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Machine learning-based design of electrocatalytic materials towards highenergy lithium||sulfur batteries development

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The practical development of Li ||S batteries is hindered by the slow kinetics of polysulfides conversion reactions during cycling. To circumvent this limitation, researchers suggested the use of transition metal-based electrocatalytic materials in the sulfur-based positive electrode. However, the atomic-level interactions among multiple electrocatalytic sites are not fully understood. Here, to improve the understanding of electrocatalytic sites, we propose a multi-view machine-learned framework to evaluate electrocatalyst features using limited datasets and intrinsic factors, such as corrected d orbital properties. Via physicochemical characterizations and theoretical calculations, we demonstrate that orbital coupling among sites induces shifts in band centers and alterations in the spin state, thus influencing interactions with polysulfides and resulting in diverse Li-S bond breaking and lithium migration barriers. Using a carbon-coated Fe/Co electrocatalyst (synthesized using recycled Li-ion battery electrodes as raw materials) at the positive electrode of a Li | |S pouch cell with high sulfur loading and lean electrolyte conditions, we report an initial specific energy of 436 Wh kg⁻¹ (whole mass of the cell) at 67 mA and 25 °C.

Lithium ||sulfur (Li ||S) batteries undergo complex reaction routes and sluggish reaction kinetics as sulfur converts into various lithium polysulfides (LiPSs) with variable chain lengths¹. The required activation energy for transforming soluble LiPSs into insoluble Li₂S₂/Li₂S restricts the efficient utilization of active materials, thereby impeding the development of high-energy-density rechargeable S-based nonaqueous batteries. Electrocatalysts such as transition-metal compounds²⁻⁴, metal nanoclusters⁵, and atom site catalysts (ASCs)⁶ have been developed to improve the kinetic of the LiPSs conversion reactions. Although isolating single atomic site catalysts (SASCs) is thought to maximize catalytic activity⁷, the complex sulfur reactions often require multiple active sites to effectively manage adsorption, activation, or chemical bond scission of LiPSs⁸.

To develop efficient multi-site catalysts useful for producing highenergy Li ||S batteries, it is necessary to deeply understand its activity origin. Previous studies have primarily focused on the interaction between catalysts and LiPSs⁹⁻¹². However, the ensemble effect–interactions among multiple active sites within catalysts–remains underexplored, which plays an important role in determining the catalyst-LiPS interaction¹³. This is partly because of the absence of effective

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approaches to analyze such complex systems, which contain numerous combination possibilities and indistinct activation mechanisms at the atomic level^{14,15}, and pose significant challenges to conventional theoretical approaches based on first principles. Machine learning has achieved significant results in materials science and chemistry¹⁶⁻¹⁹, particularly in areas such as catalysts²⁰⁻²², photovoltaics^{23,24}, synthesis planning^{25,26}, and reaction optimization^{27,28}. However, its application is often hindered by the shortage of experimental data for relevant materials. These persistent challenges impede a deep understanding of the fundamental mechanisms governing atomic interactions and the rational design of catalysts for high-energy Li ||S batteries.

Here we combine an interpretable machine learning model with density functional theory (DFT) calculations to decipher the ensemble effect and experimentally verified its influence mechanism on sulfur electrochemical reactions at the atomic level. Diatomic site catalysts (DASCs) with various geometric features and atom combinations are chosen as model materials because of their remarkably enhanced interaction between multi-sites²⁹⁻³¹. We propose an interpretable multiview machine-learned framework designed to automatically evaluate the 182-dimensional potential feature space within DASCs, which aims to identify the key indicator of the ensemble effect from limited data samples. We integrate three feature engineering modules into our framework to extract the most relevant features to the catalytic performance, such as the corrected *d* orbital electronic properties, which indicate the multifactorial influence on the performance of multi-site catalysts. Moreover, we use DFT calculations based on the indicator uncovered by machine learning, to reveal the ensemble effect of multisite catalysts in sulfur electrochemical reactions. Our study uncovers that the inter-site communication and coordination structure effects among multiple active sites promote orbital hybridization changes between these sites and LiPSs. This mechanism, distinct from the traditional single-site activation pathway, enhances Li | |S bond breaking and Li⁺ migration kinetics, thereby guiding the design of DASCs. Our designed catalysts have enabled an Ah-level Li | |S pouch cell to achieve a specific gravimetric energy of 436 Wh kg⁻¹ (based on the whole cell mass), which can be calculated for the first discharge cycle with an applied current of 67 mA. Our work deciphers the underlying impact mechanism of the ensemble effect on sulfur electrochemical reactions and provides insight into the activity origins in multi-site catalysts.

Results

Designing of electrocatalysts using machine learning

To design highly efficient multi-site catalysts for high energy density Li ||S batteries, it is necessary to understand the ensemble effect, which involves the interactions among multiple active sites. The ensemble effect is influenced by a diverse array of factors such as intrinsic physicochemical properties of different atoms, variable active sites, and inter-site communication, all of which contribute to the catalytic activity. A deep understanding of the key factors is crucial to fully comprehend the origins of catalytic activity. It is supposed that the catalytic activity of multi-site catalysts is governed more by complex atomic interactions, rather than by individual descriptors³². It is not feasible to unravel the complex nonlinear relationships by chemical intuition alone. Data-driven approaches, particularly machine learning, provide robust support in revealing these complex correlations and refining theoretical models^{20,33-35}. However, the scarcity of data and the complexity of feature spaces pose significant challenges to machine learning models.

To reveal the impact of the ensemble effect in multi-site catalysts, we chose DASCs as the model materials, with the adsorption energy of Li_2S used as the indicator of catalytic activity. DASCs were selected for their stable synthesis and characterization compared to triple active site catalysts or high entropy atom catalysts, making them more suitable for large-scale development. We integrated DFT calculations and an interpretable multi-view machine-learned framework, consisting of

three components: the filter module, the wrapper module, and the embedded module (Fig. 1a and Supplementary Note 1). A substantial proportion of our effort in the machine learning framework was devoted to constructing potential features, such as the physicochemical properties of transition metals, and to applying multi-view feature engineering for extracting the feature importance space associated with the catalytic activity of DASCs. Using different methods to collect a variety of sample features can make better use of limited datasets. This approach provides an effective solution to the problem of data scarcity in small-data machine learning scenarios. The importance space of the filter module enabled initial screening of feature, whereas the wrapper and embedded modules refined and produced statistically robust chemical rules, mapping from importance to feature spaces. This procedure progressively refined and narrowed the feature space, instrumentally in revealing key factors influencing the catalytic activity of multi-site catalysts, such as the electronegativity, the first ionization energy of metals and the corrected composite features.

