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EDGE ARTICLE**Ultrathin Nanosheets of Feroxyhyte: A New Two-dimensional Material with Robust Ferromagnetic Behavior**Pengzuo Chen,^{†a} Kun Xu,^{†a} Xiuling Li,^b Yuqiao Guo,^a Dan Zhou,^a Jiyin Zhao,^a Xiaojun Wu,^{a,b} Changzheng Wu^{*a} and Yi Xie^aReceived (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
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Two dimensional (2D) nanosheets have shown highly potential application in next-generation nanoelectronic devices. However, developing 2D nanosheets for next-generation spintronics has been blocked due to the lack of intrinsic robust ferromagnetic behavior. Here, we highlighted a robust ferromagnetic behavior in a 2D inorganic graphene-like structure. The δ -FeOOH ultrathin nanosheets, as a new 2D material, exhibit an unprecedentedly high saturation magnetization value of 7.5 emu/g at room temperature, which is the highest value among graphene and graphene analogues. Atomic-scale topochemical transformation ensures the formation of 2D δ -FeOOH ultrathin nanosheets from intermediate Fe(OH)₂ nanosheets. Moreover, δ -FeOOH ultrathin nanosheet is found to be a semiconductor with a direct band gap of 2.2 eV. Owing to advantages of robust ferromagnetism in semiconductor, δ -FeOOH ultrathin nanosheets show promising candidate for constructing next generation spintronics.

Introduction

Recently, two dimensional (2D) nanosheets, which are made of single or few layers, have received tremendous attentions due to their quantum size effect brought unique physical properties.¹⁻³ Graphene, a typical 2D nanomaterial, has been the most widely studied 2D material during the past few years owing to its exceptional electronic, thermal and mechanical properties.⁴⁻⁷ Triggered by the graphene, various 2D nanosheets with graphene-like structure including metal chalcogenides (e.g. TiS₂, VS₂ and MoS₂), metal oxides (e.g. MnO₂, SnO₂), carbon nitrides (C₃N₄) have also been developed and shown greatly potential applications in stamp-transferrable electrodes,⁸ supercapacitors,⁹⁻¹¹ sensors,¹²⁻¹⁵ field-effect transistors,^{16, 17} catalysis^{18, 19} and bioimaging.²⁰ However, most of the existing 2D compounds are intrinsically nonmagnetic and the development of these novel 2D nanosheets for next generation spin-related nanodevices are therefore extremely inhibited.²¹ Although few ferromagnetic 2D nanosheets have been gradually unravelled lately,²²⁻²⁴ there still remains an important challenge to obtain a 2D material with

robust room temperature ferromagnetism for future-generation spintronic devices.

Transition metal oxides especially iron oxides could provide rich spin-related information because of their special 3d electronic configuration. Feroxyhyte (δ -FeOOH), the metastable species in iron oxide family, has a crystallographic structure that is based on a hexagonal closed-packed oxygen lattice with Fe³⁺ ions occupying half of the available octahedral interstices similar to that of hematite.²⁵ The presence of two unequally occupied octahedral sites would induce a significant spontaneous magnetization in δ -FeOOH structure, with an almost constant Curie temperature over room temperature.^{25, 26} Moreover, the

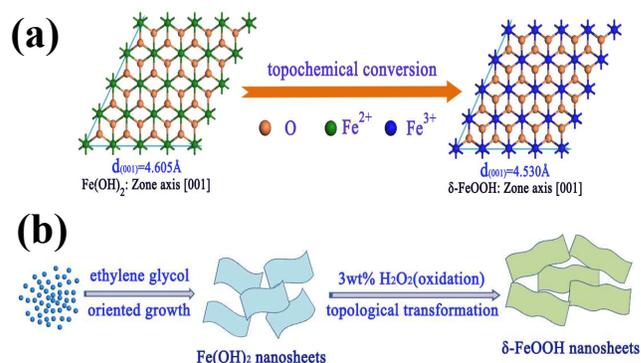


Figure 1. (a) Top-view of c-orientation showing the topochemical conversion from Fe(OH)₂ (001) plane to δ -FeOOH (001) plane. (b) Schematic illustration of the formation process of ultrathin δ -FeOOH nanosheets.

