Signature of coexistence of superconductivity and ferromagnetism in two-dimensional NbSe$_2$ triggered by surface molecular adsorption

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Ferromagnetism is usually deemed incompatible with superconductivity. Consequently, the coexistence of superconductivity and ferromagnetism is usually observed only in elegantly designed multi-ingredient structures in which the two competing electronic states originate from separate structural components. Here we report the use of surface molecular adsorption to induce ferromagnetism in two-dimensional superconducting NbSe$_2$, representing the freestanding case of the coexistence of superconductivity and ferromagnetism in one two-dimensional nanomaterial. Surface-structural modulation of the ultrathin superconducting NbSe$_2$ by polar reductive hydrazine molecules triggers a slight elongation of the covalent Nb–Se bond, which weakens the covalent interaction and enhances the ionicity of the tetravalent Nb with unpaired electrons, yielding ferromagnetic ordering. The induced ferromagnetic momentum couples with conduction electrons generating unique correlated effects of intrinsic negative magnetoresistance and the Kondo effect. We anticipate that the surface molecular adsorption will be a powerful tool to regulate spin ordering in the two-dimensional paradigm.
Since the discovery of superconductivity (SC), the interplay between SC and magnetism has been a topic of cutting-edge research in solid-state materials. Given that ferromagnetism (FM) often plays a destructive role in superconductors by disturbing the singlet correlations responsible for the pairing interaction, the coexistence of SC and FM is rare yet valuable. The well-established correlated systems that exhibit these two competing electronic states are usually prepared by fabricating two separate structures, taking advantage of the inherent properties of each individual parent ingredient. For instance, such systems include the hybrid [Ni0.66Al0.33(OH)]2[TaS2] system, which is composed of ferromagnetic cation layers and superconducting anion layers; Fe/Nb/Fe trilayers consisting of one single SC layer (Nb layer) between two FM layers (Fe layer); and the layered [(L1– xFe)0.5(FeL1– x)0.5]Se system, which consists of ferromagnetic (Li1– xFe)0.5OH and superconducting (FeL1– x)0.5Se layers. 

These fascinating findings achieved by virtue of the proximity effect have generated increased interest in investigating the interplay between SC and FM. However, further realization of the coexistence of these two competing electronic states in a single homogeneous structure promises further insight into the coupling of these two competing orderings. In this regard, the recently reported two-dimensional (2D) electron liquid LaAlO3/StrTiO3 interface represents an advance in the coexistence of SC and FM, as both ingredients are neither superconducting nor ferromagnetic in their individual states. The coexistence of these properties at a uniform interface makes this 2D electronic system an attractive platform for achieving the coexistence of SC and FM in one system. The question remains whether the coexistence of both electronic states can be designed in a single freestanding 2D electronic structure, with the expectation of unconventional SC in the ground state for the stronger interplay of FM and SC.

Recently, two-dimensional or interface superconductors with the thickness down to one unit cell or atomic layers have attracted much attention and demonstrated many intriguing behaviours. 2D transitional metal chalcogenides, as the classic prototype for superconductors, provide a promising material platform for investigation of the coexistence of SC and FM because of their unique spin configuration and richly correlated electronic phases. 2H-NbSe2, a canonical layered SC material, consists of one Nb layer sandwiched between two Se layers, forming trigonal prismatic NbSe6 with covalent Nb–Se bonds and the impairment of the Nb–Se covalent interactions, which enhance the ionicity of the tetravalent Nb with unpaired electrons and thus successfully yields ferromagnetic ordering in superconducting 2D NbSe2 nanomaterials. The coexistence of SC and FM in a single 2D nanomaterial gives rise to the fascinating coupled effects of negative magnetoresistance (MR) and the Kondo effect. This work provides a route for achieving the integration of ordered magnetism and SC in 2D systems.

