered ring;  $S_4$ , top of N atom;  $S_5$ , top of C atom;  $S_6$ , top of the six-membered ring;  $S_7$ , top of three six-membered rings. The balls in gray and blue represent the C and N atoms, respectively.

labelled as  $\text{N}_3$ . Obviously, a large N-coordinating cavity (six-fold cavity) was formed by six unsaturated N atoms of four heptazine structural motifs. In each of these heptazine structural motifs, there were two classes of non-equivalent C atoms and N atoms, respectively, which were labelled as  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{N}_1$  and  $\text{N}_2$ , as shown in Fig. 1(a).

The calculated bond lengths of  $\text{C}_1\text{-N}_1$ ,  $\text{C}_1\text{-N}_2$ ,  $\text{C}_2\text{-N}_2$  and  $\text{C}_2\text{-N}_3$  are  $1.39 \text{ \AA}$ ,  $1.33 \text{ \AA}$ ,  $1.34 \text{ \AA}$  and  $1.47 \text{ \AA}$ , respectively, are in good agreement with the results of the published literature.<sup>59,62</sup> Furthermore, it is evident from Fig. 1(b) that the optimized structure of monolayer pristine  $g\text{-C}_3\text{N}_4$  is a stable planar configuration.

### 3.2. Geometric structures of NM single atoms confined in monolayer $g\text{-C}_3\text{N}_4$

In order to find the most favourable adsorption configuration for NM single atoms confined in pristine  $g\text{-C}_3\text{N}_4$ , all kinds of adsorption sites around the six-fold cavity were considered on the  $2 \times 2 \times 1$   $g\text{-C}_3\text{N}_4$  supercell, as shown in Fig. 2. Each NM single atom species was placed at the  $S_1\text{-}S_7$  sites, respectively, forming 56 kinds of  $\text{NM}_1@g\text{-C}_3\text{N}_4$  configurations in total. The binding energies were obtained when these configurations were fully relaxed, as shown in Table 1. As can be seen from this table, the maximum binding energies are  $-5.42 \text{ eV}$ ,  $-4.08 \text{ eV}$ ,

Table 1 The binding energy ( $E_b$ ) for eight kinds of noble metal atoms at the different adsorption sites

Sites	$E_b$ for $\text{NM}_1@g\text{-C}_3\text{N}_4/\text{eV}$							
	Ru	Rh	Pd	Ag	Os	Ir	Pt	Au
$S_1$	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	-1.29	-3.28	<sup>b</sup>	<sup>b</sup>	-0.001
$S_2$	-5.42	-4.08	-3.55	<sup>a</sup>	-5.17	-3.57	-3.60	<sup>a</sup>
$S_3$	-4.19	-2.32	<sup>b</sup>	0.12	-3.71	0.65	<sup>b</sup>	0.43
$S_4$	-4.47	-1.89	-0.81	<sup>a</sup>	0.11	1.17	-0.61	0.44
$S_5$	<sup>b</sup>	-0.68	-2.49	0.27	-1.52	0.86	-0.66	0.39
$S_6$	-2.97	0.22	-0.12	0.30	-0.19	1.31	-0.13	0.15
$S_7$	<sup>c</sup>	1.06	-0.45	0.32	1.41	2.55	-0.01	0.43

<sup>a</sup> Moved to  $S_1$ . <sup>b</sup> Moved to  $S_2$ . <sup>c</sup> Moved to  $S_6$ .

