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Hetero-structure effect on Na adsorption and diffusion in two dimensional composites

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ABSTRACT

The composites of two-dimensional (2D) materials exhibit good energy storage performance, and hetero-structure plays an important role. In this study, Na adsorption on 2D graphene, silicene and transition metal dichalcogenides (TMDs) surfaces, and at TMDs/graphene and TMDs/silicene hetero-structures are systematically investigated through first-principles calculations. Two kinds of interfacial bonding characteristics in the hetero-structures are revealed. The adsorption of Na at different positions in the hetero-structures is studied. The relationship of Na adsorption with the interfacial bonding characteristics and the electronic structures of the systems is explored. The contribution of Na storage in the hetero-structures to the electrochemical performance is analyzed. Furthermore, combined with the study of Na diffusion, the microscopic mechanism of the synergistic effects in the hetero-structures on Na adsorption and diffusion are revealed. The results provide a theoretical basis for obtaining 2D composites with excellent Na storage performance through hetero-structure design.

1. Introduction

Rechargeable Na ion batteries (NIBs) are considered as promising alternatives to Li ion batteries (LIBs) due to the abundance and low price of Na element [1–3]. However, the practical applications of NIBs have been hamstrung by the lack of suitable anode materials to accommodate Na ion which has a larger radius than Li ion [4,5]. As the most widely used anode material in LIBs, graphite has a highly ordered structure while it is considered to be not suitable to host Na ion because Na hardly forms staged intercalation compounds with graphite [6–8]. The successful preparations of graphene and its analogous structures have brought new ideas for the development of NIBs [9,10].

Different anions combine with metal atoms to give different band gaps, which can promote electron transfer by regularize the structural, electronic and bonding properties. Among them, transition metal dichalcogenides (TMDs) have similar structures to graphite, and the open framework of these types of materials allows Na ion to insert reversibly with good mobility [11,12]. But some limitations impede their further applications [13,14], such as low electronic conductivity, significant volume change and mechanical stress. On the other hand, graphene has many unique advantages relative to other 2D materials, such as large specific surface area, high electric conductivity, excellent mechanical flexibility, and so on [15]. However, the pristine graphene is difficult to accept electrons from Na atoms because of electron-balance system of graphene [16]. Meanwhile, clustering is probably inevitable when depositing Na on graphene with high coverage [17]. Compounding two materials is an effective way to improve the performance of NIBs electrodes. Previous reports have shown that exfoliated MoS_2-G electrodes [18], exfoliated $MoSe_2$ into carbon nanospheres [19], $MoTe_2$/rGO composite [20], and carbon coated Sb_2S_3 hollow spheres [21] have potential as high performance electrodes for NIBs. Combining TMDs and graphene is also a convenient mean of modifying electrode materials. The composites with 2D layered hetero-structures (such as MoS_2/graphene [4,22], WS_2/graphene [23] and SnS_2/graphene [24]) exhibit more stable cycling stability, higher capacity and rate capability than pristine TMDs as anode materials for NIBs. Na storage behavior is expected to be related to 2D hetero-structures, but the influence mechanism of different 2D hetero-structures on Na storage in 2D composite

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materials is still unclear.

Silicon and carbon belong to group IV of the periodic table. Both graphene and silicene are zero-gap semiconductors and have low migration energy barriers for Na of 0.14 and 0.23 eV, respectively [25,26]. Nevertheless, silicene have a low-buckled honeycomb structure [27] and can possess many unique properties such as sp^2 and sp^3 hybridization [28], larger hexagons size [29], higher adsorption energy and theory capacity for Na than graphene [30], due to its larger atomic radius and lower electronegativity as previous studies have verified [31]. Moreover, silicene and MoS_2 composites exhibit metallic electronic properties with the geometry of silicene and MoS_2 layers slightly distorted [28]. Therefore, silicene compositing with TMDs is expected to be with excellent electrochemical performance. It is necessary to study the effect of TMDs/silicene hetero-structures on Na storage. In the meantime, a comparison investigation of the Na storage behavior in TMDs/graphene and TMDs/silicene composites is helpful to ascertain the influence mechanism of different 2D hetero-structures on Na storage, which benefits the design of new energy storage materials.

In this work, we provide a comprehensive investigation on the Na adsorption at the hetero-structures of MS_2/G and MS_2/Si (M refers to Mo, W and Sn; G refers to graphene; Si refers to silicene) through the first-principles calculations. The influence mechanisms of 2D hetero-structures on Na adsorption and diffusion are explored through the detailed energy and electronic structure analysis. The feasibility of using the composites with the 2D hetero-structures as anode material for NIBs is also discussed.

