



Theoretical study on the photocatalytic properties of graphene oxide with single Au atom adsorption



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ABSTRACT

The photocatalytic properties of graphene oxide (GO) with single Au atom adsorption are studied via the first-principles calculations based on the density functional theory. The present study addresses the origin of enhancement in photocatalytic efficiency of GO derived from single Au atom depositing. Compared with the clean one, the work function of the single Au atom adsorbed GO is lowered due to the charge transfer from Au to GO, indicating enhanced surface activity. The Au atom plays as an electron trapping center and a mediating role in charge transfer from photon excited GO to target species. The photogenerated electron–hole pairs can be separated effectively. For the GO configuration with atomic Au dispersion, there are some states introduced in the band gap, which are predominantly composed of Au 6s states. Through the in-gap state, the photo-generated electron transfer from the valence band of clean GO to the conductive band more easily. In addition, the reduction of the gap in the system is also presented in the current work, which indicates that the single Au atom adsorption improves light absorption for the GO based photocatalyst. These theoretical results are valuable for the future applications of GO materials as photocatalyst for water splitting.

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1. Introduction

After hydrogen releasing the chemical energy, the only production is water. So hydrogen is considered to be the very promising energy to solve energy crisis and environmental pollution. Absorbing the sunlight, photocatalysis using the photogenerated electrons and holes can split water into H₂ and O₂ [1], which is a good method for the conversion and utilization of solar energy. To date, various sulfide, oxide, oxynitride, and phosphide inorganic semiconductor photocatalysts have been developed for the splitting of water [2–10]. Unfortunately, many of these photocatalysts usually has some disadvantages, such as toxicity of heavy metals, limited concentration of active sites [9,10]. Conversely, the organic photocatalyst has many advantages, such as low cost, mechanical flexibility, and easy fabrication [11–13]. The GO, which is an important material to massively produce graphene with low cost, has recently attracted resurgent interests since it has been suggested as a potential photocatalytic material [14]. GO materials have excellent solubility, biocompatibility, and tunable band gap [15–17]. Furthermore, it also has mobility of charge carriers of 10 cm²/Vs and conductivity of 10,000 S/m, which are sufficiently large to migrate the photogenerated electrons fast toward surface for efficient photocatalytic reaction [18]. The GO material can be transformed from an insulator to a semiconduc-

tor and a graphene-like semimetal by adjusting the ratio of *sp*² and *sp*³ hybridized carbon [14,19]. Recently, Krishnamoorthy et al. [15] have examined photocatalytic characteristics of GO nanostructures by measuring reduction rate of resazurin into resorufin as a function of under ultraviolet (UV) irradiation time and demonstrated that GO nanostructures have very promising applications in photocatalysis. At the same time, the band gap and band position of graphite oxide have also been characterized by employing the absorption spectroscopy, electrochemical analysis, and Mott–Schottky equation [17]. It is shown that the energy levels of conduction and valence band edges of GO from appropriate oxidation are suitable for both reduction and oxidation reactions for water splitting. However, a great proportion of the GO polymers only represent high activity under UV irradiation because of its wide band gap, which greatly restricts its practical application as a photocatalyst [20]. Though the band gap of GO decreases with increasing reduction degree, the required chemical potentials may be stringent and difficult to reach [21,22].

Precipitating metal particles on photocatalysts surface has been proved to be an effective method for the sake of enhanced photocatalytic activity. Some metals, such as Au, Pt, Ag and Co/Ni, are usually adopted as co-catalysts in quest of high photocatalytic efficiencies [23–25]. It has been reported that multilayer graphene loaded with (1 1 1) facet-oriented Au nanoplatelets exhibits improved photocatalytic ac-

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tivity toward overall water splitting, under visible light irradiation. Au loading plays a positive effect, increasing the catalytic activity and light-harvesting role of Au. Visible light can only excite Au nanoplatelets, promoting charge separation with electron migration from Au nanoplatelets to graphene that in this case would act as enhancer of the charge separation [26]. What is more, the low-coordinated and unsaturated noble metal atoms always act as the active sites [27]. Unfortunately, subnanoclusters also includes some multiple active centers, which may not be the most ideal active site for specific products. The size of metal particles has become a particularly important factor to dictate the reactivity and specificity of metal catalysts supported on semiconductors [28,29]. In addition, the noble metal catalysts also have some disadvantages, such as high cost and low abundance in earth, which will greatly restrict the application. Hence, the research topic of improving the utilization efficiency of active metal components has been widely connected. There are many efforts have been made to promote the efficiency of noble metal catalysis by downsizing the particles or clusters to single atoms.

Isolated metal atoms singly distributed on the supports, presenting well-defined and uniform single-atom dispersion, which is the ultimate small-size limit for metal particles [30]. With single atoms serving as the catalytically active sites, single-atom catalysts (SACs) can offer a great potential for achieving high catalytic activity and selectivity in experiments. SACs have been widely used in the three key research fields: oxidation [31,32], water gas shift (WGS) [33], and hydrogenation [34]. Recently, with a facile one-step method, Xing et al. synthesized isolated metal atoms (i.e., Pt, Pd, Rh and Ru) stably anchored anatase TiO₂ (101) surface. They found, with the deposition of single noble atoms, the photocatalytic performance of anatase TiO₂ (101) surface for hydrogen evolution can be increased by 6–13 times over the metal clusters loaded ones [35]. Moreover, g-C₃N₄ with single atom (Pd and Pt) supported has been illustrated as an efficient photocatalyst for reduction of CO₂ under visible-light illuminating [36]. Our previous theoretical studies have been demonstrated the electronic mechanism for the improved photocatalytic activity of SrTiO₃ with single Au, Ag and Cu atom loaded [37–39]. However, systematic analyses of a theoretical point of view for the single-atom loaded GO system are absent so far. So, in the current work, we adopt Au/GO as model structure to study the origin of enhancement in photocatalytic efficiency derived from single Au atom depositing. In addition, insights into isolated Au atom adsorption are helpful to understand the metal particle growth on surface. These theoretical results are valuable for the future applications of GO materials as photocatalyst for water splitting.