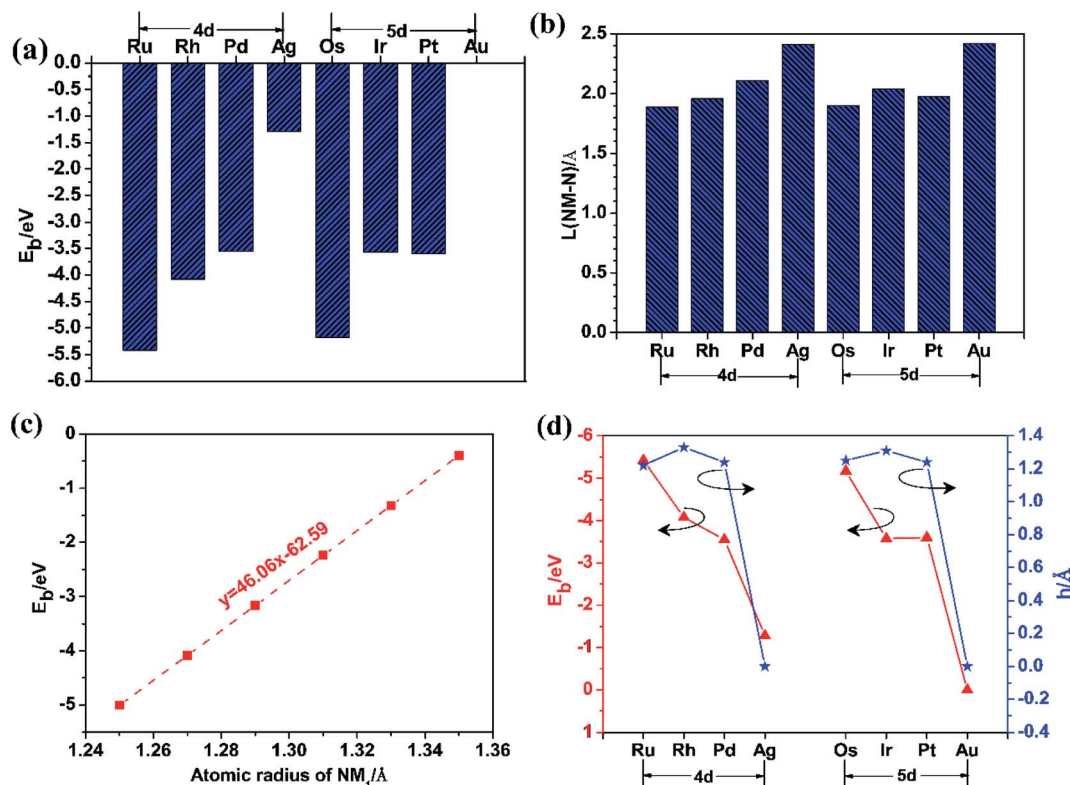


Fig. 3 (a) The binding energy ( $E_b$ ) of  $NM_1$ ; (b) the average bond length ( $L$ ) between  $NM_1$  and N atoms ( $NM-N$ ); (c) the binding energy ( $E_b$ ) of  $NM_1$  versus the atomic radius of  $NM_1$ ; (d) the binding energy ( $E_b$ ) of  $NM_1$  and the geometric deformation ( $h$ ).

−3.55 eV, −1.29 eV, −5.17 eV, −3.57 eV, −3.60 eV and −0.001 eV for Ru, Rh, Pd, Ag, Os, Ir, Pt and Au single atom at adsorption site  $S_2$ ,  $S_2$ ,  $S_2$ ,  $S_1$ ,  $S_2$ ,  $S_2$ ,  $S_2$ , and  $S_1$ , respectively. Here, the binding energies were negative, which represented exothermic processes. These results indicate that the site  $S_2$ ,  $S_2$ ,  $S_2$ ,  $S_1$ ,  $S_2$ ,  $S_2$ ,  $S_2$ , and  $S_1$  in the six-fold cavity are energetically favourable for Ru, Rh, Pd, Ag, Os, Ir, Pt and Au single atoms confined in  $g-C_3N_4$ . However, the  $Au_1@g-C_3N_4$  with positive  $E_b$  values ( $E_b \approx 0$  eV for site  $S_1$ ,  $0.15$  eV  $< E_b < 0.44$  eV for other sites) at all sites is thermodynamic instability. Therefore, it is difficult for Au single atom to be introduced into the monolayer  $g-C_3N_4$  to prepare  $Au_1@g-C_3N_4$  catalysts. Further, as can be found, the binding energy decreased with increasing atomic number and met  $4d > 5d$  trend, as shown in Fig. 3(a). Meanwhile, the average bond lengths between noble metal atoms and N atoms for eight kinds of noble metal atoms at the different adsorption sites were also obtained, as listed in Table 2. From this table, it had the shortest  $NM-N$  bond lengths for eight kinds of noble metal atoms at the site  $S_1$  or  $S_2$  in the six-fold cavity. These sites where the shortest bond lengths occurred correspond exactly to the sites where the maximum binding energies occurred. The results suggest that the shorter the bond length is, the greater the binding energy is. For instance, the Ru–N bond length of 1.89 Å is shortest with a maximum binding energy of −5.42 eV, while the Au–N bond length of 2.42 Å is longest with a minimum binding energy of −0.001 eV. As opposed to the behaviour of the bond lengths and the binding energies, the

bond length increased with increasing atomic number and meets  $4d < 5d$  trend, as shown in Fig. 3(b).

More interestingly, the binding energy for eight kinds of noble metal atoms at the site  $S_1$  or  $S_2$  in the six-fold cavity linearly decreased with increasing atomic radius of  $NM_1$ , as shown in Fig. 3(c). This indicates that the larger the atomic radius of  $NM_1$  is, the weaker the confinement effect of the six-fold cavity for  $NM_1$  is. This is because as the radius of  $NM_1$  increase, the confinement configurations become more and more unstable. Moreover, just as shown in Fig. S2 in the ESI,<sup>†</sup> the introduction of  $NM_1$  resulted in the deformation of pristine

Table 2 The average bond length ( $L$ ) between  $NM$  atoms and N atoms ( $NM-N$ ) for eight kinds of noble metal atoms at the different adsorption sites

