

Full Length Article

Adsorption of hydrogen and hydrogen-containing gases on Pd- and Ag-single atoms doped on anatase TiO₂ (1 0 1) surfaces and their sensing performance

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ABSTRACT

The Pd- and Ag-doped anatase TiO₂ (1 0 1) surfaces were investigated and the binding energies of single atom of Pd (−2.15 eV) and Ag (−2.38 eV) on the anatase (1 0 1) surfaces, respectively denoted as Pd/TiO₂ and Ag/TiO₂, were obtained. Binding sites for Pd and Ag atoms toward the TiO₂ surface atoms are three atoms (Ti_{5C} and two O_{2C} atoms) and two O_{2C} atoms of the TiO₂ (1 0 1) surface, respectively. Due to adsorptions of H₂ and hydrogen-containing (H₂O, NH₃, and CH₄) gases on the Pd/TiO₂ and Ag/TiO₂, adsorption abilities on the Pd/TiO₂ and Ag/TiO₂ are in decreasing orders: NH₃ > H₂O > H₂ > CH₄ and NH₃ > H₂O > CH₄ > H₂, respectively. Mulliken-charge transfers from the Pd and Ag atoms to adsorption atoms of the anatase TiO₂ (1 0 1) surface and the adsorption of hydrogen and hydrogen-containing gases to the Pd/TiO₂ and Ag/TiO₂ were observed. The Pd/TiO₂ and/or Ag/TiO₂ have high potentials to be NH₃ sensing materials based on the electric conductivity measurement. The Pd/TiO₂ has high potential to be CH₄ sensing device based on the electric conductivity and surface charge measurements.

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1. Introduction

Various metal oxide surfaces, such as Ga₂O₃ [1], CeO₂ [2], ZnO [3], MnO_x [4], MoO₃ [5], ZrO₂ [6], LiO₂ [7], Fe₃O₄ [8], and TiO₂ [9,10] have acknowledged a great interest in the field of gas-sensing, adsorption of hydrogen (H₂) and hydrogen-containing gases (CH₄, H₂O, NH₃). Titanium dioxide is one of the most metal oxide materials that frequently and widely used as gas-sensing material due to its outstanding stability, nontoxicity and high capacity of detecting numerous gas species [10–22]. There are many works dedicated to the improvement and focus on the interaction of the small molecules and gas-sensing efficiency of TiO₂. Nevertheless, the sensing performance of TiO₂ is highly dependent on surface and structural properties [17]. Customizing the exposed crystal facets is a feasible way to modify a gas sensing property of TiO₂. Two polymorphs of TiO₂, rutile and anatase are most widely used. In particular, anatase is commonly used for active phase and support in the molecular adsorption [23–27] and gas-sensing materials [11,16,28,29]. The (1 0 1) surface of anatase nanocrystals is thermodynamically more stable than (0 0 1) surface [30,31]. The

experimental results have reported that anatase TiO₂ is high sensing performance as compared to the rutile TiO₂ [11]. Therefore, it is extremely satisfying to explore the sensing performance of anatase TiO₂ with specific crystal facets revealing for the designing of anatase TiO₂-based gas sensing devices with better sensing capacity. However, the defects such as oxygen vacancies have been identified as surface active sites for molecular adsorption [11,32,33].

The anatase TiO₂ (1 0 1) terraces as well as oxygen vacancies were found to affect the growth of Au, and the nucleation behavior of Pt [34]. The sensing properties of anatase TiO₂ were found to be improved by modifying the surface with noble metals such as Au and Pt nanoparticles [34] and the binding of TiO₂ surfaces with noble metals can enhance the efficiency of catalytic [35,36] and photocatalytic activity [37]. The Pd adsorbed on TiO₂ nanorods [38], on anatase TiO₂ (1 0 1) [39] and loaded spider-web TiO₂ nanowires [40] were found to increase sensing performance for H₂ and volatile organic compound, adsorption for CO₂, and small molecules, respectively. The Ag/TiO₂ nanocomposite for environmental and sensing applications [41], Ag/TiO₂ nanofibers for H₂S sensing [42] and Ag nanoparticles modified TiO₂ spherical heterostructures for gas-sensing performance [43] were studied. The Ag nanoparticles on TiO₂ (1 0 1) surface were found to be an