Feature engineering holds an important role in machine learning, enhancing the performance of the final model and elucidating the intricate relationships between features and predicted outcomes. Initially, we used domain-specific knowledge in data analytics to filter a vast initial feature space, as detailed in Fig. 1b-d and Supplementary Tables 1-3. The primary strategy of the Filter module was to evaluate each feature and subsequently refining the feature space based on these evaluations. We employed the Pearson correlation coefficient as a key evaluative metric, noted for its efficiency and rapid initial filtering capability of large feature spaces. We developed a two-stage filtering process guided by Pearson correlation scores. The first stage, illustrated in Supplementary Fig. 1a, b, identified and excluded undifferentiated features, such as the electronegativity of the non-metallic atom (N), consistent across all DASCs, was irrelevant for our machine learning model. The second stage, detailed in Supplementary Fig. 1c, involved removing one feature from each pair with a Pearson coefficient above 0.7. For instance, the bond length of N and M1, as well as the mean bond length of N and M1 were deemed insufficiently impactful on LiPSs adsorption. This filtering process effectively reduced the feature space to 128-dimensional (F_{128}).

We optimized a large dataset by the filter module, but this was insufficient to select the most optimal features. The predictive performance of the F_{182} dataset model is depicted in Supplementary Fig. 2a. The R² value of 0.51 for this model indicates its predictive accuracy is unreliable. We used the wrapper module to refine feature selection with learning algorithms, directly assessing features by model performance to identify the most relevant subspace. This process further reduced feature counts³⁶⁻³⁸. As illustrated in Supplementary Fig. 2b, the enhanced model performance achieved after removing fewer contributory features resulted in an improved accuracy of 0.61.

Distinct from the prior two modules, the embedded module combines feature selection and model training in an algorithm-driven process. In this study, we used an extreme gradient boosting regression (XGBR) tree model for the final feature selection and training step. This embedding method further improved the accuracy of the model, achieving an R² of 0.63 (Supplementary Fig. 2c). This model was considered pre-trained, still including numerous reference features. We then applied the hyperparameters and weights from this model to a dataset comprising only site, structural, and component features. This adjustment significantly increased the accuracy of the final model to 0.82 (Supplementary Fig. 2d). Moreover, we extended the proposed machine learning framework to complex trimetallic sites. Supplementary Fig. 3 and Supplementary Fig. 4 are the heat map of Person correlation coefficient matrix for feature set after filter module and the performance of the final ML model, respectively. The high-accuracy prediction results ($R^2 = 0.83$) demonstrate that the machine learning





serve as the data base for pre-training). The size and color of a squares describe the feature value, and the size is mapped according to the absolute value of the difference between the feature value and 0.5 to allow visibility of the values close to 0. Thus, this means that the larger the red squares are, the values are closer to 0; the smaller the blue squares are, then the values are closer to 1. The detailed definition of features is listed in Supplementary Table 1–3. **c**, **d** Feature heat maps (including structure and component features) of the partial DASC (Main metal = Fe). The horizontal axis is the short name of DASC, the vertical axis is the number of features, and the shade of the color indicates the relative magnitude of the values. **e** Feature importance (%) of the final XGBR model based on embedded module results.

framework can efficiently and accurately predict the adsorption energy of multi-metal-center catalysts with more complex site structures, which reduces the computational cost.

Notably, throughout the interpretable multi-view machinelearned framework, the chemical patterns related to the ensemble effect were progressively uncovered. The feature importance ranking of the final prediction model revealed the key factors influencing the catalytic activity of multi-site catalysts (Fig. 1e). These factors can be categorized into two types. The first type includes electronic properties such as the electronegativity (χ_M), d-band center ($\varepsilon_{d,M}$), *d*-electron number of synergistic metals (θ_M) and the first ionization energy of central metal (II_{MI}), relating to the inter-site communication among multi-active sites. The second type comprises the atomic radius of the metals (R_{MI} , R_M) and the spacing between coordinating nitrogen atoms (L_{3N}), reflecting the coordination structure effect in multi-site catalysts. These findings offer a valuable direction for further research into the ensemble effect.

Multi-site catalysts synthesis and characterization

To systematically investigate the principles derived from machine learning for Li||S batteries, a series of Fe-based DASCs were

synthesized. Elemental Fe was selected due to its improved catalytic activity in sulfur electrochemical reactions compared to other transition metal elements within metal/nitrogen doped carbon catalysts, and its plentiful availability³⁹ Additional elements, Co, Ni, and Cu, were selected as synergistic sites to fine-tune the ensemble effect in the DASCs. The spherical aberration-correction high-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) images (Supplementary Fig. 5a-d), three-dimensional morphology images (Fig. 2a-d), and the energy dispersive spectrum (EDS) element mapping image (Fig. 2e, f and Supplementary Fig. 5e) reveal the uniform distribution of atomically dispersed atomic sites of Fe SASC and FeCo, FeNi, and FeCu DASCs on a carbon substrate, notably without the aggregation of metal or alloy nanoparticles and clusters. The X-ray diffraction (XRD) patterns of Fe SASCs and FeCo, FeNi and FeCu DASCs (Supplementary Fig. 6) show the wide diffraction peaks at 26 and 44 degrees of the (002) and (100) planes of graphitized carbon. The absence of other distinct peaks suggests an atomic level dispersion without forming nanoparticles.

The fine chemical states changes of the Fe site in DASCs were revealed by X-ray photoelectron spectroscopy (XPS). As shown in Supplementary Fig. 7, The addition of synergistic Co sites resulted in a





and FeCu DASCs and their control samples. **h** Wavelet transforms of Fe K-edge EXAFS signals for FeCo, FeNi and FeCu DASCs. **i** Fabrication process from mixed electrode crystals to metal ion solvents and DASCs. The recovery efficiency calculations for each step are provided together.