Sites	$L(NM-N)$ for $NM@g-C_3N_4/\text{Å}$							
	Ru	Rh	Pd	Ag	Os	Ir	Pt	Au
$S_1$	<i>b</i>	<i>b</i>	<i>b</i>	2.41	2.28	<i>b</i>	<i>b</i>	2.42
$S_2$	1.89	1.96	2.05	<i>a</i>	1.90	2.01	1.98	<i>a</i>
$S_3$	1.97	2.04	<i>b</i>	—	1.97	1.99	<i>b</i>	—
$S_4$	1.92	2.05	2.10	<i>a</i>	1.91	2.04	2.04	—
$S_5$	<i>b</i>	2.12	2.28	—	1.95	2.09	2.25	—
$S_6$	2.63	2.23	—	—	2.03	2.19	2.37	—
$S_7$	<i>c</i>	2.01	2.10	—	1.99	2.04	2.00	—

<sup>a</sup> Moved to  $S_1$ . <sup>b</sup> Moved to  $S_2$ . <sup>c</sup> Moved to  $S_6$ .

$g\text{-C}_3\text{N}_4$  from a flat shape to a wrinkled shape. This deformation can be characterized on the basis of the thickness ( $h$ ) of the slab  $\text{NM}_1@g\text{-C}_3\text{N}_4$  SACs, as Fig. 3(d) and S2 in the ESI.† Even more importantly, as shown in Fig. 3(d), the deformation quantity ( $h$ ) and the binding energy decreased with increasing atomic number, and followed the same variation trend on 4d and 5d. The results indicate that the larger the deformation is in each period, the larger the binding energy is; on the contrary, the smaller the deformation is, the smaller the binding strength is. This may be due to the fact that the single atoms are more easily anchored in the deformed wrinkle space than in the flat structure of  $g\text{-C}_3\text{N}_4$ . The deformed wrinkle space provided an extremely important confined environment for the single atoms. In other words, these results confirm the importance of wrinkle for  $\text{NM}_1@g\text{-C}_3\text{N}_4$  SACs.

In brief, it can be suggested from the above analysis of energy and spatial configuration that the most favourable adsorption sites are  $S_2, S_2, S_2, S_1, S_2, S_2, S_2,$  and  $S_1$  for single Ru, Rh, Pd, Ag, Os, Ir, Pt and Au atom confined in pristine  $g\text{-C}_3\text{N}_4$  catalysts, respectively. In other words, the most favourable confined sites for NM single atoms are located in the six-fold cavity, while Au single atom was hard to confine in  $g\text{-C}_3\text{N}_4$  due to its small binding energy in the monolayer  $g\text{-C}_3\text{N}_4$ . Moreover, in order to clearly show the most favourable confined configurations of

$\text{NM}_1@g\text{-C}_3\text{N}_4$ , the corresponding top view and side view of that are displayed in Fig. S1 and S2 in the ESI,† respectively.

### 3.3. Electronic structures of NM single atoms confined in monolayer $g\text{-C}_3\text{N}_4$

**3.3.1. Density of states.** The calculated density of states (DOS) for pristine monolayer  $g\text{-C}_3\text{N}_4$  and  $\text{NM}_1@g\text{-C}_3\text{N}_4$  are illustrated in Fig. 4. For pristine monolayer  $g\text{-C}_3\text{N}_4$ , it can be seen from Fig. 4(a) that the pristine monolayer  $g\text{-C}_3\text{N}_4$  exhibits semiconductor characteristics, which are in good agreement with the previous reports.<sup>63</sup> Meanwhile, from Fig. 4(a), it is found that the valance band (VB) is composed mostly of the  $\text{N}_2$  atoms around the Fermi level, while the conduction band (CB) edge is mainly made up of the  $\text{C}_1, \text{C}_2$  atoms and a few of  $\text{N}_1$  and  $\text{N}_2$  atoms. Also, most remarkably, almost no electrons on either VB or CB around the Fermi level were donated by  $\text{N}_3$  atoms, as shown in Fig. 4(a). In order to understand the above conclusions more intuitively and recognize active sites of the pristine monolayer  $g\text{-C}_3\text{N}_4$  more clearly, the corresponding highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of valance band maximum (VBM) and conduction band minimum (CBM) of the pristine monolayer  $g\text{-C}_3\text{N}_4$  was obtained, as shown in Fig. 5(a-1) and (b-1). The HOMO and LUMO obtained is consistent with the DOS results