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excellent catalytic activity for CO oxidation [36] and Ag/TiO₂ as an excellent selectivity and stability for ethanol gas [44]. The prepared Pd/TiO₂ nanofibrous membrane showing good mechanical and electrical properties and providing an excellent material for hydrogen sensing is reported [45]. The Pd/TiO₂ used as catalysts were found to promote ethylene selectivity in selective acetylene hydrogenation [46]. TiO₂ nanofiber enhancements of Pd-doped TiO₂ fibers were reported for gas sensing characteristics [47]. Sensing performances of Pd-doped TiO₂ films were tested and the doping Pd was found to improve the response sensitivity of TiO₂ sensor remarkably for CO sensing [48] and for NH₃ sensing sensitivity [49]. The mesoporous Ag-(TiO₂/SnO₂) nanostructures were found to show excellent response towards ethanol and high selectivity towards other volatile organic compounds (VOCs) including acetone, methanol, isopropanol, benzyl alcohol and ethyl acetate [50]. Several works revealed that Ag-doped TiO₂ nanomaterials provided photocatalytic properties [51–54] but almost no work on gas adsorption using Ag-doped TiO₂ material has been done. Therefore, adsorptions of H₂ and hydrogen containing gases on Ag-doped TiO₂ for gas sensing application have been included in this work.

In the present work, we have applied the periodic density functional theory (DFT) to investigate the binding of single Pd and Ag atoms onto anatase TiO₂ (1 0 1) surface, denoted as M/TiO₂, where M = Pd and Ag. The adsorption abilities for H₂ and hydrogen containing gases, (H₂O, NH₃ and CH₄) of M/TiO₂ surfaces have been investigated.

2. Computational details

All quantum-mechanical calculations were carried out using the CRYSTAL06 software packages [55] implementing a periodic LCAO (linear combination of atomic orbitals) approach with atom-centered Gaussian type basis functions. DFT (density functional theory), the B3LYP hybrid functional including Becke's three-parameter exchange [56] and Lee–Yang–Parr correlation [57] as a hybrid functional have been adopted. In terms of basis sets, the Ti and O atoms of the surface has been described by HAYWSC-411(311d)G [58] and 8-411d1G [59], respectively. The basis sets for dopants, Pd (HAYWSC-2111d31) [60], Ag (HAYWSC-311d31G) [61] were employed. For molecular gases adsorbent, H (3-1p1G) [62], O (8-411d1G) [59], N (6-31d1G) [62] and C (6-21G) [63] were used. Spin polarized calculation was incorporated in the geometry optimization for all Ag/TiO₂ systems. A Monkhorst–Pack shrinking factor of $2 \times 2 \times 1$ *k*-point was used to sample the Brillouin zone. The tolerances for geometry optimization convergence have been set to the default values and the default truncation thresholds of 10^{-6} , 10^{-6} , 10^{-6} , 10^{-6} and 10^{-12} for the coulomb-exchange screening tolerances. Fock/Kohn–Sham matrices mixing was set to 70.

The surface model of two-dimensionally (2D) periodic slab of anatase TiO₂ (1 0 1) surface, the 2D periodic (2×2) supercell slab with a thickness of twelve slab layers for a total of 48 atoms (Ti₁₆O₃₂) with all bridged oxygen atoms and Ti atoms on top of the surface as active sites was employed as accomplished in our previous work [64]. The anatase TiO₂ (1 0 1) surface which is a corrugated structure is characterized by the presence of fully coordinated, 6-fold coordinated Ti atoms (Ti_{6C}) and 3-fold coordinated oxygen O atoms (O_{3C}), coordinative unsaturated atoms, 5-fold coordinated Ti atoms (Ti_{5C}) and 2-fold coordinated bridging oxygen O atoms (O_{2C}), as shown in Fig. 1. The anatase surface was modified from the optimized geometry of 2D slab (1 0 1) surface of X-ray crystallographic structure of the anatase TiO₂ [65]. The metal atoms and molecular gases are relaxed to obtain their optimized positions. All M/TiO₂ surfaces and their adsorption struc-

