Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unveiling the anchoring and catalytic effect of $Co@C_3N_3$ monolayer as a high-performance selenium host material in lithium-selenium batteries: A first-principles study

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Contents

Section 1. Adsorption sites for cobalt on C_3N_3 monolayer

In order to determine the optimal adsorption position of cobalt on C_3N_3 material, the embedding of cobalt in the N6 cavity of the intrinsic C_3N_3 monolayer are explored, as depicted in **Fig. S1(a)**. With reference to the embedding site of cobalt in N6 cavity, three possible sites, namely the Co1 (between two nitrogen atoms), Co2 (between three nitrogen atoms) and Co3 (centre of six nitrogen atoms) are evaluated.[1,2] The configurations and relative energies and of Co atom at three embedding sites in the intrinsic C_3N_3 monolayer are presented in the **Fig. S1(b)**.

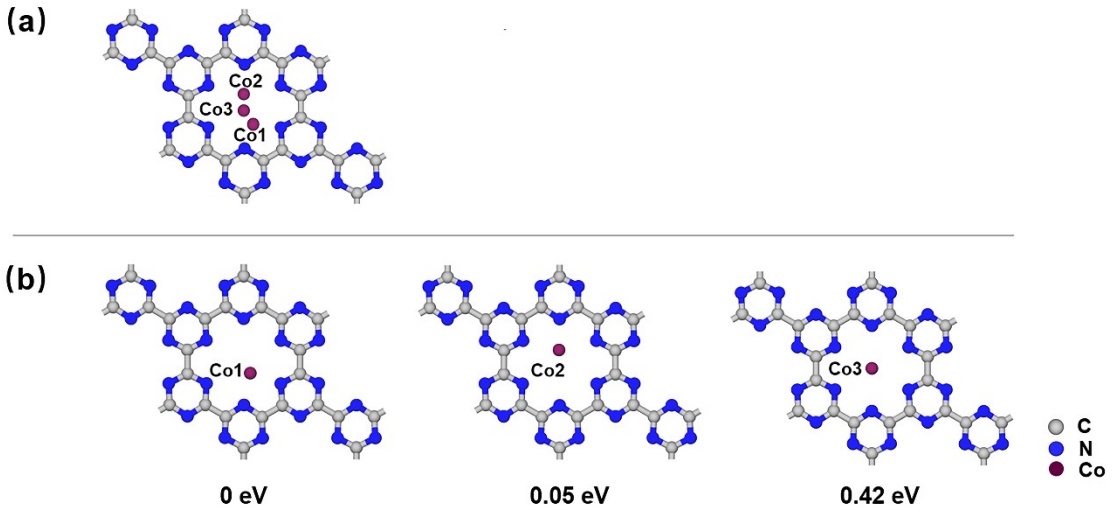


Fig. S1. (a) Three adsorption sites for Co atom on C_3N_3 monolayer. **(b)** Configurations and relative energies and of Co atom at the three embedding sites in the intrinsic C_3N_3 monolayer.

Actually, the transition metal atoms tend to agglomerate on the substrate because of the large cohesive energy.[3] Furthermore, to check the stability of Co@C_3N_3, the binding energy (contrary to the definition of formation energy) of transition metal cobalt at the three adsorption sites are further evaluated, and the calculated results and the differences (ΔE_{diff}) between the binding energies and the corresponding cohesive energies in bulk phase are surmised in **Table S1**. The binding energy (E_b) is defined as the following equation:

$$E_b = E_{C_3N_3} + E_{Co} - E_{Co@C_3N_3} \quad (1)$$

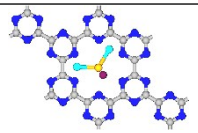
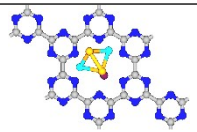
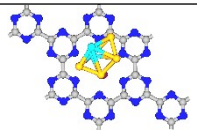
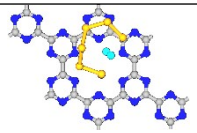
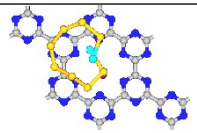
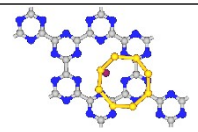
Where $E_{C_3N_3}$, E_{Co} and $E_{Co@C_3N_3}$ are the total energies of C_3N_3 monolayer, Co atom and Co@C_3N_3 system, respectively. From **Table S1**, the binding energy at Co1 site is the largest among the considered three binding sites. Notably, the binding energy at Co1 site surpasses the cohesion energy by 0.18eV, which indicates that Co could be effectively and tightly trapped at the Co1 site without the encountering any clustering issues.[4]