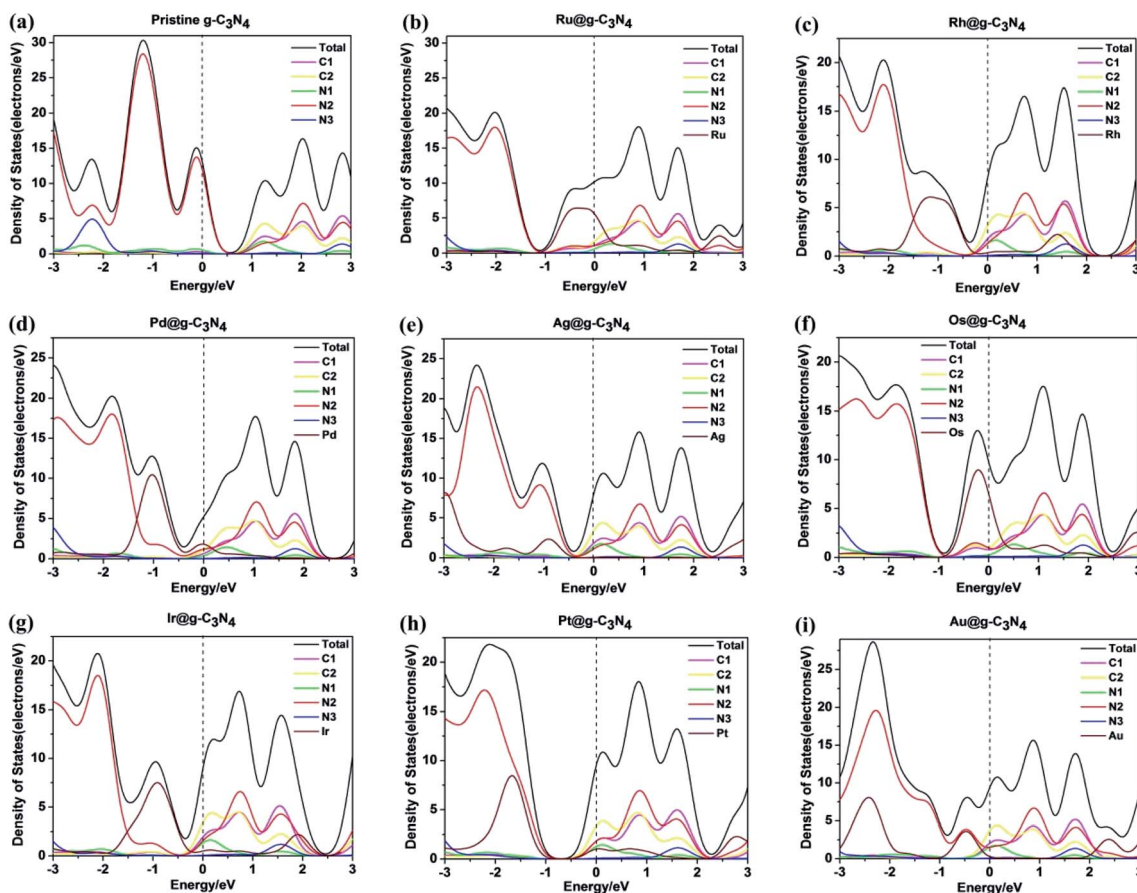


Fig. 4 Density of states for (a) pristine  $g\text{-C}_3\text{N}_4$  and  $\text{NM}_1@g\text{-C}_3\text{N}_4$ ,  $\text{NM}_1 =$  (b)  $\text{Ru}_1$ , (c)  $\text{Rh}_1$ , (d)  $\text{Pd}_1$ , (e)  $\text{Ag}_1$ , (f)  $\text{Os}_1$ , (g)  $\text{Ir}_1$ , (h)  $\text{Pt}_1$ , (i)  $\text{Au}_1$ . The Fermi energy is set to zero.