Results

Surface molecular adsorption. To enable effective adsorption of polar molecules on the negatively charged NbSe2 surface, the assembled thin film of NbSe2 ultrathin nanosheets (Supplementary Figs 1 and 2, Supplementary Notes 1 and 2) was exposed in the vapour flow of hydrazine at an elevated temperature of 70 °C, during which the gas state of hydrazine as well as elevated temperature help to overcome the adsorption energy barrier and ensure sufficient interactions between polar hydrazine with nanosheets. In our case, the strong reductive atmosphere plays a vital role in protecting inherent Se–Nb–Se lattice structure from being oxidated, while experimental results have confirmed that other polar molecules such as H2O, amines (NH3 and so on) and alcohols (CH3OH, CH3CH2OH, and so on) have the relative lower reductive capability inevitably lead to structural destruction with elemental Se particles as by-products. Of note, the assembled thin film of NbSe2 ultrathin nanosheets provides abundant interstitial sites to confine and stabilize the adsorbed hydrazine molecules (details see Supplementary Fig. 3), ensuring effective surface molecular adsorption to induce local distortions. The surface molecular adsorption of strong reductive hydrazine successfully realized the surface-structural modulation of 2D NbSe2 nanosheets as well as the preservation of the NbSe2 framework, as schematically illustrated in Fig. 1, where the adsorption site and the resultant structural distortion were highlighted in the green background. The strong polarity of 1.83 Debye of the reductive hydrazine molecules facilitated the surface molecular adsorption due to the electrostatic interactions between the surfaces of the negatively charged NbSe2 nanosheets and the adsorbed polar hydrazine molecules, which enabled the attraction of the polar hydrazine molecules to the surfaces of the NbSe2 nanosheets, as revealed by the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra. The spectrum of the pure hydrazine molecules is presented in the topmost part of Fig. 2a, where the characteristic N–H stretching bond at ~3,000 cm⁻¹ is the signature of the existence of the hydrazine molecules. As expected, the spectrum of the hydrazine-treated NbSe2 nanosheets resembles that of the pure hydrazine molecules, thus confirming the adsorption of the hydrazine molecules to the NbSe2 nanosheets. By contrast, the spectrum of the pure NbSe2 nanosheets does not exhibit a signature similar to that present in the topmost spectrum; in particular, the N–H stretching bond is absent. The hydrazine treatment enabled the adsorption of the hydrazine molecules on the surfaces of the NbSe2 nanosheets, thereby triggering local surface-structural distortions.

ultrathin NbSe2 nanosheets would be a new class of 2D electronic systems that possess coupled SC and FM.

Here we highlight a surface-structural modulation strategy for the incorporation of intrinsic FM into the superconducting NbSe2 framework, thereby accomplishing the structural integration of SC and FM in a freestanding case of 2D nanomaterial. The surface adsorption of polar reductive hydrazine molecules triggers structural modulation while the pristine structure is reserved, leading to the elongated covalent Nb–Se bonds and the impairment of the Nb–Se covalent interactions, which enhance the ionicity of the tetravalent Nb with unpaired electrons and thus successfully yields ferromagnetic ordering in superconducting 2D NbSe2 nanomaterials. The coexistence of SC and FM in a single 2D nanomaterial gives rise to the fascinating coupled effects of negative magnetoresistance (MR) and the Kondo effect. This work provides a route for achieving the integration of ordered magnetism and SC in 2D systems.

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Maintenance of pristine NbSe₂ framework after the adsorption. The pristine Se–Nb–Se layered framework was maintained after surface adsorption of the polar hydrazine molecules, as confirmed by systematic structural characterization performed via X-ray powder diffraction, Raman spectroscopy and Se K-edge X-ray absorption near-edge structure (XANES) spectroscopy of the...
hydrazine-treated NbSe₂ nanosheets. As observed in Fig. 2b, the X-ray diffraction pattern of the hydrazine-treated nanosheets parallels that of the pure nanosheets, thereby confirming the retention of the NbSe₂ lattice framework. The high-resolution (0.35 cm⁻¹) Raman spectra further confirm that the in-plane structural framework of 2H-NbSe₂ was well preserved. As observed in Fig. 2c, the Raman spectra of the pure and hydrazine-treated NbSe₂ nanosheets exhibit two prominent peaks corresponding to the $A_{1g}$ and $E_{1g}$ modes of 2H-NbSe₂ (ref. 35). The slight energy shift (0.9 cm⁻¹) of hydrazine-treated NbSe₂ nanosheets to the lower energy revealed the releasing energy of the out-of-plane vibration $A_{1g}$ mode, indicating local elongation of Nb–Se covalent bonds that is consistent with X-ray absorption fine structure (XAFS) measurement results in the following discussions. In addition, the Se K-edge XANES spectra (Fig. 2d) of the pure and hydrazine-treated NbSe₂ nanosheets confirm the nearly invisible effect of the hydrazine treatment on the valence states of the element, indicating that there is no electron transfer between the surface-adsorbed hydrazine molecules and the outmost Se layers. In a word, the structural comparison between the pure and hydrazine-treated NbSe₂ nanosheets revealed that the 2H-NbSe₂ lattice framework was well preserved at the macroscopic level after the hydrazine treatment.