decrease in Fe²⁺ from 20% to 15%, while the Fe²⁺ content increased to 42% and 32% in the presence of Ni and Cu, respectively. The sequence of oxidation states is as follows: FeCo>Fe>FeNi>FeCu. The distribution of metal atoms in FeCo DASC was further investigated through the analysis of intensity profiles derived from high-resolution HAADF-STEM images in Supplementary Fig. 8a. The bright dots highlighted with white circles represent metal atoms in pairs, confirming the successful synthesis of diatomic site catalysts. The measured distance between these atom pairs is approximately 2.1-2.2 Å. Similar observations for FeNi and FeCu DASCs are shown by HAADF-STEM in Supplementary Fig. 8b, c. Figure 2g, h shows the Fourier transform and wavelet transforms of Fe K-edge extended X-ray absorption fine structure (EXAFS) signals by k²-weight for Fe SASCs and FeCo, FeNi and FeCu DASCs along with their control samples. The Fe SASC only shows a main peak at approximately 1.5 Å in R space, which is indicative of the Fe-N scattering path. In contrast, the main peak for FeCo, FeNi and FeCu DASCs is located at a higher R-value (around 1.8 Å), suggesting a longer Fe-N bonds. Additionally, an obvious sub-peak at about 2.2 Å corresponds to the Fe-M coordination in the first shell. The spin states of Fe in FeCo DASC were analyzed using ⁵⁷Fe Mössbauer spectroscopy at 6.2 K. The results revealed a reduction in the content of high-spin Fe^{2+} architecture (isomer shift (IS): 1.16 mm s⁻¹, quadrupole splitting value (ΔE_0): 3.0 mm s⁻¹) in FeCo DASC compared to Fe SASCs (Supplementary Fig. 9).

Notably, the metallic precursors in this work were obtained through the recycling of waste lithium-ion batteries (LIB), which were able to produce metal ions solution at the ton scale. The recycling process, depicted in Fig. 2i, involved extracting materials from various LIB positive electrodes and waste current collectors obtained from battery recycling companies. When using 5 g LiFePO₄ and 5 g LiCoO₂ as precursors, we obtain 1.7 g FeCo DASC and 1.3 g Co SASC after metal extraction and thermal treatment, achieving 96% crystal-to-catalyst recovery. This sustainable strategy greatly reduces the production cost of ASCs to two-thirds compared with conventional methods (further information is provided in Supplementary Tables 4, 5; Supplementary Note 2 and Supplementary Fig. 10). The design of the production line is shown in Supplementary Fig. 11, showing the potential scalability for large-scale DASC production.

Mechanistic investigations via computational modeling

Based on the important features and underlying mechanisms from our interpretable multi-view machine-learned framework, we applied DFT to decipher the specific mechanism of ensemble effect using Fe-based ASCs as model systems. In contrast to the coordination environment of SASCs, DASCs exhibit not only metal-nitrogen bonds but also metalmetal bonds. Electron localization functions provide the visualization of lone pairs and bonding pairs, verifying the existence of *d*-*d* orbital hybridization between the two metal sites (Fig. 3a, b), which is mainly among orbitals between d_{x2-y2} , d_{z2} , and d_{yz} (Supplementary Fig. 12). The hybridization can be quantified by the integrated Crystal Occupation Hamiltonian Population (ICOHP) between metal sites. It is noteworthy that the FeCo DASC has the highest absolute value of ICOHP (-0.97) than FeNi DASC (-0.42) and FeCu DASC (-0.35), indicating the highest bond strength and thus the strongest *d*-*d* orbital hybridization between Fe and Co sites. Experimental validation is provided through X-ray Absorption Near Edge Structure (XANES) data (Fig. 3c). Compared with Fe SASC, the XANES profiles of FeCo DASC show an obvious shift toward higher energy, experimentally validating the influence of *d*-*d* orbital hybridization. This suggests a more oxidative state for the Fe center metal site, which can be attributed to the electronic interaction with the Co metal site.

The adsorption configurations show that metal sites with lower atomic numbers act as the central metal to interact with sulfur in LiPSs because of their stronger d-p hybridization (Supplementary Fig. 13a–d)¹². The charge density difference analysis reveals the strong

interfacial charge interaction in the center metal-sulfur and coordinated nitrogen-lithium, respectively (Supplementary Fig. 13e-h). In the bonding interactions of metal-sulfur, the primary mechanism involves the coupling of *d-p* orbitals. Previous work has demonstrated that the d_{z2} and $d_{xz/vz}$ states of the SASC are more stable for square planar coordination of D4h symmetry. As illustrated in Fig. 3d, e, the order of energy levels of the Fe metal center can be changed with the synergistic metal site introduction. The introduction of the Co atom decreases the energy levels of d_{x2-y2} and changes the filling state. In contrast, the energy levels of d_{z2} are increased with partial filling of the spin-down d_{z2} orbital of Fe. Moreover, it also leads to the increased delocalization of the d_{yz} and d_{xz} orbitals, as well as partial filling of the spin-down orbitals of $d_{\nu z}$ (Supplementary Fig. 14). This leads to the change in the spin state of the Fe sites, consistent with the Mössbauer spectroscopy (Supplementary Fig. 9). Based on the d-p orbital hybridization theory, the antibonding (π^* and σ^*) states will be gradually occupied with the increasing number of d_{z2} and d_{yz} electrons of Fe in FeCo DASC, leading to weaker binding strength for Fe-S bond compared to that observed in Fe SASC system. Furthermore, we observe that the synergistic metal affects the central position of the Fe d-band and subsequently modulates the strength of the Fe-sulfur binding (Fig. 3f; Supplementary Fig. 15a; Supplementary Table 6). With the decrease of the *d*-band center in the Fe site and moving away from Fermi levels, the binding strength between Fe and sulfur is weakened.

In light of the interfacial charge interaction between coordinated nitrogen and lithium in LiPSs (Supplementary Fig. 13e-h), an investigation was conducted to elucidate the role of coordinated nitrogen. Two-dimensional differential charge density analyses demonstrate that the introduction of the synergistic metal leads to new forms of coordinated nitrogen between metal sites (Fig. 3g-j). In the FeCo DASC, Bader charge analysis reveals the coordinated nitrogen atoms where Li adsorbs exhibit intermediate average charges (6.13 e), in contrast to those in Fe SASC (6.21 e), FeNi DASC (6.19 e), and FeCu DASC (6.23 e). This difference is attributable to the inter-site communication among the catalysts. The introduction of the synergistic metal raises the *p*-band center of coordinated nitrogen towards Fermi levels, leading to an increase in nitrogen-lithium binding energy (Fig. 3k, Supplementary Figs. 15b, 16, and Supplementary Table 6). Additionally, Projected Density of States (PDOS) reveals that the nitrogen in the FeNi DASC and FeCu DASC exhibits spin-polarized status, which is beneficial for increasing the adsorption energy with Li⁴⁰ (Fig. 3l). As the electronegativity of the synergistic metal increases, the p-band center of coordinated nitrogen rises, explaining the influence mechanism of extracted important features by our interpretable multi-view machine-learned framework. A moderate p-band center and the absence of spin polarization result in an optimal adsorption energy, which weakens the Li-S bonds while ensuring rapid lithium transport. The moderate nitrogen-lithium binding energy of the FeCo DASC can weaken the Li-S bonds in LiPSs and ensure fast lithium migration on the catalyst surface. (Figs. 3l, 4a, b).