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absorption edge of the δ -FeOOH located in the vicinity of 600 nm presents a semiconductor behavior.²⁷ In this respect, the ferromagnetism and semiconductor states coexisting in δ -FeOOH ultrathin nanosheets make these nanosheets as new inorganic graphene analogues and highly promising candidates for future-generation spintronics.

Atomic structure analyses give us inspiration that δ -FeOOH ultrathin nanosheets could be obtained by a facile topochemical transformation strategy. As shown in **Figure 1a**, the $\text{Fe}(\text{OH})_2$ and δ -FeOOH possess the similar crystal planes when viewed from the c -axis. More interestingly, the $\{001\}$ facets ($d=4.605 \text{ \AA}$) of $\text{Fe}(\text{OH})_2$ matches well with the $\{001\}$ facets ($d=4.530 \text{ \AA}$) of δ -FeOOH, which offers the possibility for realizing the topochemical conversion from $\text{Fe}(\text{OH})_2$ to δ -FeOOH. In this regard, the controllable synthesis of $\text{Fe}(\text{OH})_2$ ultrathin nanosheets provide the feasibility for achieving the δ -FeOOH ultrathin nanosheets.

Despite the topochemical transformation strategy is feasible, 2D δ -FeOOH ultrathin nanosheet has not been achieved up to date, greatly hampering further investigation of the unique magnetic behaviors. Herein, we demonstrate the first synthesis of 2D δ -FeOOH ultrathin nanosheets with less than three unit cells, as a new inorganic graphene analogue, undergoing an atomic-scale topochemical transformation strategy, through the oxidation of $\text{Fe}(\text{OH})_2$ ultrathin nanosheets. As for the δ -FeOOH ultrathin nanosheets, the intrinsic ferromagnetic behavior has been investigated. The δ -FeOOH ultrathin nanosheets show a robust ferromagnetic behavior at room temperature and present a semiconductor state. To the best of our knowledge, the saturation magnetization value of our δ -FeOOH ultrathin nanosheets is the highest value among the graphene and graphene analogues.

Results and discussion

The δ -FeOOH ultrathin nanosheets were achieved by an atomic-scale topochemical transformation process, through the oxidation of $\text{Fe}(\text{OH})_2$ ultrathin nanosheets at room temperature. The phase

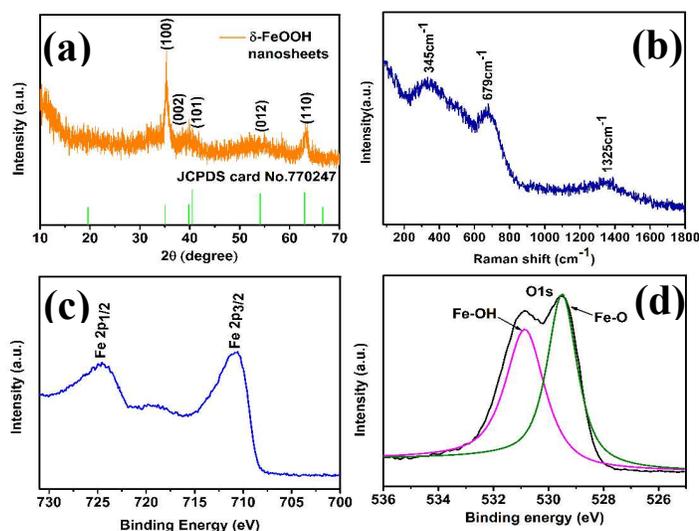


Figure 2. (a) XRD pattern of the δ -FeOOH ultrathin nanosheets. (b) Raman spectra of δ -FeOOH ultrathin nanosheets. XPS of high-resolution Fe 2p (c), O 1s (d) core level regions.

