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Theoretical investigations of the interaction between transition-metal and benzoquinone: Metal dispersion and hydrogen storage

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ABSTRACT

The dispersion of transition metals (TM) has been an ongoing challenge for quasi-molecular H₂ storage. Here we have investigated the adsorption of TM (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) on benzoquinone (BQ), by using the first-principles methods. It is found that Sc or Ti (Sc/Ti) atom is energetically favored to bind with ortho-BQ (OBQ) to form OBQ–Sc/Ti complex when compared to their bulk structures. Notably, the coordination number of Sc/Ti is only two, thereby providing enough empty *d* orbitals for H₂ storage without geometrical blocking. Four H₂ molecules can be accommodated by each OBQ–Sc complex via Kubas-like interaction, with the adsorption energy of 0.20 eV/H₂ and the H₂ storage capacity of ~5.0 wt%. For practical application, two types of structures have been proposed for H₂ storage using BQ molecule as building block, which would guarantee the dispersing of Sc atom and avoid clustering of OBQ–Sc complexes. In particular, for Sc-decorated oxygen-terminated zigzag graphene nanoribbons, the capacity of H₂ storage reaches up to 6.0 wt%.

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Introduction

The Kubas-like interaction mechanism, derived from hybridization between *d*-orbitals of transition metal (TM) and H₂'s σ/σ^* orbitals [1], is dominant for quasi-molecular H₂ storage based on TM-decorated nanomaterials [2–6]. A suitable binding energy of H₂ with TM (0.2–0.6 eV/H₂) endows these materials some outstanding properties, such as fast adsorption-desorption kinetics, good reversibility, and suitable

desorption temperature [7–11], thus showing remarkable advantages towards nanostructure and metal hydride materials. To reach a higher H₂ storage, a better dispersion of TMs on adsorbent is required, which has been pointed out by the previous theoretical studies [12–14]. A typical illustration is Ti-decorated cis-polyacetylene [12,15,16], on which each isolated Ti atom could adsorb 5H₂ molecules with binding energy as large as 0.46 eV/H₂. However, only 2H₂ can be accommodated by a Ti clustered dimer via Kubas-like interaction with a weakened binding strength of 0.26 eV/H₂. Similar cases have

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been also reported for the system of Ti-decorated fullerene [3,13], where the clustering of Ti atoms does not only change the nature of H₂ bonding but also reduce the weight percentage of H₂ storage. Therefore, the search for novel supporting matrices that can disperse TMs has become the key issue for the design of H₂ storage media through Kubas-like interaction mechanism.

In the past decades, carbon-based nanostructures, BN nanostructures, organic polymers, and porous networks have been proposed as candidates to disperse TMs [2–4,14,17–21], considering their high surface-to-weight ratio and light weight. However, a serious obstacle is that the TM clustering is difficult to overcome, since the binding energy of TM with these materials is much smaller than its corresponding cohesive energy. A number of tactics for stabilization on surface have been attempted, such as doping via substituting C atom by B or N atom [6,22], introducing mono or double-vacancy [23], or their combinations [21,24]. In addition, using strain modulation [25] or curvature of nanostructure [26] has also been explored. However, a general confliction seems exist between the H₂ adsorption capacity and structural stability. A strong binding between TM and adsorbent is often accompanied with a large TM coordination number, and subsequently the number of adsorbable H₂ molecules and the binding strength via Kubas-like interaction are both significantly reduced [21,27]. For instance, through incorporating porphyrin unit as TM dispersants in graphene, TMs from Sc to Zn can be dispersed with each TM bonded with four N atoms, while each TM could adsorb no more than two H₂ molecules [21]. Thus, for an ideal H₂ storage media, the number of TM coordination should be small enough to enhance the H₂ adsorption, and meanwhile the binding between TM and adsorbent should be strong enough to maintain the system's stability.

In this paper, we have proposed an organic molecule benzoquinone (BQ) to disperse TM (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) atoms. In the formed ortho-BQ–Sc or ortho-BQ–Ti (OBQ–Sc/Ti) complex, the binding energy is remarkably larger than Sc/Ti's cohesive energy and the coordination number of Sc/Ti is only two, indicating a well dispersion of TM and enough empty *d* orbitals for further H₂ uptake. Four H₂ molecules can be accommodated by each OBQ–Sc molecule via Kubas-like interaction, with adsorption energy of 0.20 eV/H₂ and H₂ storage capacity of 5.0 wt%. Using BQ molecule as building block, two types of structures have been designed for H₂ storage, the capacity of which are 3.8 and 6.0 wt%, respectively.