In addition, guided by the extracted structural features (R_{M} , R_{MI} , and L_{3N}) of machine learning, we investigate the implied mechanism. The structural feature combinations that determine the lattice strain in the multi-site catalysts, change with the synergistic metal sites and can be measured by the ratio of the sum of metal sites and L_{3N} . The alterations in the Fe-N bond length, in conjunction with inter-site communication among the synergistic metal sites, collectively led to the change in the *d*-band center of the Fe sites. The influence of synergistic metal (Co, Ni, and Cu) on the electronic structure of the central Fe extends beyond the intrinsic electronic properties and atomic radii of the coordinating metals. Furthermore, it encompasses the overall environment within the coordination structure, such as the distance between three nitrogen atoms. These factors collectively define the characteristics of the coordination environment, thus embodying the ensemble effect.



Fig. 3 | **Identification of ensemble effect by DFT. a**, **b** Electron localization functions of Fe SASC (**a**) and FeCo DASC (**b**). **c** XANES of Fe SASC, FeCo DASC, FeNi DASC, and FeCu DASC. **d**, **e** Schematic energy-level diagrams of the S *3p* states as an Li₂S adsorbs to the Fe SASC (**d**) and FeCo DASC (**e**). **f** *d*-band center of Fe and ICOHP of Fe-S bond in various Fe-based SASC and DASCs for Li₂S. **g**-**j** Two-dimensional

differential charge density of Fe SASC (**g**), FeCo DASC (**h**), FeNi DASC (**i**), and FeCu DASC (**j**). **k** *p*-band center of N, and ICOHP of N-Li bond in various Fe-based SASC and DASCs for Li₂S. **I** PDOS on *s* orbitals for lithium in Li₂S and *p* orbitals for nitrogen in Fe SASC, FeCo DASC, FeNi DASC, and FeCu DASC.

In summary, guided by the indicators identified through machine learning, we applied DFT to reveal the ensemble effect in multi-site catalysts for sulfur electrochemical reactions, focusing on inter-site communication and coordination structure effect. Specifically, FeCo DASCs demonstrated an improved *d-d* coupling effect, leading to a higher central metal-sulfur binding energy compared to other diatomic catalysts. Moreover, a critical activation mechanism involving coordinated nitrogen in DASCs resulted in a marked increase in nitrogen-lithium binding energy, surpassing that of single-metal catalysts. In FeCo DASC, the nitrogen-lithium binding energy is optimally balanced, effectively weakening the Li-S bonds and enhancing the Li⁺ migration kinetics. Notably, FeCo DASC stands out in comparison to single-metal and other diatomic systems, particularly in weakening Li-S bonds.

Influence of ensemble effect to catalytic activity

Taking FeCo DASC as a representative example, we explored the mechanism of sulfur-based electrochemical reactions under the influence of the ensemble effect, contrasting it with Fe SASC, where ensemble effects are absent (Fig. 4c and Supplementary Fig. 17). The presence of the ensemble effect results in a markedly different activation degree of the LiPSs on FeCo DASC compared to LiPSs on Fe



Fig. 4 | Evaluation of the influence of ensemble effect on catalytic reactivity. a, b Top-view schematic representations of the corresponding diffusion pathways for Fe SASC (a) and FeCo DASC (b). c The sulfur-based electrochemical reaction mechanism on FeCo DASC with ensemble effects. d Apparent activation energies of the Li₂S to Li₂S_n conversion for Fe SASC, FeCo DASC, FeNi DASC, FeCu DASC, and catalyst-free sample calculated from the CV profiles. e The overpotential obtained from the CV profiles of symmetric cells with Li₂S₆-containing electrolyte. The error

bars for all catalysts were determined from the standard deviation. **f** *Ea* at different potentials at a given discharge voltage for Fe SASC and FeCo SASC. The error bars for all catalysts were determined from the standard deviation. **g** The overall workflow diagram, showing the steps of revealing ensemble effect by multi-view machine-learned framework. The detailed definition of features is listed in Supplementary Table 1–3.

SASC without ensemble effects. Fe atoms still act as the central site interacting with the sulfur atom in LiPSs because of their stronger *d-p* orbital hybridization than Co atoms. Moreover, the coordinated nitrogen atoms between Fe and Co atoms are activated and interact with lithium atoms in LiPSs, showing a smaller N-Li distance compared to those in Fe SASC.

Subsequently, we conducted a series of kinetic tests to validate the impact of the ensemble effect on the sulfur-based electrochemical reactions. The cyclic voltammetry (CV) curves were first tested to probe the cathodic peak current under various temperatures². A linear correlation was observed between the logarithmic peak current and the reciprocal of the absolute temperature across all the investigated materials (Supplementary Fig. 18). The calculated apparent activation energy (E_a) values from CV curves exhibited the following order: FeCo DASC < FeNi DASC < FeCu DASC < Fe SASC < catalyst-free (Fig. 4d), which is in good agreement with the DFT estimations. The FeCo DASC exhibits the best catalytic activity due to the presence of the ensemble effect. Then equal quantities of each catalyst were loaded on the electrode and the CV curves were measured using symmetric cells with Li₂S₆-containing electrolyte (Supplementary Fig. 19). The electrodes with DASCs exhibited reduced polarization compared to those with SASC, indicating the important role of ensemble effects in enhancing the electrode reaction kinetics (Fig. 4e). The FeCo DASC showed the lowest overpotential among the different DASCs, suggesting improved catalytic activity. Supplementary Fig. 20 presents contour plots of CV patterns for Fe SASC, FeCo DASC, FeNi DASC, and FeCu DASC, respectively. Two cathodic peaks at approximately 2.30 V (Peak A) and 2.04 V (Peak B), respectively, correspond to the reduction of S₈ to LiPSs and Li₂S₂/Li₂S. The peak at about 2.37 V (Peak C), observed during the anodic sweep, represents the transition from Li₂S₂/Li₂S to

LiPSs and S_8 . It is notable that the positive electrodes employing FeCo DASC exhibit a higher current response compared to positive electrodes employing Fe SASC and other Fe-based DASCs. Moreover, even when the scanning speed is reduced, the positive electrode with FeCo DASC consistently demonstrates a current response, suggesting improved catalytic activity attributed to the ensemble effects. Subsequently, we employed FeCo DASC and Fe SASC as representative catalysts, with and without ensemble effects, respectively.