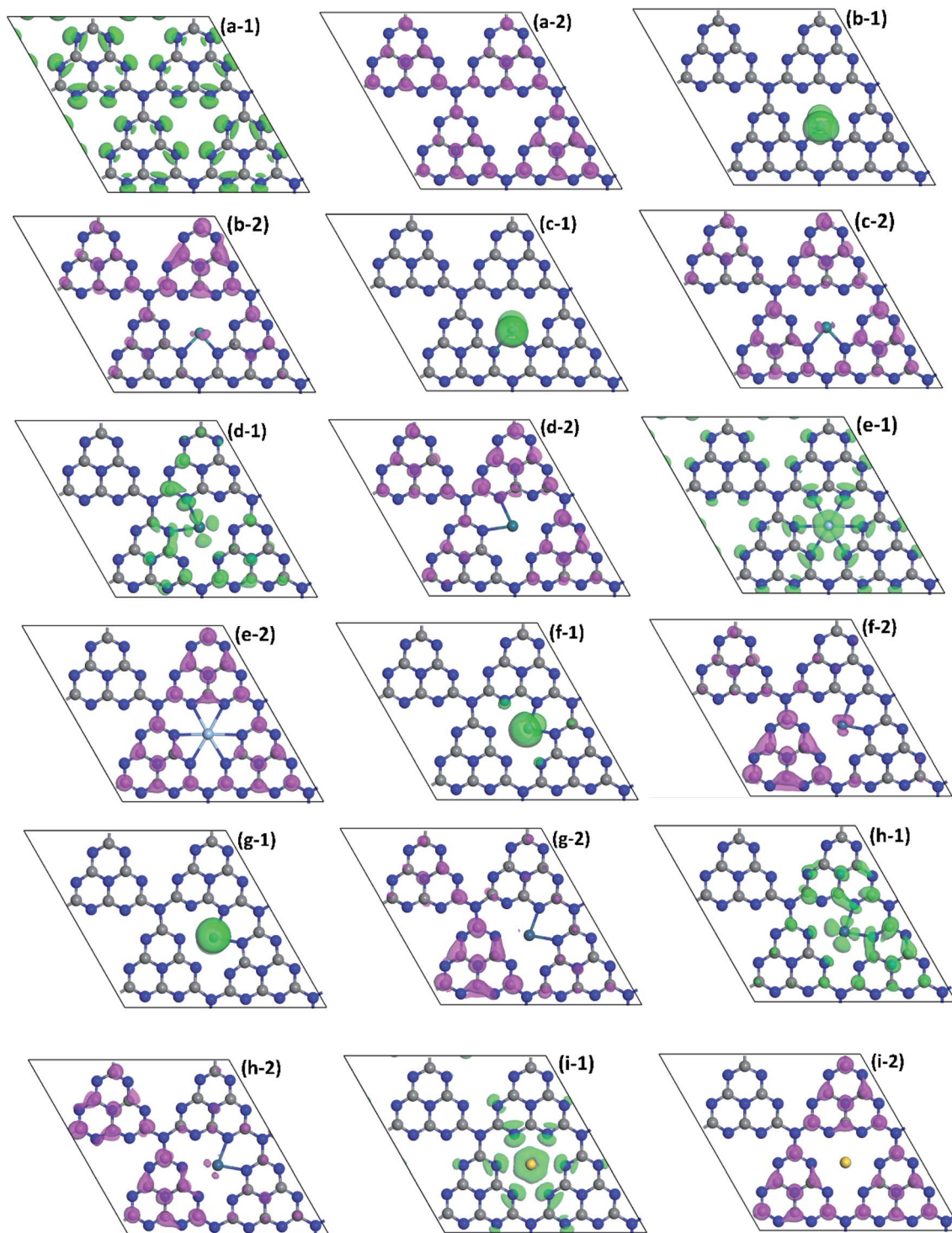


Fig. 5 HOMO (green part) of (a-1) pristine  $g\text{-C}_3\text{N}_4$  and  $\text{NM}_1@g\text{-C}_3\text{N}_4$ ,  $\text{NM}_1 =$  (b-1)  $\text{Ru}_1$ , (c-1)  $\text{Rh}_1$ , (d-1)  $\text{Pd}_1$ , (e-1)  $\text{Ag}_1$ , (f-1)  $\text{Os}_1$ , (g-1)  $\text{Ir}_1$ , (h-1)  $\text{Pt}_1$ , (i-1)  $\text{Au}_1$ ; LUMO (purple part) of (a-2) pristine  $g\text{-C}_3\text{N}_4$  and  $\text{NM}_1@g\text{-C}_3\text{N}_4$ ,  $\text{NM}_1 =$  (b-2)  $\text{Ru}_1$ , (c-2)  $\text{Rh}_1$ , (d-2)  $\text{Pd}_1$ , (e-2)  $\text{Ag}_1$ , (f-2)  $\text{Os}_1$ , (g-2)  $\text{Ir}_1$ , (h-2)  $\text{Pt}_1$ , (i-2)  $\text{Au}_1$ . The isovalue is set as  $0.05 \text{ e } \text{\AA}^{-3}$ . The balls in gray and blue represent the C and N atoms, respectively.

mentioned above. From Fig. 5(a-1) and (b-1), the HOMO was only found on  $\text{N}_2$  atoms around the six-fold cavity, while the LUMO was found on  $\text{C}_1$ ,  $\text{C}_2$ , and  $\text{N}_1$  atoms adjacent to  $\text{N}_2$  atoms in every heptazine unit. The results indicate that  $\text{N}_2$  atoms exhibit oxidation activities while  $\text{C}_1$ ,  $\text{C}_2$  and  $\text{N}_1$  atoms exhibit

reduction activities in a photocatalytic reaction, which are consistent with previous reports.<sup>60</sup> Meanwhile, it can be concluded that those localized distributions of the HOMO and the LUMO can lead to low separation efficiency of photo-induced electron-hole pairs. In addition, it is noted that the

bridge N<sub>3</sub> atoms are not covered by either the HOMO or the LUMO. The results show that the electrons cannot be excited and transferred on and by the N<sub>3</sub> atoms under visible-light irradiation. The bridge N<sub>3</sub> atoms only play the role of connecting three adjacent heptazine units instead of acting as a charge transmission channel. In other words, the photo-induced carriers are completely localized in each isolated heptazine unit, resulting in the outstanding recombination of photo-induced carriers and low photocatalytic activity of the pristine monolayer g-C<sub>3</sub>N<sub>4</sub>.