2. Computational method

Vienna ab initio Simulation Package (VASP) [32] based on the projector augmented wave (PAW) formalism [33] of the density functional theory (DFT) is used in the calculations. The exchange correlation functional is depicted by the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerh (PBE) [34]. In order to get a better picture of weak interaction [35], we choose a computationally cost-effective“optB86b-vdW″method for vdW interactions [36]. Fig. 1 shows MoS_2, WS_2, SnS_2, G, Si and the related hetero-structure models adopted in our study, and the optimized lattice parameters of MoS_2, WS_2, SnS_2, G and Si are in agreement with previous results (Table 1). For MoS_2/G and WS_2/G (Fig. 1(e)), MS_2 monolayer with 4 × 4 supercell containing 16 M and 32 S atoms and G with 5 × 5 supercell containing 50 C atoms are used, and the lattice mismatches are about 2.57% and 2.29%, respectively. For SnS_2/G (Fig. 1(f)), SnS_2 monolayer with 2 × 2 supercell containing 4 Sn and 8 S atoms and G with 3 × 3 supercell containing 18 C atoms are used, and the lattice mismatch is about 0.13%. For MoS_2/Si and WS_2/Si (Fig. 1(g)), MS_2 monolayer with 5 × 5 supercell containing 25 M and 50 S atoms and Si with 4 × 4 supercell containing 32 Si atoms are used, and the lattice mismatches are about 2.59% and 2.28%, respectively. For SnS_2/Si (Fig. 1(h)), SnS_2 monolayer with 4 × 4 supercell containing 16 Sn and 32 S atoms and Si with 4 × 4 supercell containing 32 Si atoms are used, and the lattice mismatch is about 4.15%. G and Si expand or shrink to fit the MS_2 supercell.

Table 1
Lattice parameters (Å) of MoS_2, WS_2, SnS_2, G and Si monolayers from the present studies and previous reported results.

	MoS_2	WS_2	SnS_2	G	Si
GGA	3.17	3.16	3.70	2.47	3.86
	3.19 [38]	3.13 [39]	3.67 [40]	2.46 [41]	3.85 [31]
Experiment	3.16 [42]	3.15 [43]	3.64 [44]	2.46 [45]	3.80 [46]

The vacuum layer in the perpendicular direction is set above 20 Å. For geometry optimizations, the Brillouin zone [37] is sampled using gamma-centered Monkhorst-Pack scheme with 1 × 1 × 1 k-point grid, and the energy cutoff is 400 eV. All the internal coordinates, as well as the cell shapes are relaxed until the Hellmann-Feynman forces are less than 0.01 eV/Å. The 5 × 5 × 1 k-point mesh is used for the calculation of the system energy.

3. Results

3.1. Interface interaction of MS_2/G and MS_2/Si hetero-structures

The interface interaction energies of the MS_2/G and MS_2/Si hetero-structures are defined as:

$$E_I = E_G + E_M - E_T, \tag{1}$$

where E_G, E_M and E_T represent the energies of G (Si), MS_2 monolayers, and the corresponding MS_2/G (Si) hetero-structures, respectively.

As listed in Table 2, the values of E_I per C are relatively small, suggesting weak interactions between G and MS_2 monolayers. The E_I of MS_2/Si (>0.1eV) are bigger than that of MS_2/G (<0.1eV), and the distance between Si and MS_2 is reduced, compared with that between G and MS_2. Thus, the mixed sp^2-sp^3 hybridization in Si can provide stronger bindings with their neighboring MS_2 layers. The

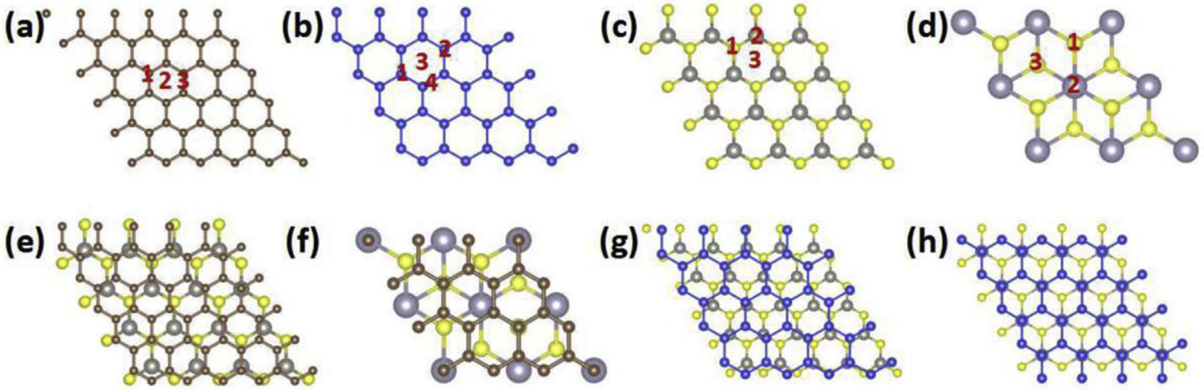

Fig. 1. Atomic structures (top view) of (a) G, (b) Si, (c) Mo(W)S_2, (d) SnS_2, and the hetero-structures of (e) Mo(W)S_2/G, (f) SnS_2/G, (g) Mo(W)S_2/Si and (h) SnS_2/Si. Light gray, dark gray, yellow, sapphire blue and brown spheres represent Mo (W), Sn, S, Si, and C atoms, respectively. The Na atom adsorption positions on G, Si and MS_2 monolayers are numbered in (a), (b), (c) and (d). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)