Electrochemical impedance spectroscopy (EIS) measurements were conducted at various temperatures to determine Ea at different potentials. The charge transfer resistance at varying temperatures was fitted using a simplified-contact Randles-equivalent circuit, revealing a linear correlation between the reciprocal of absolute temperature and the logarithm of the reciprocal of the charge transfer resistance (Supplementary Fig. 21). Subsequently, the activation energy was derived following the Arrhenius reaction. The resulting Ea values indicate that the conversion of S₈ molecules into soluble LiPSs is relatively facile (Fig. 4f). Conversely, the transformation of LiPSs into the ultimate insoluble products needs a higher activation energy, representing the rate-determining step in Li ||S batteries. The derived activation energy values show that cells with FeCo DASC exhibit lower activation energies compared to those with Fe SASC, consistent with the relative free energy landscape during the discharge process (Supplementary Fig. 22). It is noteworthy that the Co SASC shows a higher reaction barrier than FeCo DASC. In the FeCo DASC, interactions between Fe-S and Li-N bonds can be observed, indicating that Co plays a crucial role in modulating the electronic structure of the Fe sites and the coordinated nitrogen.

Then we set a reductive potential of 2.05 V to drive LiPSs convert to Li₂S production and observed the distribution of solid Li₂S particles influenced by the ensemble effect after the deposition of LiPSs. We calculated specific capacities for Li₂S precipitation on the positive electrodes with Fe SASC and FeCo DASC by integrating the currenttime curve during deposition, resulting in values of 325.0 and 384.8 mAh g⁻¹, respectively (Supplementary Fig. 23). The enhanced Li₂S precipitation capacity observed on positive electrodes with FeCo DASC implies improved reaction kinetics from LiPSs to Li₂S, which is attributed to the ensemble effect. After Li₂S precipitation, we examined the positive electrode surfaces (Supplementary Fig. 24). In comparison to samples with Fe SASC, FeCo DASC surfaces displayed thicker Li₂S deposition, consistent with a higher deposition capacity. The divergent deposition morphology, while employing the same solvent, can be attributed to the presence of highly active FeCo DASC⁴¹. Furthermore, we also investigated the oxidation of the deposited Li₂S through a potentiostatic charging process (Supplementary Fig. 25). Remarkably, FeCo DASC exhibited a higher dissolution capacity in comparison to Fe SASC, suggesting a more effective oxidation process on the surfaces with FeCo DASC.

We then employed in situ Raman spectroscopy to provide insights into the regulation of the shuttle effect by FeCo DASC⁴². In assessing the diffusion of LiPSs towards the lithium negative electrode side, we only observed limited signals corresponding to $S_6^{2^\circ}$ throughout the discharge and charge processes for positive electrodes with FeCo DASC (Supplementary Fig. 25a). This observation indicates the effective mitigation of the shuttle effect. In contrast, positive electrodes without FeCo DASC exhibited two prominent peaks at 281.6 cm⁻¹ attributed to $S_8^{2^\circ}$ at the initiation of the discharging process (Supplementary Fig. 25b). Upon discharging, signals of $S_6^{2^\circ}$ and $S_4^{2^\circ} + S_3^{2^\circ}$ emerged. The notable signals for $S_6^{2^\circ}$, $S_4^{2^\circ}$, and $S_3^{2^\circ}$ indicate the presence of severe LiPSs shuttling, which is responsible for the capacity loss.

In summary, we introduce an integrated framework that combines machine learning, DFT, and electrochemical testing to reveal the ensemble effect and guide the design of effective catalysts. Our multiview machine learning model was developed to identify key features that impact the ensemble effect within a vast feature space of multi-

Assembly and testing of Li | |S batteries

To validate the impact of the ensemble effect on devices, the electrochemical performance test of Li||S batteries was conducted. In Supplementary Fig. 26, we present the electrochemical characteristics of Li||S batteries using the developed catalysts. Various DASCs enabled higher capacities than the Fe SASC, highlighting the important role of the ensemble effect in improving the battery performance. Notably, the FeCo DASC with the most effective ensemble effect enabled the highest capacity of 1468 mAh g⁻¹ among all the atomic catalysts at a specific current of 167.5 mA g⁻¹ for the 1st cycle of the Li || S cells (Supplementary Fig. 26a). We also assessed the rate capabilities of positive electrodes with Fe SASC and various Fe-based DASCs to compare their reaction kinetics for Li-S chemistry, using a sulfur loading of approximately 2 mg cm⁻² (Supplementary Fig. 26b). At specific currents of 335, 837.5, 1675, and 3350 mA $g^{\mathchar`-1}$, the discharge capacities for the 1st cycle the Li | |S cells with FeCo DASC were 1112, 980, 916, and 828 mAh g⁻¹, respectively, considerably surpassing those of other samples. Furthermore, the EIS measurements of the cell with FeCo DASC also revealed the lowest charge-transfer impedance, indicative of the lowest charge-transfer resistance at the FeCo DASC/LiPS interface, contributing to the rapid conversion of LiPSs (Supplementary Fig. 26c).

To illustrate the practical potential of FeCo DASC, we conducted performance assessments using Li||S batteries with varying sulfur loadings (Supplementary Fig. 26d). The results revealed stable cycling performance, characterized by high first cycle-areal capacities of 3.12, 6.27, and 9.51 Ah g⁻¹ for sulfur loadings of 3.0, 4.7, and 8.5 mg cm⁻², respectively. Additionally, we tested Li||S cells with FeCo DASC to long-cycling stability tests at 1675 mA g⁻¹ (Supplementary Fig. 26e). After 500 cycles, the Li||S cells with the FeCo DASC retained a discharge capacity of 0.56 Ah g⁻¹, with an average capacity decay rate of only 0.05% per cycle. In contrast, the Li||S cells without FeCo DASC experienced rapid capacity degradation. These improvements in cycling stability can be attributed to the ensemble effect of FeCo DASC.

