



Role of electron localisation in H adsorption/hydride formation in the Mg basal plane under aqueous corrosion: A first-principles study

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Introduction

Understanding hydrogen-metal (H-M) interactions is important in various fields of surface science, including the aqueous corrosion of metals [1].

The interaction between atomic H and Mg surface is a key process for the formation of sub-surface Mg hydride, which may play an essential role in Mg aqueous corrosion [2].

We reveal that the electron localisation function (ELF) can be a promising indicator for predicting the possible stable adsorption sites of atomic H in the Mg (0001) surface.

We find that the ELF pattern of the Mg surface can be modified by the on-surface atomic or radical adsorptions. The sub-surface H adsorption and sub-surface hydride layer in the Mg (0001) surface are thus stabilized by the on-surface adsorption with some sub-surface ELF enhanced regions (or local H traps).

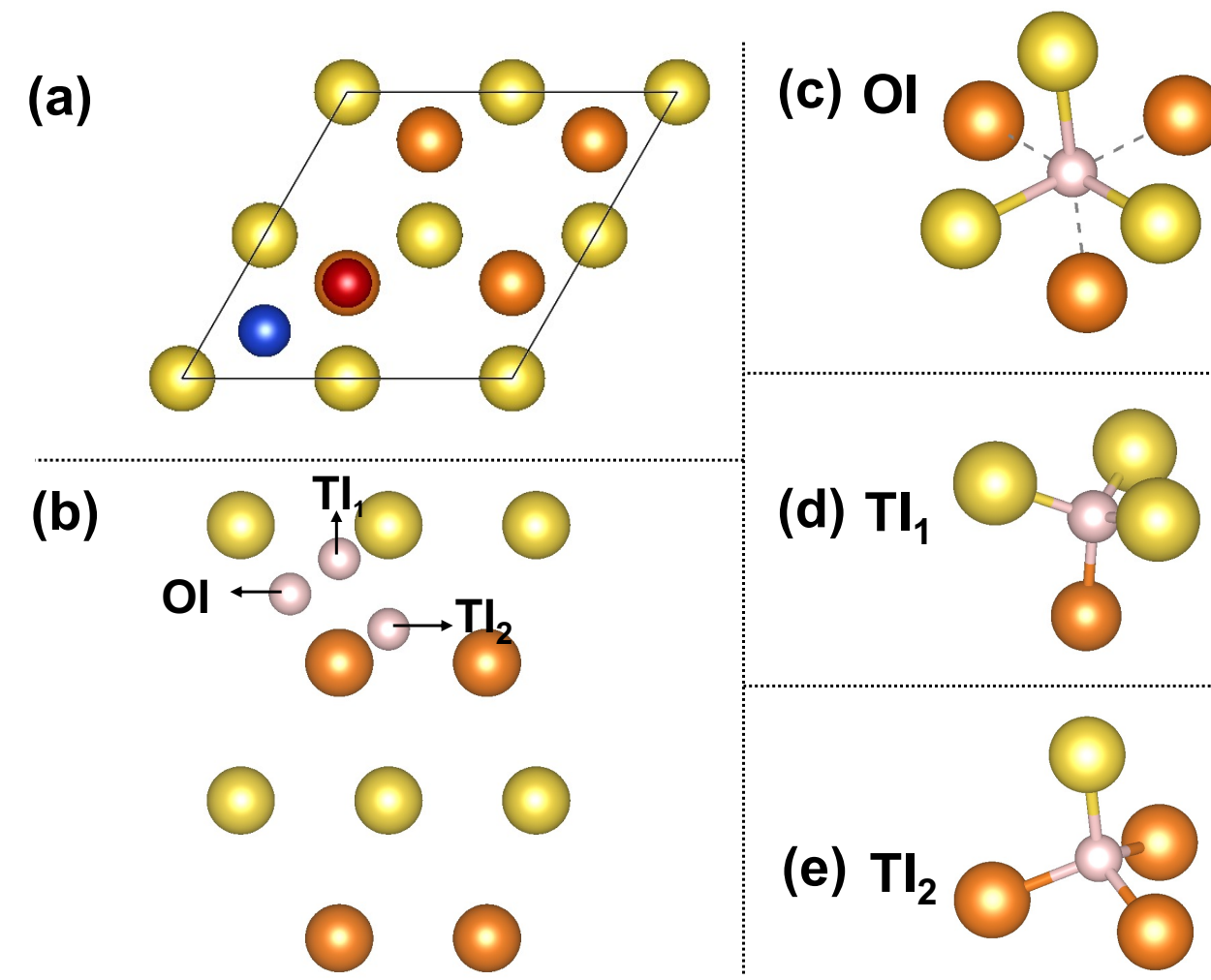


Figure 1 (a) and (b) correspond to the top view and the side view of the Mg (0001) surface. The on-surface FCC and Hcp site are represented by the blue and red sphere. Top layer (TL) Mg atoms and second layer (SL) ones are indicated by different colours. (c)-(e) demonstrate the octahedral (OI), tetrahedral-I (TI₁) and tetrahedral-II (TI₂) interstitial within the subsurface region of the Mg basal plane.