Table S1: The binding energy of cobalt atom embedded at Co1, Co2 and Co3 sites (E_b, eV), the cohesive energy of the cobalt metal bulk (E_{coh}, eV), and the difference between E_b-Co1 and cohesive energy of the cobalt crystal (ΔE_{diff}, eV). * From reference.[5,6]

	E_b-Co1	E_b-Co2	E_b-Co3	E_{coh}*	ΔE_{diff}
Energy **(eV)**	4.57	4.52	4.15	4.39	0.18

Section 2. $Co@C_3N_3$-LiPSes structure and the binding energies

Table S2. Structures and the binding energies of LiPSes clusters on $Co@C_3N_3$ monolayer at the different adsorption positions.

E_b \ structures	Li_2Se-$Co@C_3N_3$	Li_2Se_2-$Co@C_3N_3$	Li_2Se_4-$Co@C_3N_3$	Li_2Se_6-$Co@C_3N_3$	Li_2Se_8-$Co@C_3N_3$	Se_8-$Co@C_3N_3$
						
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	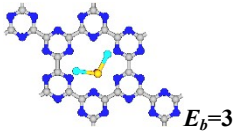	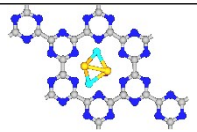	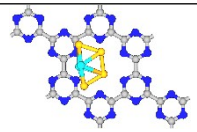	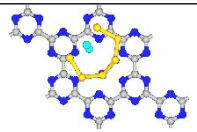	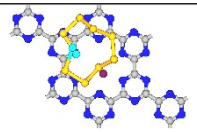	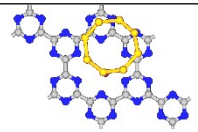
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	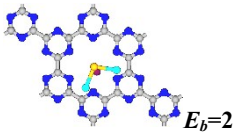	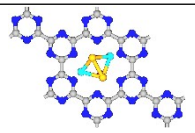	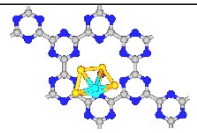	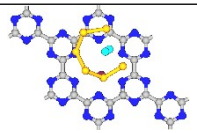	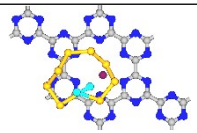	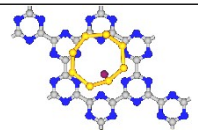
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	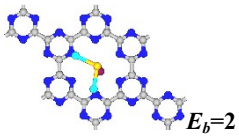	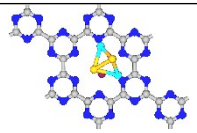	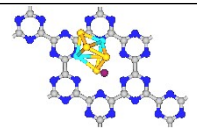	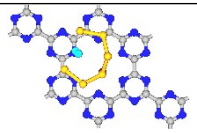	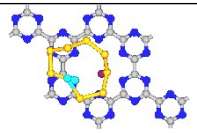	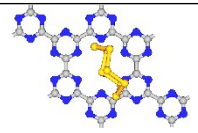
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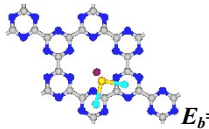
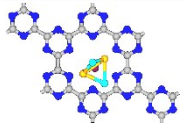
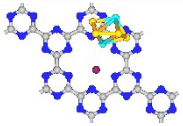
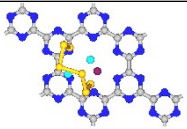
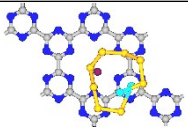
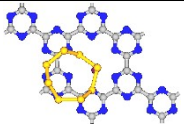
	 E_b=2.36 eV	 E_b=0.18 eV	 E_b=0.74 eV	 E_b=0.05 eV	 E_b=0.91 eV	 E_b=0.56 eV

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