To assess the practical applicability of the proposed ensemble effect in Li | |S cell format with high electrode area, pouch cell assembly and testing were conducted. The internal detailed physicochemical processes of Li ||S pouch cells have previously been described as black box behavior⁴³. In this study, we conducted the FEM simulations for a comprehensive visualization and comparative analysis of Li | |S pouch cell performance, both with and without the ensemble effect (Supplementary Note 3 and Supplementary Tables 7-9). The model featured a sulfur positive electrode with a double-sided areal loading of 14 mg cm⁻², a 150 μ m thick lithium negative electrode, and an electrolyte-to-sulfur (E/S) ratio of 2.8. The ensemble effect was found to enhance the kinetics of the sulfur positive electrode reaction, thereby accelerating the conversion of polysulfides. Figure 5a illustrates that in the absence of the ensemble effect, intermediate polysulfides at the positive electrode inefficiently convert into lower-order LiPSs, migrating towards the negative electrode and accumulating due to the electric field. With the ensemble effect, active sulfur converts promptly into lower-order LiPSs, precipitating on the positive electrode surface, thereby reducing polysulfide concentrations in the electrolyte and minimizing the shuttling effect. This effectively mitigates lithium negative electrode corrosion, decreases lithium





deposition morphology at end of discharge. **d** Photograph of the Li ||S pouch cell. **e**, **f** Discharge-charge profiles (**e**) and cycle performance (**f**) of the Li ||S pouch cell. **g** State-of-the-art performance of high-energy-density Li ||S pouch cells (over 300 Wh kg⁻¹) in published literature and this work. **h** Performance comparison between this work and previously reported Li ||S pouch cells (N/P ratio: negative/ positive, indicating anode to cathode capacity ratio).

consumption, and prevents the development of dendritic lithium morphologies (Fig. 5b). These observations are supported by in situ Raman spectroscopy analysis (Supplementary Fig. 25). Simulations further demonstrate that the ensemble effect enhances sulfur utilization and alters Li₂S deposition within the positive electrode. Without the ensemble effect, the active materials near the separator are efficiently utilized, and Li₂S tends to deposit in a two-dimensional mode during discharge (Fig. 5c). Conversely, the ensemble effect

significantly improves performance in high-sulfur-loading positive electrodes under practical conditions by engaging the entire electrode in the reaction process, even in thick electrodes distant from the separator. This transition to a three-dimensional deposition mode facilitates subsequent reactions, enhancing discharge capacity and confirming the observed differences in deposition capacity and morphology (Supplementary Fig. 23).

Furthermore, a 1.6 Ah Li ||S pouch cell was assembled using the winding stacking method, with parameters similar to those used in the earlier described FEM simulations (Fig. 5d and Supplementary Fig. 27). This cell achieved an initial specific energy of 436 Wh kg⁻¹ at 67 mA (Fig. 5e, f), showing stable cycling performance. This specific energy value is well aligned with the state-of-the-art literature of lab-scale Ahlevel Li | |S pouch cells (Fig. 5g)^{6,44-50}. Detailed calculations are provided in the Supplementary Fig. 27. Moreover, the ensemble effect of FeCo DASC enables the cell to achieve a high specific capacity of 1214.9 mAh g⁻¹ for a low electrolyte-to-sulfur (E/S) ratio of 2.8 µL mg⁻¹, high sulfur content (76.1%), high areal sulfur loading (12.7 mg cm⁻²), and a low negative/positive (N/P) ratio of 1.29. The Li ||S pouch cell performance we present here is better when compared with selected state-of-the-art Ah-level Li ||S pouch cells reported in the literature (Fig. 5h)^{6,44,46,51,52}. It is noteworthy that the specific energy and cycling performance of our Li||S pouch cell could be further improved by optimizing positive electrode design parameters, such as tortuosity and porosity, along with advancements in Li-metal protection and electrolyte formulation.

In summary, by combining an interpretable multi-view machinelearned framework and DFT, we deciphered the inter-site communication mechanism and coordination structure effect among multicatalytic sites, thereby proposing the ensemble effect in sulfur electrochemical reactions. The influence of the ensemble effect was experimentally validated, offering universal insights for the design of efficient multi-site catalysts for Li ||S batteries. Previous research has primarily concentrated on clarifying the adsorption and interaction processes between catalysts and LiPSs. Our experimental and simulation results highlight the fundamental role of inter-site communication and coordination structure effect among multiple active sites in influencing the kinetics of sulfur electrochemical reactions at the atomic level. The orbital coupling between active sites causes shifts in band centers and changes in spin states, thereby affecting interactions with polysulfides and leading to variations in Li-S bond breaking and lithium migration barriers. The visualization of the internal physicochemical processes in Li | |S pouch cells underscores the key role of the ensemble effect in boosting reaction kinetics, reducing polysulfide shuttling, and enhancing sulfur utilization. As proof-of-concept for practical scalability, we assemble and test an Ah-level Li | |S pouch cell containing the catalyst which was capable of deliver an initial specific energy of 436 Wh kg⁻¹ at a current of 67 mA.

Methods

Extraction of metal from spent lithium-ion battery

The steps for extracting cobalt ions from spent lithium cobalt oxide $(LiCoO_2, LCO)$ positive electrodes are as follows. First, 0.5 g of spent LCO and 0.05 g of waste graphite (10 wt%) were mixed and evenly ground, then sintered at 800 °C for 3 h in an argon atmosphere, resulting in a mixture of cobalt oxide and lithium oxide. Next, leveraging the difference in water solubility, the decomposition product was dispersed in deionized water and filtered to obtain a cobalt oxide precipitate and a lithium-containing aqueous solution. Finally, the cobalt oxide obtained was dissolved in dilute nitric acid, and the pH was adjusted to neutral to obtain a cobalt nitrate solution, which is used for the synthesis of ASCs. The steps for extracting iron ions from spent lithium iron phosphate (LiFePO₄, LFP) positive electrodes are as follows: First, 0.5 g of spent LFP material was mixed with 0.5 g of oxalic acid and 1 mL of deionized water in a ball mill jar. The mixture was then

ground for 2 h at 500 rpm with a ball to material ratio of 20:1. Then, based on the difference in water solubility, the ball milled products were dispersed in deionized water and filtered to obtain an iron oxalate precipitate and a solution containing lithium and phosphorus. Finally, the iron oxalate was dissolved in dilute nitric acid and the pH was adjusted to neutral to obtain an iron nitrate solution, which is then used for the synthesis of ASCs. The steps for extracting nickel ions from spent ternary nickel-cobalt-manganese (LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂, NCM811) positive electrodes are as follows: First, 0.5g of spent NCM811 was mixed with 0.05 g of waste graphite, and then the mixture was sintered at 650 °C for 3 h under an argon atmosphere to obtain nickel-cobalt-manganese oxides and lithium-containing compounds. Next, based on the difference in water solubility, the decomposition products were dispersed in deionized water and filtered to separate the transition metal oxides from the lithium-containing solution. Finally, the aforementioned oxides were dissolved in dilute nitric acid and the pH was adjusted to neutral to obtain a nickel nitrate solution, which is then used for the synthesis of ASCs.