As shown in Fig. 4(b)–(i), after introducing noble metal single atoms into the monolayer g-C<sub>3</sub>N<sub>4</sub>, the DOS of NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> had been changed greatly compared with that of the pristine g-C<sub>3</sub>N<sub>4</sub> in Fig. 4(a). For all NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> systems, noble metal single atoms participated mainly in the constitution of VB, while the compositions of CB were almost unchanged compared with the pristine g-C<sub>3</sub>N<sub>4</sub>. Significantly, only a handful of noble metal single atoms participated in the constitution of CB. In particular, as for Ru<sub>1</sub>@, Rh<sub>1</sub>@, Pd<sub>1</sub>@, Os<sub>1</sub>@ and Ir<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>, the VB is contributed by noble metal single atoms and a few of N<sub>2</sub> atoms. As regards Ag<sub>1</sub>@, Pt<sub>1</sub>@ and Au<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>, the VB is contributed by the N<sub>2</sub> atoms and a part of noble metal single atoms. Most remarkably, the CB moved down and passed through the Fermi level due to the introduction of noble metal single atoms, resulting in narrowing the band gap of the NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> systems. This will effectively improve the visible light response of the systems.

Similarly, to better understand the structure of band edges, the corresponding HOMO and LUMO of VBM and CBM of monolayer NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> are shown in Fig. 5(b)–(i). As can be seen from these figures, the HOMO and LUMO of all the monolayer NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> had been redistributed compared to that of pristine monolayer g-C<sub>3</sub>N<sub>4</sub> in Fig. 5(a). The redistribution of HOMO and LUMO resulted in the variation of the active sites. Meanwhile, the separation of the HOMO and LUMO can effectively promote the photocatalytic performance of 2D materials. More specifically, the distributions of the HOMO and LUMO can be roughly divided into four categories. For monolayer Ru<sub>1</sub>@, Rh<sub>1</sub>@, Os<sub>1</sub>@ and Ir<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>, the HOMO mainly covered the noble metal single atoms, while the LUMO covered almost all triazine units except the N<sub>2</sub> and N<sub>3</sub> atoms. In this case, the non-localized distribution of the HOMO and LUMO can effectively promote the separation of photo-generated electron–hole pairs. Photo-generated carriers, however, cannot move freely in adjacent heptazine units because there is neither the HOMO nor the LUMO on the N<sub>3</sub> atoms and the N<sub>2</sub> atoms next to the noble metal single atoms, resulting in short carrier lifetime and poor photocatalytic activity. For monolayer Ag<sub>1</sub>@ and Au<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>, the HOMO is distributed on the noble metal single atoms and the N<sub>2</sub> atoms, while the LUMO is located on three adjacent heptazine units around Ag and Au single atoms except the N<sub>2</sub> atoms. In this instance, the distribution of the HOMO and LUMO are localized mainly in Ag and Au atoms and three adjacent heptazine units around them. From Fig. 5(e) and (i), after introducing Ag and Au single atoms, photo-generated carriers can be transported through Ag and Au single atom channels among three adjacent heptazine units under visible-

light irradiation. Thus, the introduction of Ag and Au single atoms will enhance the carrier mobility on g-C<sub>3</sub>N<sub>4</sub> to some extent. For Pd<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>, the HOMO mainly covered on the noble metal single atom and two adjacent heptazine units including it, while the LUMO covered almost all triazine units except Au single atoms, the N<sub>2</sub> and N<sub>3</sub> atoms. For Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>, the distributions of the HOMO are similar to that of Pd<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>, while the LUMO is distributed on two heptazine units that is not adjacent to Au single atoms. Obviously, for Pd<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> and Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>, because of the remarkable delocalized distribution of the HOMO and LUMO, photo-generated electron–hole pairs can be effectively separated. And more notably, as can be found clearly from Fig. 5(d-1) and (h-1), the HOMO is distributed on the N<sub>2</sub> atoms next to Pd and Pt atoms. Therefore, it is reasonable to believe that photo-generated carriers can be transported freely between two adjacent heptazine units through the channels formed by C–N–Pd–N–C or C–N–Pt–N–C chains. This will effectively prolong the carrier lifetime and reduce the recombination rate of photo-generated electron–hole pairs, resulting in high photocatalytic activity. These results are in good agreement with the DOS analysis. In a word, based on the above discussions, it can be inferred that Pd<sub>1</sub>@, Pt<sub>1</sub>@, Ag<sub>1</sub>@ and Au<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> may have better photocatalytic activity than Ru<sub>1</sub>@, Rh<sub>1</sub>@, Os<sub>1</sub>@ and Ir<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub>.