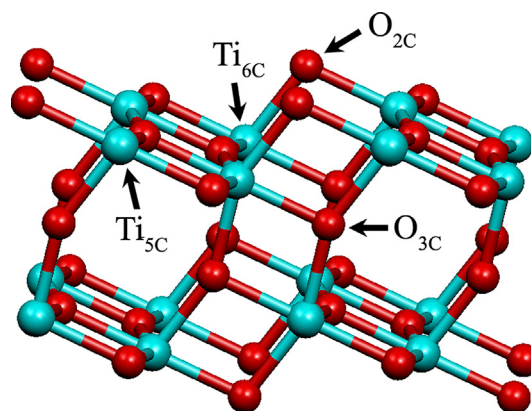


Fig. 1. Optimized surface structure of the anatase TiO₂ (1 0 1) surface. The cyan and red spheres are Ti and O atoms, respectively.

tures with molecular gases were obtained by geometry optimizations with fixing all the positions of TiO₂ atoms to retain TiO₂ (1 0 1) surface structures.

The binding energy (ΔE_{bind}) for the metal (M) atom adsorbed on the TiO₂ surface and the adsorption energy (ΔE_{ads}) of H₂, CH₄, H₂O, NH₃ and CH₄ gases on the M/TiO₂ surfaces, are computed using Eqs. (1) and (2), respectively.

$$\Delta E_{\text{bind}} = E_{\text{M/TiO}_2} - (E_{\text{M}} + E_{\text{TiO}_2}) \quad (1)$$

$$\Delta E_{\text{ads}} = E_{\text{gas/M/TiO}_2} - (E_{\text{gas}} + E_{\text{M/TiO}_2}) \quad (2)$$

where $E_{\text{M/TiO}_2}$ is total energy of the M/TiO₂ surface. E_{M} and E_{TiO_2} are total energies of single M metal atom and the TiO₂ surface, respectively. $E_{\text{gas/M/TiO}_2}$ and E_{gas} are total energies of gas molecules (H₂, H₂O, NH₃ and CH₄) adsorbed on the M/TiO₂ surface and the isolated molecular gases, respectively. Within this definition, a negative value of ΔE_{ads} indicates to a stable adsorption. The detail of Mulliken population analysis is carried out.

3. Results and discussion

3.1. The binding of single metal atoms supported on the anatase TiO₂ (1 0 1) surface (M/TiO₂)

According to the previous studies [66–68], undercoordinated Ti_{5C} and O_{2C} atoms of the anatase TiO₂ surface can act as active sites and more reactive than Ti_{6C} and O_{3C} atoms, see in Fig. 1. Therefore, the initial configurations of a single Pd and Ag atoms were added above the anatase TiO₂ (1 0 1) surface in between Ti_{5C} and O_{2C} atoms. Their final configurations obtained from full structure optimizations using periodic DFT method are the adsorption of Pd at Ti_{5C} and two O_{2C} sites, and Ag at O_{2C} site of anatase TiO₂ (1 0 1) surfaces. Fig. 2 presents the optimized structures of metal atom adsorptions on the anatase TiO₂ (1 0 1) surface to form Pd/TiO₂ (1 0 1) and Ag/TiO₂ (1 0 1), and their corresponding geometric parameters as listed in Table 1. The optimized structure of the Pd/TiO₂ shown in Fig. 2(a), Pd atom binds to the Ti_{5C} atom and two O_{2C} atoms which Pd–Ti_{5C} and Pd–O_{2C} bond lengths are 2.58 and 2.81 Å, respectively. The binding energy of single Pd atom on the perfect TiO₂ (1 0 1) surface (–2.15 eV) is close to the previous work using generalized gradient approximation (GGA) calculations (–2.18 eV) [69] but smaller than that of Pt adsorbed on the anatase TiO₂ (1 0 1) surface (–2.84 eV) [70]. The value of our work is much larger than the value obtained from the periodic supercell using a GGA approach of the Pd atom adsorbed on the perfect rutile TiO₂ (1 1 0) surface, using a four-layer thick slab

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