Local distortions induced by the adsorption. To examine the local structural modulation after the hydrazine treatment, XAFS measurements were performed to determine the local atomic and electronic structures of the hydrazine-treated NbSe₂ nanosheets. The $k^3\chi(k)$ oscillation curve presented in Fig. 3a for the hydrazine-treated NbSe₂ nanosheets exhibits a spectral shape similar to that of the pure nanosheets; however, a noticeable reduction in the oscillation amplitude is observed. Such an amplitude reduction is also evident in the corresponding Fourier transform (FT) functions. In Fig. 3b, the FT curve of the pure NbSe₂ nanosheets displays two peaks at ~2.26 and 3.09 Å, which can be attributed to Se–Nb and Se–Se correlations, respectively. For the hydrazine-treated NbSe₂ nanosheets, the intensities of these two peaks are significantly decreased, accompanied by a noticeable shift in the position of the Se–Nb peak towards the high-R side and a shift of the Se–Se peak in the opposite direction. The high-quality extended XAFS spectra enabled us to perform further least-squares fittings of the Se K-edge data, and the quantitative results thus obtained are summarized in Supplementary Fig. 4 and Supplementary Table 1. Evidently, compared with the pure NbSe₂ nanosheets, the interatomic distance of the Se–Nb coordination in the hydrazine-treated NbSe₂ nanosheets was elongated by 0.02 Å, whereas that of the Se–Se coordination was shortened by 0.03 Å. The resulting remarkable increase in the degree of disorder may have resulted in the damping of both peaks. Notably, in our fitting process, the Se–Se coordination referred to the Se atoms in the $a$–$b$ plane, whose coordination number was much greater than that of other types of Se–Se coordination and contributed greatly to the extended X-ray absorption fine structure (EXAFS) signal. Moreover, the negligible hydrazine content was out of consideration in the fitting process. On the basis of these structural parameters, the structural models for hydrazine-treated NbSe₂ nanosheets are displayed in Fig. 3c, which clearly illustrates the distorted bond lengths and bond angles of the Nb–Se, Nb–Nb and Nb–Se–Nb coordination geometries. It is apparent that, compared with the pure NbSe₂ nanosheets, the Nb–Se bond length in the hydrazine-treated NbSe₂ nanosheets was relatively elongated, thus impairing the covalent Nb–Se interactions and augmenting the unpaired electrons around the Nb atoms.

Surface-structural modulation. As indicated by the comprehensive structural characterizations of the pure and
Hydrazine-treated NbSe2 nanosheets, the adsorption of the polar hydrazine molecules resulted in local modulations in the 2H-NbSe2 structure. The electrostatic interactions between the surface charge of the nanosheets and the polar hydrazine molecules successfully triggered local structural modulation while preserving the integrity of the pristine structure. In our case, the hydrazine molecules played a vital role in inducing the structural modulation process. On the one hand, the strong reductive property ensured the structural integrity of NbSe2 nanosheets during the experimental process. Notably, representative and available polar molecules with oxidative potentials, such as H2O, amines (NH3 and so on) and alcohols (CH3OH, CH3CH2OH, and so on), can demolish NbSe2 nanosheets, producing Se nanoparticles on the NbSe2 nanosheets. The Se 3d spectra of H2O/CH3CH2OH/NH3-treated NbSe2 nanosheets consisted of quadruple peaks, suggesting the mixed selenium valence states, especially the additional doublet peak of Se0 3d5/2 (55.7 eV) and Se3 3d3/2 (54.9 eV), as shown in Supplementary Fig. 5 and Supplementary Note 3, which in turn confirmed the protective role of reductive atmosphere produced by hydrazine molecules. On the other hand, the N atom in the hydrazine molecule is threefold coordinated with its counterpart N atom and two H atoms, and this threefold coordination, together with the structural asymmetry of the molecule, results in the strong polarity of the hydrazine molecule of 1.83 Debye. As a result, the strongest polarity among the available reductive vapour molecules and advantageous over other counterparts. The strong polarity boosts the surface molecular adsorption, which is beneficial to the surface-structural modification. Hence, the adsorption of polar reductive hydrazine molecules successfully induced surface-structural modulation via the elongation of the Nb-Se bonds, which impaired the Nb-Se covalent interaction and enhanced the ionicity of the tetravalent Nb with unpaired electrons, endowing the distorted 2D NbSe2 with an intriguing magnetic response.

