Large Magnetic Anisotropy of Single Transition Metal Ad-atoms on Monolayer WS_2

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Design of novel single ad-atom magnets with large magnetic anisotropy energy (MAE) hold out the promise to overcome the difficulties of bit-miniaturization for high-density data storage. In this work, we perform systematic density functional theory calculations to study the structural stability and magnetic properties of single transition metal ad-atoms adsorbed on monolayer WS_2. We found that Re ad-atom adsorbed on hollow site of WS_2 is stable and demonstrate large perpendicular MAE up to ~30 meV/atom. Analysis of electronic structure and rigid band model reveal that this large MAE originates from the spin-orbital coupling between the d_{xz} and d_{yz} orbitals near Fermi level through cross spin channel. Our work provides useful guidance to achieve single ad-atom magnets for potential application of nanoscale magnetic devices.

1 Methods & Model

Density functional theory (DFT) calculations were performed using the Vienna *ab initio* simulation package (VASP). The exchange-correlation were included using spin-polarized local density approximation (PBE+U) and spin-orbit coupling (SOC) was invoked self-consistently in the non-collinear mode of VASP. The interaction between valence electrons and ionic cores was described within the framework of the projector augmented wave (PAW) method. The energy cutoff for the plane-wave expansion was set to 500 eV and a 5 × 5 × 1 k-mesh was sampled in the Brillouin Zone for the lattice and ionic relaxations, where the force acting on each atom was reduced to less than 0.01 eV/Å.

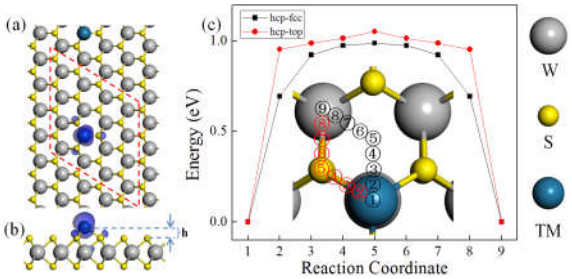

Fig. 1. (a) Top and (b) side views of TM ad-atoms(large blue sphere) on monolayer WS_2. The large grey and small yellow spheres represent the W and S atoms, respectively. The most stable binding sites of the transition metal (TM) ad-atom on monolayer WS_2 is the hollow site that is surrounded by three sulfur atoms and with a W atom below. Blue isosurface represent the spin density of TM ad-atom. (c) The reaction pathway of Re atoms on monolayer WS_2, insets shows the atomic structures corresponding to different transition states.

2 Results & Discussion

2.1 Binding Energy, Magnetic Moment and Height of Ad-atom

To evaluate the stabilities of TM@WS_2, we calculated their binding energies as defined by the following equations:

$$E_b = E_{TM@WS2} - E_{WS2} - E_{TM} \quad (1)$$

where $E_{TM@WS2}$ and E_{WS2} are the total energies of TM@WS_2 and pristine WS_2, respectively. E_{TM} is the total energy of an isolated TM atom.

(PBE+U)	E_b(eV)	M (μB)	h(Å)
Hf@WS_2	2.313	2.0	1.694
Ta@WS_2	2.459	1.0	1.433
W@WS_2	1.303	2.0	0.988
Re@WS_2	1.222	3.0	1.199
Os@WS_2	2.706	2.0	1.033
Ir@WS_2	3.223	1.0	1.065
Pt@WS_2	2.588	0.0	1.183
Ru@WS_2	3.079	2.0	1.145
Fe@WS_2	2.337	2.0	0.932
Co@WS_2	3.013	1.0	0.931

Table. 1. Calculated binding energies (E_b), magnetic moments (M) and adsorption height (h) for different TM ad-atoms on monolayer WS_2.

The MAE is mainly determined by the SOC (namely, the magneto-crystalline anisotropy) and can be calculated from the differences between perpendicular and in-plane contributions of SOC as expressed by

$$MAE = \xi^2 \sum_{u,o,\alpha,\beta} (2\delta_{\alpha\beta} - 1)\left[\frac{|\langle u,\alpha | L_z | o,\beta \rangle|^2}{\varepsilon_{u,\alpha} - \varepsilon_{o,\beta}} - \frac{|\langle u,\alpha | L_x | o,\beta \rangle|^2}{\varepsilon_{u,\alpha} - \varepsilon_{o,\beta}}\right] \quad (2)$$

where ξ is the strength of SOC, $\varepsilon_{u,\alpha}$ and $\varepsilon_{o,\beta}$ are the energy levels of the unoccupied states with spin α and occupied states with spin β, respectively.

2.2 Spin & Orbital Moment and MAE

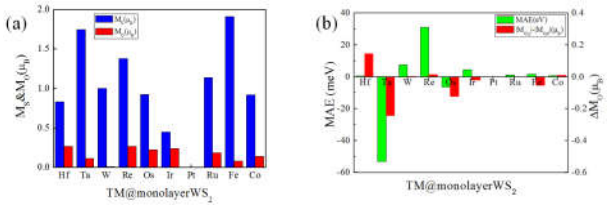

Fig. 2. (a) Spin and orbital moment of TM@monolayer WS_2. (b) Magnetic anisotropy energies(MAE) and Orbital Moment difference $|M_{O\perp}|$ - $|M_{O\parallel}|$ (μB) of TM@monolayer WS_2

2.3 P-DOS and Total & spin-decomposed MAE

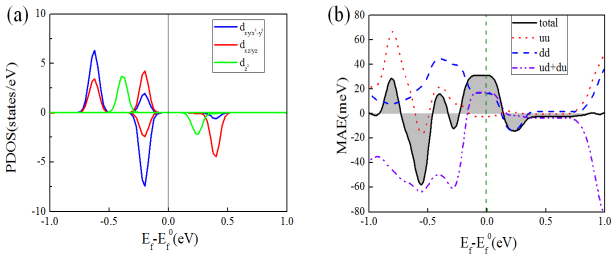

Fig. 3. (a) The calculated projected-DOS for Re ad-atom in Re@WS_2. (b)Total and spin-decomposed MAE of Re@WS_2.

These results show the importance of SOC between key pair orbitals near Fermi level in order to obtain large MAE.

2.4 Band structure and distribution of Berry curvature

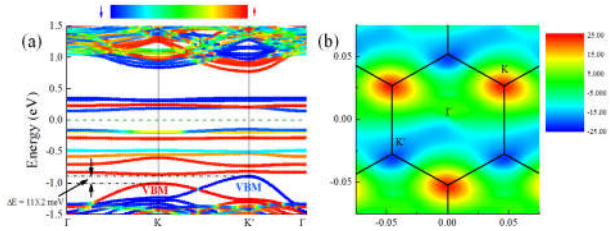

Fig. 4. (a) Calculated band structure of Re@monolayer WS_2. The color code in (a) represent weights in two spin channels. (b) The distribution of Berry curvature of Re@monolayer WS_2. Red and blue colors in (b) show positive and negative Berry curvatures, respectively.

3 Conclusion

Re ad-atoms can stably adsorbed on monolayer WS_2, making Re@WS_2 exhibit a large perpendicular MAE up to an order of ~30 meV/atom. This large perpendicular MAE mainly comes from the SOC interactions between key pair states in the d_{xz} and d_{yz} orbitals through cross spin channel near Fermi level. The dynamical stabilities and large MAE are the key factors to achieve single ad-atom magnets and realize bit-miniaturization for potential applications in nanoscale magnetic storage and quantum information processing.

P. Zuo, H. Wang, Z. Wang, and R. Wu, ***Journal*** of ***Magnetism*** and ***Magnetic Materials*** **506**, 166796 (2020)