Photocatalytic activity of carbon nanotube/Ag₃PO₄ hybrid from first-principles study

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Abstract

Pure silver phosphate (Ag₃PO₄) is an indirect semiconductor which has super photooxidative capabilities under visible light irradiation. Also, it can be used as a photocatalyst due to the rapid recombination of electron–hole pairs. The low structural stability of pure Ag₃PO₄ is the major factor militating against its use for practical applications. Under visible light irradiation, carbon nanotubes (CNTs) can increase the stability and photocatalytic activity of Ag₃PO₄. This study investigated the photocatalytic activity and stability of the CNT (6, 0)/Ag₃PO₄ hybrid by analyzing the geometric, electronic and optical properties with the density functional theory method. Semimetallic single-walled carbon nanotubes (SWCNT) (6, 0) may chemically or physically interact with the Ag₃PO₄ surface depending on its relative orientations. As its surface is exposed by SWCNT (6, 0), Ag₃PO₄ becomes a direct band gap semiconductor. The small band gap makes the CNT/Ag₃PO₄ hybrid absorb sunlight from the ultraviolet to the infrared region.

Keywords: single wall carbon nanotube (6, 0), silver phosphate, density functional theory method, photocatalyst

Classification number: 3.02

Introduction

Ag₃PO₄ is an excellent visible light photocatalyst with high photooxidative capability [1]. It is used to degrade organic contaminants and serves as a photofunctional material for wastewater cleaning [2]. This photocatalyst has high quantum efficiency under visible light irradiation, but, it is unstable under irradiation [3]. Numerous methods have been explored for improving and increasing the stability and photocatalytic activity of this photocatalyst. This includes the combination of Ag₃PO₄ with different materials, including SnO₂ [4], AgX (X = Cl, Br and I) [5], TiO₂ [6], Fe₃O₄ [7] and GO [8, 9].

The Ag₃PO₄/g – C₃N₄ composite was synthesized for water oxidation [10], oxygen production and pollutant degradation [11]. Also, g – C₃N₄ nanorod/Ag₃PO₄ composites have been considered as one of the most effective techniques for achieving the conversion of clean and sustainable sunlight to solar fuel [12]. The bifunctional TiO₂/Ag₃PO₄/graphene (GR) composites exhibited highly efficient visible light photocatalytic activity toward organic dye molecule degradation and showed excellent bactericidal performance [13]. Under LED illumination, Ag₃PO₄/Ag/graphene/graphitic carbon nitride (g – C₃N₄) hetero structured materials can drive photocatalytic water oxidation efficiently [14].

As a result of the exceptional structure and properties of CNT, it could be used as a dopant for improving the photocatalytic degradation efficiency. The electronic properties of a CNT prepare continuous electronic states in the conduction band (CB) for donating the transferring electrons [15].

The capabilities of charge transfer of CNT can promote the excited electron in the conduction band of the semiconductor to drift into the CNTs, thereby decreasing the ability of electron–hole pairs to recombine [16], and increasing the photocatalytic activity under visible light. Some composite materials have been proven to be effective, such as CNT/ZnO [17], CNT/C₃N₄ [18] and CNT/TiO₂ [19, 20]. CNT could be used
as electron capture agents to increase the activity and stability of Ag$_3$PO$_4$. The photocatalytic activity of CNT/Ag$_3$PO$_4$ has been investigated with Rhodamine B (RhB) as a model contaminant by experimental method. The experimental results showed that CNT/Ag$_3$PO$_4$ displayed much higher photocatalytic activity than the pure Ag$_3$PO$_4$ [16]. The chemical bonds according to covalent interaction at the interface are supposed to be charge transfer channels [21] and the Van der Waals (vdW) forces between CNTs and the semiconductor were also revealed at the interfaces [22], thereby increasing the photocatalytic activity of Ag$_3$PO$_4$ hybrids. Various mechanisms have been suggested for increasing the photocatalytic properties of CNT/Ag$_3$PO$_4$ hybrids. One is that in the time of photocatalysis, a high-energy photon stimulates an electron from the valence band (VB) to the CB of Ag$_3$PO$_4$, and the generated electrons formed in the space-charge districts are carried into the CNTs, thereafter holes stay on Ag$_3$PO$_4$ to take part in redox reactions [23, 24]. In this work, the interaction between Ag$_3$PO$_4$ and SWCNT (6, 0) was investigated using large-scale density functional theory (DFT) computations to disclose the enhanced photocatalytic performance.

**Computational method**

The most stable Ag$_3$PO$_4$ surface, cubic Ag$_3$PO$_4$ (100) surface and metallic CNT (6, 0) were selected. The theoretical calculations were performed using the plane wave pseudopotential DFT method, as implemented in the CASTEP code [25]. The generalized gradient approximation (GGA) was used to describe the exchange and correlation energy of the electrons [26]. Geometry optimizations and single-point energy calculations were performed. The calculated supercells consisted of a Ag$_3$PO$_4$ (100) surface which contained 32 O, 8 P and 24 Ag atoms and the (6, 0) tube which contained 108 atoms, length of 12.8 Å in its axial direction.