Theory & Modelling

ELF is calculated as the possibility of finding an electron in the vicinity of another like-spin electron [3].

The formula of ELF could be written as :

$$ELF_{\sigma} = \frac{1}{1+\chi_{\sigma}^2} \text{ with } \chi_{\sigma} = \frac{2(\tau_{\sigma} - \tau_{\sigma}^W)}{\tau_{\sigma}^{UEG}}$$

The numerator of χ_{σ} describes the kinetic energy density difference between a Fermionic system and a Bosonic system. The denominator is the kinetic energy density of a uniform electron gas.

The on-surface adsorption sites could be covered with OH radicals, atomic O or atomic H which are dissociated from water molecules.

The sub-surface adsorption sites are only available for atomic H because of its small size and high mobility within Mg substrate.

	FCC	HCP	OI	TI ₁	TI ₂
@ELF	0.66	0.79	0.35	0.69	0.67

Table 1 Onsite ELF value at different adsorption site of a pristine Mg (0001) surface. An ELF value approaching 0.5 means the local electron localisation is similar to a uniform electron gas. A higher ELF value indicates that electrons is highly localised onsite.

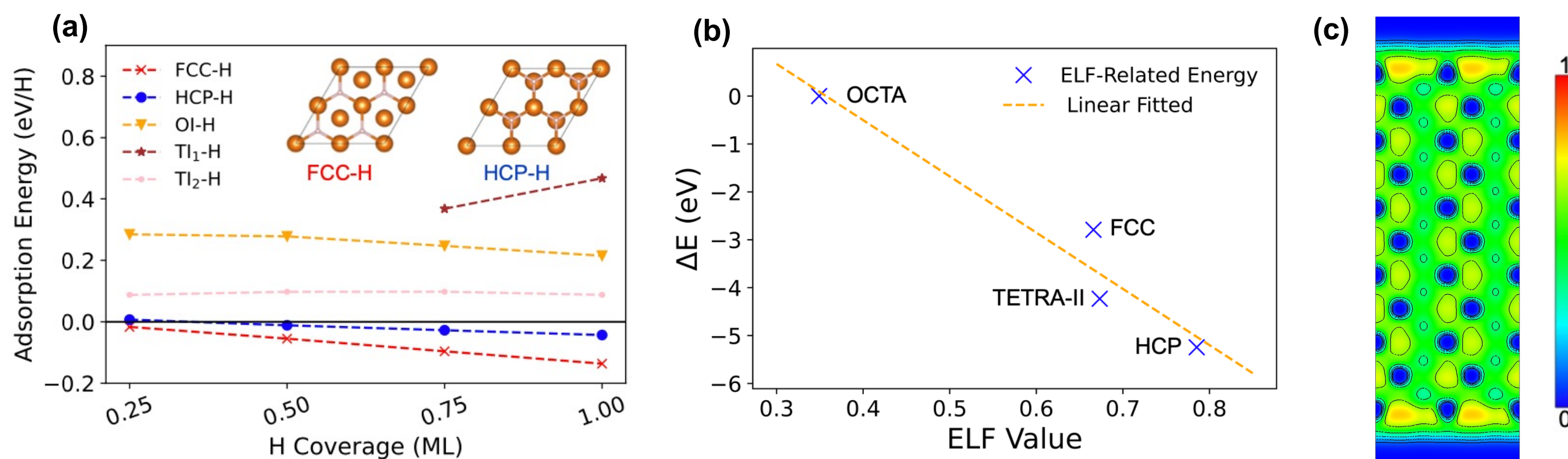


Figure 2 (a) Adsorption energy of H on the pristine Mg (0001) surface or in the sub-surface interstitial sites when the H coverage is less than 1 ML. (b) Linear fit of the estimated ELF-related energy with respect to the onsite ELF value. The ELF-related energy is calculated as the energy reminder of the total H adsorption energy subtracting the H₂ dissociation energy, lattice distortion energy and the Coulomb interaction energy, then calibrated by the highest value. (c) The side-view ELF contour of the Mg (0001) surface (blue spheres indicate the position of Mg atoms).

Low H Coverage

At low H coverage (less than 1 monolayer), on-surface Hcp site on the Mg (0001) surface is the most stable adsorption site for atomic H with a negative adsorption energy.

The total adsorption energy of hydrogen atom on the Mg (0001) surface could be decomposed into four individual components: H₂ dissociation energy, lattice distortion energy, Coulomb interaction energy and the ELF-related energy.

The ELF-related energy of H at each adsorption site is linearly correlated to the onsite ELF value (higher the ELF value, stronger the H-electron interaction, thus more negative the correspondent energy).

High ELF region (local maxima) within metal surface could be treat as proton-attractors (traps for H). Therefore, ELF is a good indicator in predicting the possible adsorption sites for atomic H in the Mg (0001) surface.

Sub-surface H Adsorption

When the Mg (0001) surface is pre-adsorbed with atomic H at Fcc sites, the electron localisation at the sub-surface TI₁ is enhanced, leading to energetically favourable sub-surface adsorption and a stable H(Fcc)-Mg-H(TI₁) tri-layer structure.