2. Computational details

The first-principles calculations based on the density functional theory (DFT) are performed with the periodic supercell plane-wave basis approach implemented in the Vienna ab initio Simulation Package (VASP) [40,41]. Interactions between valence and frozen core electrons are simulated with the projector augmented wave (PAW) pseudopotential and generalized gradient approximation (GGA) in the formulation of Perdew–Burke–Ernzerhof (PBE) functional is employed to treat the exchange and correlation potentials [42–44]. The electron wave functions are expanded into a basis set of plane waves with a kinetic energy cutoff of 500 eV. Spin-polarized calculations are adopted to properly describe the total energies and the electronic structures with regard to Au adsorption. Geometry relaxation is performed until the residual forces experienced by each ion converged to be smaller than 0.01 eV/Å and the convergence threshold for self-consistence field iteration is set at 10⁻⁴ eV. A 5 × 5 × 1 Monkhorst–Pack mesh of k points is used to sample the integration in the Brillouin zone [45]. The calculations are performed under the periodic boundary conditions, with the vacuum separation distance set to 20 Å along the z-direction, to avoid interactions between the images. Considering the dipole moment induced by metal atoms adsorption, dipole correction is adopted to describe the total energies and electronic structures. The PBE + D2 (D stands for dispersion)

method with the Grimme vdW correction is adopted to describe long-range vdW interactions [46]. All the geometries were optimised with PBE + D2. Due to the underestimate of the band gaps by using the PBE functional, the Heyd–Scuseria–Ernzerh (HSE06) [47] hybrid functional were employed to calculate the electronic and optical properties with the PBE + D2-optimised geometries. The ion-core interaction contains two parts in this functional: one for the short-range (SR), the other for the long-range (LR). The exchange correlation energy could be expressed as

$$E_{XC}^{HSE} = \chi E_X^{SR}(\mu) + (1 - \chi) E_X^{PBE,SR}(\mu) + E_X^{PBE,LR}(\mu) + E_C^{PBE}$$

where χ and μ stand for the mixing coefficient and the screening parameter, respectively. The mixing exchange parameter of 0.25 and screening parameter of 0.2 Å⁻¹ are adopted in our calculations.

3. Results and discussion

There are various structural models proposed in the literature [48–50] for GO. The existence of sp² C units, C–O–C (epoxide), and C–OH (hydroxyl) has been confirmed by recent high-resolution solid-state ¹³C NMR measurement, which further indicate that a large fraction of C atoms in the hydroxyl and epoxide units are bonded to each other, and that a large portion of sp² C atoms are bonded directly to C atoms in the hydroxyl and epoxide groups [51]. In addition, a atomic force microscope (AFM) measurement states that the thickness of the GO sheets appear to equal to integer multiples of 6.7 Å [52], indicating that epoxide and hydroxyl are most likely to be distribute on both sides of the graphene layer.

Our simulations investigate three cases of GO and the functional groups are epoxy only, hydroxyl only, and both epoxy and hydroxyl, respectively. Compared with the chemisorption energy of oxygen atoms and hydroxyl groups at different coverage, Boukhvalov et al. demonstrated the coverage of 100%, 75%, and 75% are most stable for the three cases mentioned above, and the configuration is the displayed in Fig. 1 (**e**, **h**, and **he**), respectively (see reference 22 for the detailed calculation process) [22].

For the configuration **e**, we can see the oxygen forms a bridge between two carbon atoms, as shown in Fig. 1(a). As well as for the case of hydrogen, the chemisorption leads to distortions of graphene sheets when the atoms coupled to oxygen are shifted up and their neighbors are moved in the opposite direction. This makes chemisorption of the next oxygen atom from the opposite side of graphene sheet energetically stable. For the configuration **h**, hydroxyl groups are bonded with graphene, sitting at neighboring carbon atoms from opposite sides of the graphene sheet shown in Fig. 1(b). H points toward the neighboring O atom on the same side, yielding a configuration characterized by a hydrogen bond. These adsorbed units prefer to aggregate on the graphene surface. This is in full agreement with the experimental results inferred from the NMR data [49–51]. The structure of configuration **he**, as shown in Fig. 1(c), contains separate regions of sp² and sp³ C. The sp³ strips consist of double hydroxyl chains and one epoxide. The length of bonds between functionalized carbon atoms in configuration **e**, **h**, and **he**, grows from the standard value for graphene, 1.42 Å, to 1.46 Å, 1.53 Å, and 1.50 Å, respectively. The stretching corresponds to the transition from planar sp² to distorted sp³ hybridization of carbon atoms, when a new bond formed between C and O. Distortion of the configuration **h** is stronger than in the configuration **e**, perhaps because of interaction between the hydroxyl groups leading to ordering of distortion. The structure obtained in our calculation is in good agreement with that reported in previous theoretical studies [22].

As shown in Fig. 1, we consider many adsorption sites of configuration **e**, **h**, and **he** for Au atoms to determine the most stable position, such as hollow, bridge, and so on. The adsorption energies of Au adsorbed graphene oxide are defined the following equation:

$$E_{\text{ads}} = E_{\text{GO}} + E_{\text{Au}} - E_{(\text{Au-GO})}$$

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