Polarized spin calculations. Spin-polarization calculations were performed to gain an understanding of the anticipated FM of the surface-distorted NbSe2. In the inset of Fig. 3e, the purple isosurface represents the spin density, which is rather spherical around the Nb atoms, thereby revealing the ferromagnetic order incorporated into the distorted NbSe2 nanosheets. The densities of states, shown in Fig. 3d,e, provide further evidence for this phenomenon: the significant asymmetry in the density of states (DOS) between the spin-down channel and the spin-up channel provides direct evidence of the intrinsic FM in the distorted NbSe2 nanosheets. By contrast, the densities of states for the spin-up and spin-down channels of the pure NbSe2 nanosheets are degenerate, answering for the nonmagnetic property of the pure NbSe2 nanosheets. From examining the atomic site-projected DOSs, it is apparent that the states near the Fermi level for the distorted NbSe2 are primarily contributed by Nb d states. The polarized spin calculations suggest that the delicate surface distortions caused by the elongated Nb-Se bond induce ordered spin behaviour.

Induced FM in the distorted NbSe2. The modulation of the covalent Nb-Se interaction in the hydrazine-treated NbSe2 nanosheets induced ordered spin in this SC system, as verified by magnetic measurements. Figure 4a shows the temperature dependence of the magnetic susceptibility (\(\chi\)) from 2 to 300 K for the hydrazine-treated NbSe2 nanosheets. These data were collected under a magnetic field of 200 Oe using both zero-field-cooling (ZFC) and field-cooling (FC) processes performed on the assembled film of NbSe2 ultrathin nanosheets. Both the ZFC and FC curves of the hydrazine-treated nanosheets exhibit a diamagnetic signal (superconducting transition) at \(T_c\) of 6.8 K, providing evidence for the preservation of SC after treatment. For comparison, the corresponding pure NbSe2 sample, the diamagnetic signal appeared at 7.4 K and the behaviour of \(\chi\) in the normal state were weakly temperature-dependent, as observed in Supplementary Fig. 6a. It is clearly evident that after the treatment not only did the superconducting transition temperature decrease but also the behaviour of \(\chi\) in the normal state was more strongly temperature-dependent. There was an obvious transition at \(T_c\) of 6.8 K, as shown in Fig. 4b, where the susceptibility \(\chi\) of the FC process notably increased below 40 K, thus indicating the onset of FM behaviour. To identify the antiferromagnetic FM of the hydrazine-treated SC system, the iso-thermal magnetization curves (\(M-H\) curves) at 30 and 2 K were measured; these curves are presented in Fig. 4c,d, respectively. The \(M-H\) curve at 30 K shown in Fig. 4c consists of a typical hysteresis loop, which clearly implies the successful introduction of FM into the SC NbSe2 system. Furthermore, the isothermal magnetization curve in the normal state of SC (2 K) suggests the coexistence of SC with the ferromagnetic ordering. Of note, considering the 2D feature of NbSe2 nanosheets and the random configuration of surface molecular adsorption, the induced ferromagnetic state in our case is not the conventional long-range spin ordered states but the short-range magnetic domains. As observed in Fig. 4d, the \(M-H\) curve at 2 K exhibits an obvious diamagnetic signal in the low-field region, whereas the diamagnetic behaviour eventually transforms into FM with an increasing applied field.