**Results and discussion**

The experimental lattice parameter $a = 6.013$ Å of cubic Ag$_3$PO$_4$ with space group $P4 – 3n$ (NO. 218) was taken to get the crystal cell [27]. By minimizing the total crystal energy, the equilibrium lattice parameter was calculated using the GGA method and the results are presented in table 1 with the experimental values. The lattice parameter includes $a = 6.004$ Å, which is slightly overestimated less than the experimental values. There is a strong correlation between structural parameters and the experimental values.

For the noncovalent hybrid, the equilibrium distances between the CNTs and the top layer of the Ag$_3$PO$_4$ (100) surface after optimization was calculated to be 2.450 Å for CNT (6, 0) /Ag$_3$PO$_4$. A side view of the hybrid of CNT and the cubic Ag$_3$PO$_4$ (100) surface is shown in figure 1. The strength of the CNT/Ag$_3$PO$_4$ hybrid can be evaluated by their formation energy, which is defined as:

$$E_{formation} = E_{hybrid} - (E_{CNT} + E_{Ag_3PO_4})$$

where $E_{hybrid}$, $E_{CNT}$ and $E_{Ag_3PO_4}$ display the total energy of CNT/Ag$_3$PO$_4$ (100), pure CNT, and clean Ag$_3$PO$_4$ (100) surfaces, respectively. By this definition, negative $E_{formation}$ shows that the interface is steady and stable. The interface formation energy was calculated to be $-1.020$ eV, indicating a rather strong interaction between CNTs and the Ag$_3$PO$_4$ (100) surface, and the thermodynamic stability of this hybrid.

The density of states (DOSs) of Ag$_3$PO$_4$ and CNT, before and after the formation of the hybrid, was calculated so as to determine the effect of the type of interfacial interaction on the electronic properties of hybrid.

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**Table 1. Structure parameters of Ag$_3$PO$_4$: lattice parameters and atom positions.**

| Method     | Bond length/Å | Bond angle (deg) | Fractional coordinates |
|------------|---------------|------------------|------------------------|
| Exp [22]   | 6.013         | 2.45             | P-O: 1.539, Ag-O: 2.345, O-P-O: 109.470, O-Ag-O: 93.660 |
|            |               |                  | Ag: 0.231, 0.000, 0.500 |
| GGA-PBE    | 6.004         | 0.285            | P-O: 1.549, Ag-O: 2.364, O-P-O: 109.307, O-Ag-O: 92.995 |
|            |               |                  | Ag: 0.250, 0.000, 0.500 |

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**Figure 1.** Side view of the hybrid of CNT and the cubic Ag$_3$PO$_4$ (100) surface.
Pure Ag₃PO₄ is an indirect semiconductor with a band gap \( (E_g) \) of 2.45 eV and its CB bottom is very diffusive, causing smaller useful masses of the photogenerated electrons in pure Ag₃PO₄ [1]. While the surface of Ag₃PO₄ is exposed, Ag₃PO₄ becomes a direct band gap semiconductor and \( E_g \) declines to 2.15 eV [28].

The DOS of pure Ag₃PO₄ is presented in figure 2. Also, the DOS of single metallic (6, 0) CNT showed 0eV band gap, which corroborates previous studies [22]. Figure 3 shows that the DOS of (6, 0) CNT/Ag₃PO₄ hybrid changes a little from individuals. The interaction between the metallic (6, 0) CNTs and Ag₃PO₄ may interact via a noncovalent vdW force. The band gap of CNT/Ag₃PO₄ hybrid is small (0.16 < 0.3eV) mentioning that the hybrid can absorb the most sunlight, thus raising their photocatalytic activity. For the noncovalent CNT/Ag₃PO₄ hybrid, the CB bottom is formed mainly from Ag 5s orbitals, which can be more clearly observed from the electron density distributions of the lowest-unoccupied level (LUL), while the HOL is only composed of the C 2p orbitals.

Conclusions

The interaction in CNT (6, 0) and Ag₃PO₄ hybrid depends on the nature of CNTs and their relative orientations. Metallic CNT (6, 0) may physically interact with the Ag₃PO₄ (100). In the Ag₃PO₄ hybrid, the band gap is small which causes the CNT/Ag₃PO₄ hybrid to absorb sunlight from the ultraviolet to the infrared region. Moreover, CNTs are not only
effective sensitizers, but are also highly active co-catalysts in hybrids. This study is useful for developing highly efficient carbon-based nanophotocatalysts. During photocatalysis, the Ag₃PO₄ can be excited to yield photon-generated carriers and photoinduced electrons from the valence band (VB) are transferred to the conduction band (CB), leaving the holes in the VB. In hybrid of the Ag₃PO₄ and CNT, the photo-generated electrons are effectual trapped by CNT. The CNT can be increased photocatalytic activity and stability due to the fact that the introduction of CNT significantly improves the separation of photogenerated charge carriers. Thus, electrons and holes could be usefully divided so that the photocatalytic performance of the catalyst would be modified. The optical absorption of CNT/Ag₃PO₄ hybrids in the visible-light region can be greatly increased owing to their small band gap. Fascinatingly, it was realized that the CNTs are not only effective sensitizers, but also highly active co-catalysts in hybrids.

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