The ELF in the sub-surface region of Mg basal plane could also be modified by the on-surface OH radicals and atomic O, thus stabilising the sub-surface adsorption and resulting in the formation of OH(Fcc)-Mg-H (TI₁) structure for the hydroxylated Mg surface and O(Hcp)-Mg-H(TI₂) structure for the oxidised Mg surface.

The adsorbate-generated ELF variation within the Mg (0001) surface drives the formation of local H traps within the sub-surface region. Therefore, the sub-surface H adsorption and the formation of the hydride layer underneath the top surface become stable.

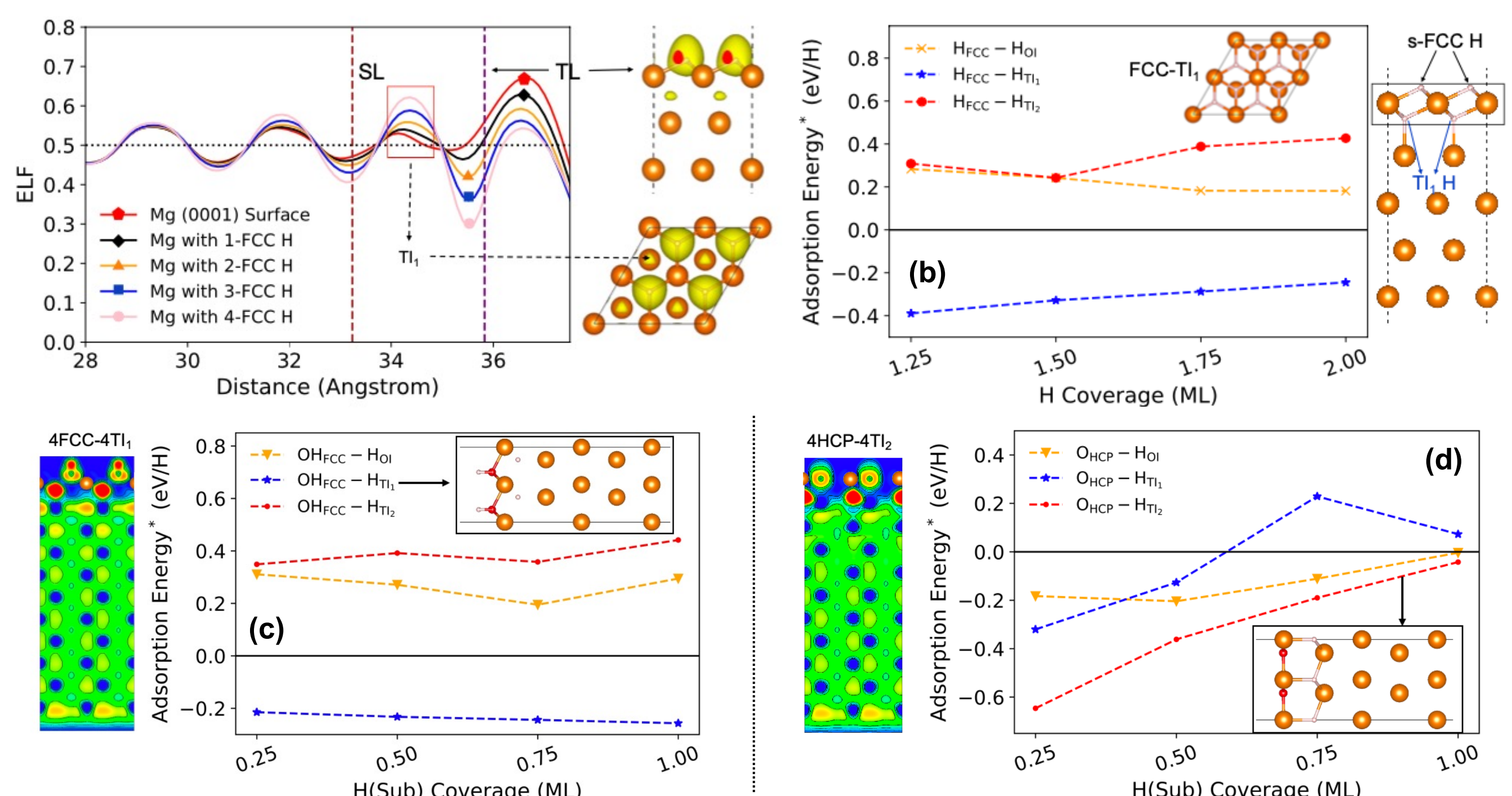


Figure 3 (a) Planar-average ELF of H covered Mg (0001) surface along Z-axis as the increase of H coverage. (b) Adsorption energy (* refers to using the pre-covered Mg surface and hydrogen gas molecule as the reference) per adsorbed atomic H in the sub-surface interstitials of the H(Fcc)-covered Mg (0001) surface. (c) Adsorption energy per adsorbed atomic H in the sub-surface interstitials of the OH(Fcc)-covered Mg (0001) surface. (d) Adsorption energy per adsorbed atomic H in the sub-surface interstitials of the atomic O(Hcp)-covered Mg (0001) surface.