Discussion

To probe the interplay between the induced FM and the inherited SC, the magnetic response of the transport properties of the 2D NbSe2 was investigated, of which the optical image is shown in Supplementary Fig. 2. As observed in Fig. 4e,f, as the temperature was decreased, the resistivity of the treated NbSe2 sample slowly decreased, similar to the result obtained for pure NbSe2 (see Supplementary Fig. 6d). However, there were three significantly different \(R-T\) behaviours of the hydrazine-treated and pure samples. First, the value of the resistivity at zero magnetic field for the treated sample was larger than that for the pure sample. Second, the pure sample exhibited an ordinary positive MR, defined as \((R_{\text{H0}} - R_{\text{H}})/R_{\text{H0}}\) where \(R_{\text{H}}\) and \(R_{\text{H0}}\) represent the resistivity under a magnetic field and the primitive resistivity, respectively. This ordinary positive MR commonly exists in metals. By comparison, the hydrazine-treated sample exhibited an abnormal negative MR of \(-6\%\) in the non-superconducting region. Third, the pure NbSe2 sample exhibited normal metal behaviour (that is, positive coefficient of resistance to temperature) until the superconducting transition at 7.4 K, whereas the resistivity of the hydrazine-treated sample initially decreased with decreasing temperature until a minimum was reached at \(T_c\) of 30 K and subsequently increased as the temperature approached the superconducting temperature. The abnormal increase in the resistivity below \(T_c\) can be well fitted to the model of the Kondo effect, revealing a logarithmic temperature dependence for the resistivity, as shown in Supplementary Fig. 7.

We believe that the different \(R-T\) behaviours of the pure NbSe2 and hydrazine-treated NbSe2 nanosheets can be attributed to the introduction of local magnetic momentum via hydrazine treatment in the metal NbSe2 matrix. The increased resistivity of the hydrazine-treated NbSe2 compared with that of the pure NbSe2 is interpretable when considering the scattering effect between the induced local magnetic momentum and the
conduction electrons. Besides, the external magnetic field increased the effective arrangement of the localized spins and thus suppressed the fluctuations of the local spins in space and time, thereby leading to a decrease in the scattering effect between the local magnetic momentum and conduction electrons and explaining the negative MR observed in the hydrazine-treated NbSe₂ sample. Furthermore, the observation of the Kondo scattering in the FM onset temperature region, where the susceptibility exhibited an obvious increase, also confirms the presence of ferromagnetic scattering centres at low-temperature region in the hydrazine-treated NbSe₂ nanosheets. Those unique phenomena of the negative MR and the Kondo effect observed in a uniform 2D nanomaterial indicate direct interaction between the conducting electrons and the local magnetic moment, beyond the proximity effect. Therefore, FM and SC were observed simultaneously in the distorted NbSe₂ nanosheets as a result of surface-structural modulation, based on the electronic phase separation model, where the hydrazine absorption region serves as the ferromagnetic building block and the pristine Se–Nb–Se framework as the superconducting building block (Supplementary Fig. 8), representing the successful structural integration of SC and FM in a 2D nanomaterial.

In conclusion, we demonstrate the surface molecular adsorption of polar reductive hydrazine molecules to induce structural distortion in 2D NbSe₂ nanosheets, which led to the successful expression of the magnetic moment of the Nb ions with ordered spin behaviour, thus representing freestanding case of the coexistence of SC and FM in one 2D nanomaterial. The surface distortion triggered by this molecular adsorption resulted in an elongated Nb–Se covalent bond, which weakened the covalent Nb–Se interaction and reduced the hybridization of Nb with Se atoms, thereby augmenting the unpaired electrons around the Nb ions and thus resulting in FM. Within this 2D superconducting framework, the induced ferromagnetic momentum coupled with conduction electrons to generate unique correlated effects of intrinsic negative MR and the Kondo effect. We anticipate that this strategy for surface-structural modification via polar molecular adsorption will provide versatile paths for the preparation of correlated systems with coexisting electronic phases.

Methods

Materials. Niobium powder (99.9%), selenium powder, iodine (analytical grade) and n-butyl-lithium (n-BuLi; 2.5 M in hexane) were purchased from...
Hydrazine treatment. The hydrazine treatment was similar to that applied to obtain reduced graphene oxide. First, 4 ml of a dispersion of highly exfoliated NbSe2 nanosheets in cyclohexane was sonicated at 70°C for 2 h in a 150-μL pore size to form a homogenous thin film, the thickness of which could be tuned by modifying the filtration time, and the thickness of the film in the experiments was controlled to be 200 nm. Afterwards, the film was transferred onto a Si/SiO2 substrate cleaned with ultraviolet oxygen radiation. The as-obtained film was subsequently treated via 5 min of exposure to hydrazine vapour generated at 70°C. The transport measurement was performed on the assembled film with four-probe connections to the gold contacts with silver paste to serve as the leads, which were connected to the sample through a stencil mask, and gold wires were embedded and attached. The laser power of 0.5 mW.