**3.3.2. The d-band centres of NM<sub>1</sub> in NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs.** As an effective evaluation parameter, the d-band centre of noble metal single atoms in NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs can be used to semi-quantitatively estimate the photocatalytic activities of photocatalysts.<sup>64,65</sup> This was because the  $\sigma \rightarrow d$  interaction and the  $d \rightarrow \pi$  interaction between the d-band of metals and the adsorbates (for example, CO, CO<sub>2</sub>, H<sup>+</sup> and so on) directly affect the binding strength between noble metal single atoms and the adsorbates. The d-band centre is expressed as follows

$$E_d = \varepsilon_d + \frac{\int_{-\infty}^{+\infty} (x - \varepsilon_d)\rho(x)dx}{2 \int_{-\infty}^{+\infty} \rho(x)dx} \quad (2)$$

where

$$\varepsilon_d = \frac{\int_{-\infty}^{+\infty} x\rho(x)dx}{\int_{-\infty}^{+\infty} \rho(x)dx} \quad (3)$$

The d-band centres of noble metal single atoms in NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs are shown in Fig. 6. As we know, the d-band centres

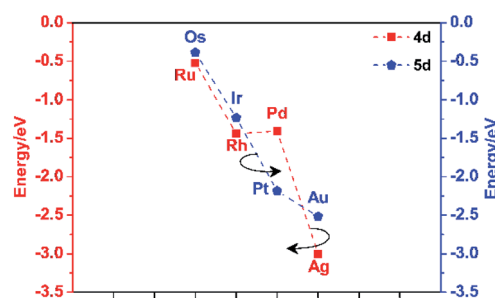


Fig. 6 The d-band centres of noble metal single atoms in NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs.

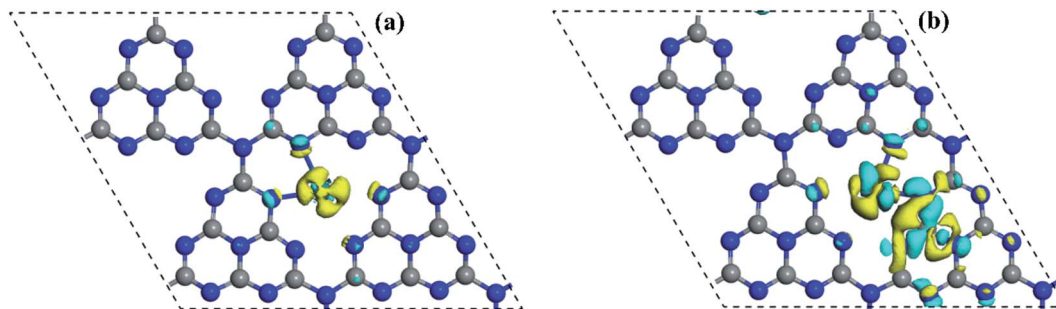


Fig. 7 Plots of 3D charge density difference of (a) Pd<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> and (b) Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> at isosurfaces of  $\pm 0.05 \text{ e } \text{\AA}^{-3}$ . The blue and yellow colours represent charge accumulation and depletion, respectively. The balls in gray and blue represent the C and N atoms, respectively.

cannot be too large or too small, otherwise it will not match well with the energy levels of the adsorbates. As can be seen from Fig. 6, the d-band centres show similar change tendency for 4d and 5d noble metals. And, the energy curves for 4d and 5d noble metals cross near the d-band centres of Rh<sub>1</sub>@, Pd<sub>1</sub>@, Ir<sub>1</sub>@ and Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs. Meanwhile, the d-band centres of Rh<sub>1</sub>@, Pd<sub>1</sub>@, Ir<sub>1</sub>@ and Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs are located in the middle, while the other d-band centres are either too large or too small. In other words, the energy levels matching between Rh<sub>1</sub>@, Pd<sub>1</sub>@, Ir<sub>1</sub>@ and Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs and the adsorbates are better than that between Ru<sub>1</sub>@, Ag<sub>1</sub>@, Os<sub>1</sub>@ and Au<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs and the adsorbates. Therefore, it can be predicted that Rh<sub>1</sub>@, Pd<sub>1</sub>@, Ir<sub>1</sub>@ and Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs may have better photocatalytic performance than Ru<sub>1</sub>@, Ag<sub>1</sub>@, Os<sub>1</sub>@ and Au<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs.

Combined with the above discussions, it is reasonable to believe that Pd<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> and Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs may have more excellent photocatalytic activity than the other NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> (NM = Ru, Rh, Ag, Os, Ir, Au) SACs.