Computational methods

The spin-polarized calculations were carried out based on density functional theory (DFT) as implemented in Vienna *ab initio* simulation package (VASP) [28]. The exchange and correlation potential with the generalized gradient approximation of Perdew, Burke, and Ernzerh (GGA-PBE) [29] was combined with the projector-augmented wave method (PAW) [30] to solve the Kohn–Sham equations. Dispersion correction, which takes van der Waals interaction into account, is adopted at DFT-D2 level of Grimme method [31], which is

known to give a better description of geometries and corresponding energies than those from the standard DFT [32].

The binding of TMs on OBQ and the H₂ molecules' adsorption on OBQ–Sc complex were simulated in a cubic box of 20 × 20 × 20 Å at Γ point with a cutoff energy of 480 eV. All the structures were relaxed until the force on each atom is less than 0.01 eV/Å. The optimized bond lengths of C₁–O, C₁–C₂, C₂–C₃ of para-BQ (PBQ) molecule are 1.24, 1.48, 1.35 Å, respectively, well consistent with the experimental data [33,34], and those of C₁–O, C₁–C₁, C₁–C₂, C₂–C₃, and C₃–C₃ of OBQ molecule are 1.23, 1.57, 1.47, 1.36, and 1.46 Å, in good agreement with previous theoretical studies [35] (cf. Fig. 1 and Table 1). The variation in total energy of configuration OBQ–Sc–4H₂ (cf. Fig. 2d) with the cell size increasing from 20 to 30 Å is within 3 meV. The binding energy of TM is defined as $E_b = (E_{OBQ} + nE_M - E_{OBQ-nM})/n$, where E_{OBQ} , E_M , and E_{OBQ-nM} represent the total energies of isolated OBQ molecule, isolated TM atom, and OBQ with adsorbed TMs respectively, and n is the number of TMs. The binding energies are listed in Table 2, combined with TMs' cohesive energies from theoretical calculations and experiments [36]. The Sc–O bond length in OBQ–Sc complex is 1.91 Å, close to ~2.07 Å in Sc₂O₃ compound [37]. The calculated cohesive energy of Sc is 4.14 eV, in agreement with the experimental value of 3.90 eV.

The O-terminated zigzag graphene nanoribbons (O-ZGRNs) is simulated by a periodical structure of C₁₆O₈ along the X-axis direction, the vacuum layers in Y and Z directions are both ~15 Å. The Brillouin zone is sampled using a Γ point centered *k*-mesh of 8 × 1 × 1. The lattice constant is 10.06 Å. In the optimized configuration (shown in the inset of Fig. 5), the bond lengths of C=O, C–C, and C=C are 1.23, 1.49, and 1.37 Å, consistent with the previous theoretical study [38].

Results and discussion

Transition metal dispersion and hydrogen adsorption

The BQ molecule (C₆H₄O₂) contains two isomers, i.e., 1, 4-BQ (PBQ) and 1, 2-BQ (OBQ). Structurally, they can be regarded as two H atoms of benzene (C₆H₆) at para or ortho -position replaced by two O atoms, as shown in Fig. 1a. The O atom is bonded with C atom via a C=O double bond. Consequently, the circular π -bond of benzene is broken. Instead, it appears as a planar structure with localized, alternating C=C (~1.36 Å), C–C (~1.47 Å), and C=O (~1.23 Å) bonds (c.f. Table 1). The OBQ is about 0.32 eV less stable than PBQ. It is likely ascribed to the electrostatic repulsion between two neighboring O atoms.

The BQ molecule exhibits a strong ability of capturing electron. When each carbonyl O atom obtains an extra electron, the double bond of C=O breaks and a *p* electron is released at the end of each carbonyl C atom. Together with four *p* electrons located at two C=C bonds, a circular π -bond forms on the ring plane, leading to an unsaturated carbon-ring transformed to a benzene. To illustrate this tendency quantitatively, we consider a reaction of H₂ dissociated to bond with two O atoms of OBQ to form 1, 2-benzenediol (C₆H₆O₂). The exothermic energy is 2.18 eV, in good agreement with the previous studies [39,40].

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