The steps for extracting copper ions from discarded copper current collectors are as follows: The waste copper foil was sintered at 500 °C for 3 h in a muffle furnace, then after grinding, the above product was dissolved in dilute nitric acid, and heated with stirring (at ~90 °C). Once completely dissolved, the pH was adjusted to neutral to obtain a copper nitrate solution, which was used for the synthesis of ASCs. The steps for extracting aluminum ions from discarded aluminum current collectors are as follows: Place the waste aluminum foil in dilute nitric acid, heat with stirring (at ~90 °C), and after complete dissolution, adjust the pH to neutral to obtain an aluminum nitrate solution, which is used for the synthesis of ASCs.

Synthesis of diatomic site catalysts

Take FeCo DASC as an example, 288 mg of $C_6H_{12}O_6$, 0.011 mmol Fe(NO₃)₃, 0.011 mmol Co(NO₃)₂, and 1.38 g of (NH₃OH)Cl were ultrasonically dissolved in a 20 mL mixture of ethanol and ultrapure water in a 1:1 ratio for 10 min. The mixture was then dried at 70 °C for 12 h, followed by carbonization in a crucible heated to 600 °C at a rate of 5 °C min⁻¹ under an Ar atmosphere for 4 h. The resulting FeCo DASC were milled into a fine powder for further characterization. FeCo DASC can also be loaded to carbon felt by dripping the mixture onto the support material. Similarly, FeNi and FeCu DASCs were synthesized using similar procedures like FeCo by changing the metal precursors to specific types. The Fe SCA was prepared using 0.022 mmol Fe(NO₃)₃ metal precursor, while keeps the other parameters and procedures consistent.

Ex situ physicochemical characterization

The samples for ex situ physicochemical characterization were transported without sample holder protection except for a special explanation. The XRD measurement for DASCs was performed using a Bruker D8 Advance diffractometer, utilizing Cu Ka emission $(\lambda = 1.5406 \text{ Å})$. The morphology and elemental composition were examined through field-emission scanning electron microscopy (SU 8010) at 5 kV, accompanied by energy-dispersive X-ray spectroscopy. Specifically, the samples used to observe Li₂S deposition morphologies were prepared in an Ar-filled glove box. After Li₂S deposition, the coin cells were disassembled, washed with DME, and naturally dried for 2 h. The electrodes were then attached to the sample holder using conductive tape under Ar protection and directly transferred to the SU 8010 device without air exposure. High-resolution transmission electron microscopy investigations, using a FEI Titan G2 80-200 microscope, provided detailed insights into the microstructure. Elemental distribution and HAADF-STEM imaging were conducted at a voltage of 200 kV. Cold-field-emission spherical aberration corrected transmission electron microscope (Thermo Fisher Scientific, Spectra 300) operated at 80 kV. The quantitative analysis of mass content was performed using inductively coupled plasma atomic emission

spectroscopy (ICP-AES, MDTC-EQ-M29-01). XPS measurements, conducted on an ESCALAB 250Xi system, were utilized to explore the catalyst compositions. Furthermore, the EXAFS measurements were carried out on the sample at 21 A X-ray nanodiffraction beamline of Taiwan Photon Source (TPS), National Synchrotron Radiation Research Center (NSRRC). This beamline adopted a 4-bounce channel-cut Si (111) monochromator for mono-beam X-ray nanodiffraction and X-ray absorption spectroscopy. The end-station is equipped with three ionization chambers and Lytle/SDD detector after the focusing position of the KB mirror for transmission and fluorescence mode X-ray absorption spectroscopy. The photon flux on the sample ranges from $1 \times 10^{11} \sim 3 \times 10^{9}$ photon/sec for X-ray energy from 6–27 keV.

In situ Raman test

In situ Raman spectroscopy (Lab RAM HR Evolution) was employed. A hole was made in the negative electrode shell and the lithium metal foil, allowing the 532 nm laser to pass through a quartz window and illuminate the separator. This setup enabled the detection of lithium polysulfide diffusion toward the lithium negative electrode.

Li₂S₆ symmetric cells measurements

Symmetric coin cells were assembled using carbon paper electrodes loaded with 1 mg of various DASCs. Each cell was filled with 30 μ L of a 0.5 M Li₂S₆ solution as the electrolyte. The Li₂S₆ solution was prepared by reacting solid Li₂S (~2–5 μ m, 99.9%, MACKLIN) with S powder (AR, Shanghai Huzheng Industrial Co., Ltd.) in a mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 vol%) by a stoichiometric ratio of 1:5. DOL (99.9%) and DME (99.9%) were sourced from Suchow DoDoChem. Co., Ltd. The reaction mixture was continuously stirred at 60 °C for 12 h in an Ar-filled glovebox. An additional 10 μ L of electrolyte was dropped on the separator. The CV profiles of these cells were tested at a scanning rate of 1 mV s⁻¹ within a voltage range of –1.0 to 1.0 V at 25 °C.

Li₂S deposition test

A mixture of sulfur and lithium disulfide in a 7:1 molar ratio was prepared in tetraglyme (>99%, Sigma-Aldrich) under vigorous stirring to produce a $0.5 \text{ M Li}_2\text{S}_8$ solution. 20 µL of this solution was dropped onto the positive electrode (carbon paper loaded with various DASCs), and 20 µL of standard electrolyte was applied to the lithium negative electrode (500 µm in thick, and 16 mm in diameter, China Energy lithium Co., Ltd.). The standard electrolyte (LS-002, 1M dilithium (trifluoromethane sulfonylimide) imide (LiTFSI) in DME:DOL = 1:1 Vol% with 1% LiNO₃) was sourced from Suchow DoDoChem. Co., Ltd.), The test was conducted at 25 °C using coin cell. After discharging the cells galvanostatically to 2.06 V at 0.134 mA, the cells were further discharged potentiostatically at 2.05 V until the current dropped below 0.001 mA. The specific capacities were calculated by integrating the current-time curve during deposition.

Li₂S dissolution test

Post Li₂S deposition, the coin cells were disassembled in an argon-filled glove box, and the positive electrodes were rinsed with DME (99.9%, Suchow DoDoChem. Co., Ltd.) to eliminate residual LiPSs. These positive electrodes were then reassembled into new coin cells with lithium negative electrodes (500 μ m in thick, and 16 mm in diameter, China Energy lithium Co., Ltd.) and standard electrolytes (1 M LiTFSI in DME:DOL = 1:1 Vol% with 1% LiNO₃, Suchow DoDoChem. Co., Ltd.) for Li₂S dissolution. The cells were charged potentiostatically at 2.35 V and 25 °C until the charge current fell below 0.001 mA to ensure complete Li₂S dissolution.