Preparation of NbSe2 nanosheets. In a typical procedure, LiNbSe2 was synthesized via lithium insertion using 90 mg of NbSe2 powder in 1 ml of n-BuLi (2.5 M) diluted with 8 ml of hexane in a customized glass vacuum system reacted at 60°C and washed for 12 h to obtain Li-inserted NbSe2. The resultant dispersions were filtered, washed with cyclohexane and anhydrous ethanol several times, and then vacuum-dried at 60°C for the subsequent experimental procedures. Afterwards, 20 mg of the as-obtained LiNbSe2 was dispersed in 20 ml of distilled water. Then, the solution was bubbled with nitrogen to expel any dissolved oxygen molecules to avoid oxidation. The LiNbSe2-containing dispersions were filtered and washed after 1 h. Afterwards, the resultant water-dispersion suspension was centrifuged at 2,000 r.p.m. for 20 min. The supernatant was then decanted into another container to remove unexfoliated flakes, and a high-quality dispersion of [NbSe2]n− nanosheets was thus prepared.

Characterization. X-ray diffraction was performed using a Philips X’Pert Pro Super diffractometer with Cu Kα radiation (λ = 1.5418 Å). Transmission electron microscopy (TEM) images were acquired with a JEOL JEM-2100 transmission electron microscope at an acceleration voltage of 200 kV. Field-emission scanning electron microscopy (FE-SEM) images were acquired with a JEOL JSM-6700F SEM. HR-TEM images were acquired with a JEOL 2010 microscope at an accelerating voltage of 200 kV. Scanning TEM (STEM) images and energy-dispersive X-ray spectra (EDS) were obtained using a JEM 2100F (field emission) transmission electron microscope equipped with an Oxford INCA X-sight EDS Si/Li detector at an acceleration voltage of 200 kV. A Shimadzu IRPremiere-21 spectrometer with a standard 45°ZnSe ATR cell (Specac Ltd., Woodstock, GA) and a ZnSe grating polarizer (PIKE Technologies Inc., Madison, WI) was used to collect ATR-FTIR spectra. The XAFS measurements at the Nb K-edge (12 658 eV) were performed in fluorescence mode at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), China. The storage ring of SSRF was operated at 3.5 GeV with a maximum current of 210 mA. The magnetization was characterized using a Quantum Design physical property measurement system (PPMS) at 70°C. The background signal of SiO2 substrate was treated by deducting the data of blank SiO2 substrate. The magnetic-transporting property was measured via the four-probe technique using a Quantum Design physical property measurement system (PPMS-9) with the van der Pauw method. Gold contacts were evaporated on the sample through a stencil mask, and gold wires were embedded and connected to the gold contacts with silver paste to serve as the leads, which provided a strong electrical contact and consequently a small contact resistance. The transport measurement was performed on the assembled film with four-probe configuration. High-resolution Raman spectra were recorded at room temperature using a LARBRAM-HR confocal laser micro Raman spectrometer at 750 K with a laser power of 0.5 mW.

Density functional theory calculations. Electronic structure calculations and geometric optimizations were performed using density functional theory as implemented in VASP.37,38 The exchange-correlation energy was treated using the projector augmented wave (PBE)-type GGA functional, which has been proven to be able to describe this system very well.39 The ion–electron interaction was treated using the projector-augmented wave technique. A cutoff energy of 520 eV was adopted. For geometric optimization, both the lattice constants and the atomic positions were relaxed until the forces on the atoms were less than 0.02 eV Å−1 and the total change in energy was less than 1.0 × 10−5 eV. The Brillouin zone was sampled using k-points with a 0.02 Å−1×1 spacing in the Monkhorst–Pack scheme39 for geometry optimization, and for the DOS calculations, a denser grid with a 0.01 Å−1 spacing was used.40

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Author contributions
C.W. conceived the idea and experimentally realized the study, co-wrote the paper and supervised the entire project and is responsible for the infrastructure and project direction. X.Z. and Y.G. contributed equally to this work; they experimentally realized the study, analysed the data and co-wrote the paper, and these authors were assisted by X.A., J.Z. and K.T. XAFS data collection, analysis and fitting were performed by H.C. and S.W. The theoretical calculations were performed by J.D. and X.C.Z. Y.X. supervised the whole experimental procedure and co-wrote the paper. All authors discussed the results and commented on and revised the manuscript.

Additional information
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