**3.3.3. Differential charge density and Mulliken population analysis.** In order to further study the catalytic activity of Pd<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> and Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs, the 3D differential charge densities of that are shown in Fig. 7. As can be seen from the figure, the charge depletion (the yellow colour) occurred mainly on Pd single atom in Pd<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> in Fig. 7(a), while the charge accumulation (the blue colour) and depletion occurred simultaneously on Pt single atom in Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> in Fig. 7(b), which indicate that the charge transfer existed between noble metal

single atoms and the N<sub>2</sub> atoms, resulting in strong interaction between noble metal single atoms and the N<sub>2</sub> atoms. Further, in order to describe quantitatively the charge transfer, Mulliken charges were calculated, as listed in Table 3. As can be seen from Table 3, the oxidation states of Pd and Pt single atom are +0.44 and +0.31, respectively. Recent studies suggest that it is very important for the charge transfer between transition metal atoms and g-C<sub>3</sub>N<sub>4</sub> during catalytic process.<sup>66</sup> In general, the transition metal atoms that can maintain a lower valence states have a stronger ability to capture the adsorbates, resulting in their higher photocatalytic activity.<sup>67</sup> Hence, Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs may have higher photocatalytic activity than Pd<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs. Moreover, it can be seen from Table 3 that the bond populations of Pd and Pt single atom were 0.18 and 0.25, respectively, indicating that the interaction between Pt single atom and g-C<sub>3</sub>N<sub>4</sub> is greater than that between Pd single atom and g-C<sub>3</sub>N<sub>4</sub> due to the stronger covalent bonds between Pt single atom and the N<sub>2</sub> atoms. This result is consistent with the result that the binding energy of Pt single atom (−3.60 eV) is greater than that of Pd single atom (−3.55 eV) in Table 1, and the result that the Pt–N bond length (1.98 Å) is less than the Pd–N bond length (2.05 Å) in Table 2.

In brief, based on all the above discussion, it is reasonable to believe that Pt<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs may have higher photocatalytic activity than the other NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs under the same conditions, and can be considered as one of the most promising NM<sub>1</sub>@g-C<sub>3</sub>N<sub>4</sub> SACs.

## 4. Conclusions

In summary, the geometric structures and electronic structures of pristine monolayer g-C<sub>3</sub>N<sub>4</sub> and eight types SACs of the noble metal single atom confined in g-C<sub>3</sub>N<sub>4</sub> were studied systematically by using DFT calculations. The calculation results of the geometric structures show that the most favourable confined sites for NM single atoms are located in the six-fold cavity. Remarkably, Au single atom is difficult to be confine in g-C<sub>3</sub>N<sub>4</sub> due to its small binding energy. At the same time, the deformed wrinkle space of g-C<sub>3</sub>N<sub>4</sub> contributed to the stability of the noble metal single atom in the six-fold cavity of g-C<sub>3</sub>N<sub>4</sub>. The “confining” not only means that the noble metal single atom is constrained by the coordination environment of g-C<sub>3</sub>N<sub>4</sub>, but

Table 3 Mulliken charges and the bond population of noble metal single atoms in the six-fold cavity of g-C<sub>3</sub>N<sub>4</sub>. The unit of Mulliken charge is “e”

Species	Mulliken charges	Bond population
Ru	+0.71	0.23
Rh	+0.69	0.25
Pd	+0.44	0.18
Ag	+0.31	0
Os	+0.60	0.34
Ir	+0.52	0.33
Pt	+0.31	0.25
Au	+0.25	0.01



also means that new electronic state are formed due to the strong electron interaction between the noble metal single atom and  $g\text{-C}_3\text{N}_4$ , so as to realize the modulation of the photocatalytic activity. After introducing the confined noble metal single atoms into the monolayer  $g\text{-C}_3\text{N}_4$ , the CB of the systems moved down and crossed through the Fermi level, causing the band gap of the  $\text{NM}_1@g\text{-C}_3\text{N}_4$  systems to be narrowed, thus increasing its response to visible light. Meanwhile, photo-generated electron-hole pairs can be effectively separated for  $\text{NM}_1@g\text{-C}_3\text{N}_4$  due to the remarkable delocalized distribution of the HOMO and LUMO. Moreover, after introducing the confined Ag and Au single atoms, photo-generated carriers can be transported through Ag and Au single atom channels among three adjacent heptazine units under visible-light irradiation. And, for  $\text{Pd}_1@g\text{-C}_3\text{N}_4$  and  $\text{Pt}_1@g\text{-C}_3\text{N}_4$  SACs, photo-generated carriers can be transported freely between two adjacent heptazine units through the channels formed by C–N–Pd–N–C or C–N–Pt–N–C chains, thus prolonging the lifetime of photo-generated carriers. Especially,  $\text{Pt}_1@g\text{-C}_3\text{N}_4$  single-atom catalysts are considered to have higher photocatalytic activity than the other  $\text{NM}_1@g\text{-C}_3\text{N}_4$  single-atom catalysts. These results provide a new insight into understand single-atom confinement effects of noble metals on monolayer  $g\text{-C}_3\text{N}_4$  for photocatalytic applications, and a new idea for preparing high-efficiency photocatalysts.

## Author contributions

Cheng Yang: investigation, data curation, writing-original draft; Zong-Yan Zhao: methodology, software; Qing-Ju Liu: supervision, conceptualization, methodology, software.

## Conflicts of interest

There are no conflicts to declare.

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