Assembly and testing of Li | |S cells

Sulfur (Shanghai Huzheng Industrial Co., Ltd, AR) was impregnated into CNT ($5 \sim 8 \text{ nm}$ in diameter, $8 \sim 20 \mu \text{m}$ in length, >99% purity,

Guangdong Canrd New Energy Technology Co. Ltd.) via a meltdiffusion process at 155 °C for 10 h. resulting in S/CNT composites with 70 wt% sulfur. Positive electrodes were fabricated by mixing S-CNT powder (70 wt% sulfur), conductive carbon (CNT, 5~8 nm in diameter, $8 \sim 20 \,\mu\text{m}$ in length, >99% purity, Guangdong Canrd New Energy Technology Co. Ltd.), polyvinylidene fluoride (PVDF, >99.5%, Guangdong Canrd New Energy Technology Co. Ltd.), and ASCs (Fe SASC, and FeCo, FeNi and FeCu DASCs) in a 7:1:1:1 ratio in 1-Methyl-2pyrrolidinone (NMP, 99.9%, MACKLIN) to create a slurry by continuous magnetic stirring for 12 h in air, subsequently spread onto Al foil $(>99.6\%, 25 \,\mu\text{m}$ in thick, Guangdong Canrd New Energy Technology Co. Ltd.) and dried under vacuum at 60 °C. Lithium metal foil (500 µm in thick, and 16 mm in diameter, China Energy lithium Co., Ltd.) served as the negative electrode. The conventional electrolyte was DOL and DME (1:1 by volume) solution containing 1 M LiTFSI and 1 wt% LiNO₃. DOL, DME, LiTFSI and LiNO₃ were sourced from Suchow DoDoChem. Co., Ltd. The water content in all the non-aqueous electrolytes solution is less than 20 ppm. Each coin cell contained 40 µL of electrolyte and was assembled in an argon-filled glove box, where the content of O₂ and H₂O are lower than 0.1 ppm. A LAND 2001A battery testing system evaluated the galvanostatic charge-discharge performance within a voltage range of 1.7 V to 2.8 V (vs. Li/Li⁺). CV and EIS tests were performed using a VMP3 electrochemical workstation (Bio Logic). A potentiostatic signal at different temperatures and potentials were used for EIS measurement with a frequency between 10 MHz and 0.1 Hz and a 5 mV amplitude. CV tests were conducted using the coin cells between the electrochemical window of 1.7-2.8 V and the scan rate from 0.1 to 0.5 mV s⁻¹. The apparent active energy was calculated from the relationship between the inverse of absolute temperature (T) and the logarithm of the reciprocal of the peak current according to the Arrhenius equation ($j \propto k = Ae^{-\frac{La}{RT}}$). Where A is the pre-exponential factor, R is the universal gas constant, k is the rate constant and T is the absolute temperature (Kelvin). For the pouch cell construction, the sulfur positive electrode was fabricated by dispersing a mixture of S/ carbon composite, FeCo DASC, Super P (40 nm, >98%, Guangdong Canrd New Energy Technology Co. Ltd.), and LA133 binder (<1 µm, 15% of solids content, Guangdong Canrd New Energy Technology Co. Ltd.) in deionized water, maintaining a mass ratio of 8.43:0.15:0.4:0.6. This slurry was then casted on Al foil and subsequently dried under vacuum at 60 °C for 12 h. The Al foil was ultrasonically welded to the Al tab, while the Li foil was pressed to the Ni tab. The pouch cell was assembled by coiling the sulfur positive electrode, Celgard 2400, and lithium foil in a sandwich configuration, forming a total of seven layers. The assembly was carried out in a Dry Room with a size of 8 square meters and a dew point of -50 °C. After injecting 3.61 g of standard electrolyte, the cell was left to rest for 24 h before testing. During testing, the cell was clamped using a fixture to maintain a pressure of 0.19 MPa. All the electrochemical measurements were conducted in environmental room equipped with air conditioner under 25 °C. The coulombic efficiency was calculated by the ratio of discharge capacity to charge capacity per cycle. For coin cell, the specific capacity and specific current refers to the mass of active materials. For pouch cell, the specific energy refers to the whole mass of the cell.

DFT calculations

Spin-polarized DFT calculations were conducted using the Vienna Ab initio Simulation Package (VASP) with the Projector Augmented Wave (PAW) method. The calculations employed a cutoff energy of 450 eV and utilized the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional⁵³. The Gaussian smearing method was used and the width of smearing was chosen as 0.05 eV. In the vertical direction, a vacuum layer of about 15 Å in thickness was introduced for all the surfaces. For the binding energy and adsorption conformation simulations, we used the DFT-D3 functional to include the physical van der Waals interaction⁵⁴, which was demonstrated to be very important in the

simulation of Li₂S adsorption⁵⁵. The optimized lattice constants of graphene are 2.47 Å, consistent with the experimental results. A $6 \times 6 \times 1$ model of graphene is adopted in this work. The Brillouin zone was sampled using Monkhorst-Pack scheme with a k-point mesh of $2 \times 2 \times 1$ in the Gamma-centered grids for the structural relaxation⁵⁶. The structure relaxation was continued until the forces on all the atoms were converged to less than 0.01 eV/Å.

FEM simulations

Based on the practical conditions of assembling pouch cell, we calculated the relevant parameters within the Li ||S battery and simulated its electrochemical performances using COMSOL Multiphysics 6.0 software. The polysulfide distribution evolution, Li₂S deposition behaviors as well as the polysulfide corrosion with Li negative electrode were detailed simulated, in which the governing equation^{57,58} were described in the Supplementary Information. By adjusting the relevant parameters with reaction kinetics, we achieved the simulation for the ensemble effect on Li ||S battery performance.

Data availability

The data used in this study have been deposited in the Zenodo repository (DOI: 10.5281/zenodo.13786952). Source data are provided with this paper.

Code availability

The codes of machine learning models and data processing used in this study are available on Zenodo⁵⁹ and at: https://aimslab.cn/#/soft_materials_imvf.

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Author contributions

G.Z. and Z.H. conceived the idea and designed the project. G.Z., T.W., and J.L. supervised the experiments and edited the paper. Z.H., Z.L., L.Y., R.G., Y.J., G.J., and Z.L. performed the catalyst synthesis and tested the catalysts. T.W. contributed to the DFT calculations parts. A.C., Z.W., K.T., and J.G. contributed to the machine learning analysis. M.Z. conducted the COMSOL simulations. W.L. contributed to the material synthesis equipment. All authors analyzed the data and discussed the results.

Competing interests

The authors declare no competing interests.

Additional information

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