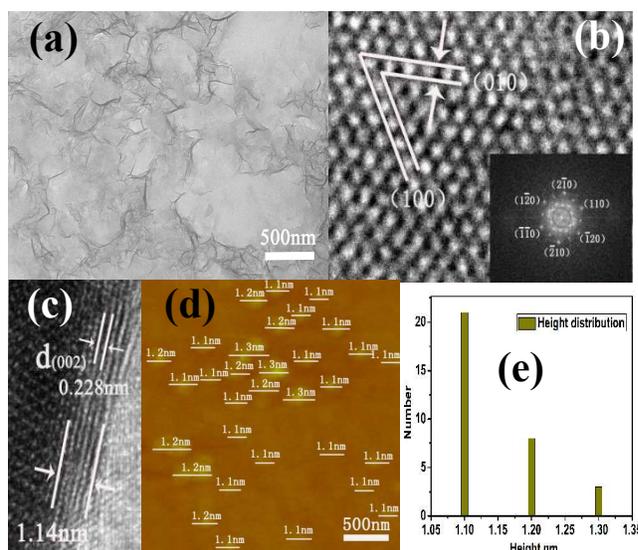


Figure 3. (a) TEM image of δ -FeOOH ultrathin nanosheets. (b) HRTEM image and (inset) corresponding FFT pattern of δ -FeOOH ultrathin nanosheets. (c) HRTEM image of the edge of an ultrathin nanosheet. (d) Tapping-mode AFM image of δ -FeOOH ultrathin nanosheets. (e) The corresponding height distribution.

and purity of the as-obtained sample were confirmed by X-ray diffraction (XRD) analysis. As shown in **Figure 2a**, the XRD pattern of as-synthesized sample could be readily indexed to the pure hexagonal δ -FeOOH (space group P-3m1, $a=b=2.95 \text{ \AA}$, $c=4.53 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$; JCPDS card No.77-0247), indicating that the obtained δ -FeOOH ultrathin nanosheets were of high quality. In addition, the δ -FeOOH structure was also verified by the means of Infrared spectroscopy (**Figure S2**) and Raman spectrum. The Raman spectrum of the δ -FeOOH ultrathin nanosheets in **Figure 2b** shows the peaks at 345, 679, 1325 cm^{-1} , which match exactly with the spectrum of δ -FeOOH reported in a previous literature spectrum.²⁸ Furthermore, chemical

composition and element valence of the sample were studied by the XPS. **Figure S3** shows the survey XPS spectrum, which clearly demonstrates the sample constitutive of Fe and O elements (H element couldn't be detected by the XPS). The high-resolution core spectrum of Fe 2p was presented in **Figure 2c**, which excludes the possibility of Fe^{2+} or Fe^0 in the synthetic sample. The peak at 710.7 eV along with a weak satellite peak at 719.4 eV can be assigned to Fe^{3+} 2p3/2, and the binding energy of Fe^{3+} 2p1/2 at 724.4 eV demonstrates the Fe^{3+} state of the δ -FeOOH structure.²⁹ The O1s region in **Figure 2d** is consists of two parts at 529.6 eV and 530.8 eV respectively, which can be ascribed to Fe-O and O-H bonding behavior of the synthetic products.²⁹

To illustrate the outlook and structural information of the as-synthesized δ -FeOOH ultrathin nanosheets, microscopic characterization were carried out. Field-emission scanning electron microscopy (FESEM) image presented in **Figure S4** clearly demonstrated ultrathin nanosheet morphology with a typical size ranging from 200 nm to several micrometers for as-obtained samples. The transmission electron microscopy (TEM) image (**Figure 3a**) shows a large-area wrinkled and nearly transparent nanosheets as

graphene, which also confirm the ultrathin nanosheet morphology of the as-synthesized δ -FeOOH nanosheets. As illustrated in **Figure 3b**, HRTEM image and corresponding fast Fourier transform (FFT) pattern reveal the nature of hexagonal single crystal nanosheet with a [001] preferential orientation. Moreover, the edge-area HRTEM image shown in **Figure 3c** gives solid evidence that the δ -FeOOH nanosheets were ultrathin nanostructures with the height of about 1.2 nm. The thickness of the as-synthesized δ -FeOOH nanosheets was also evaluated by tapping-mode atomic force microscopy (AFM). The AFM image and corresponding height distribution (**Figure 3d, e**) showed that the measured height was ranging from 1.1 nm to 1.3 nm, consistent with the edge-area HRTEM measurement. The above characterization results clearly demonstrate that the purity and high quality of δ -FeOOH ultrathin nanosheets have been successfully synthesized.

The ultrathin nanostructure of the δ -FeOOH nanosheets endow it

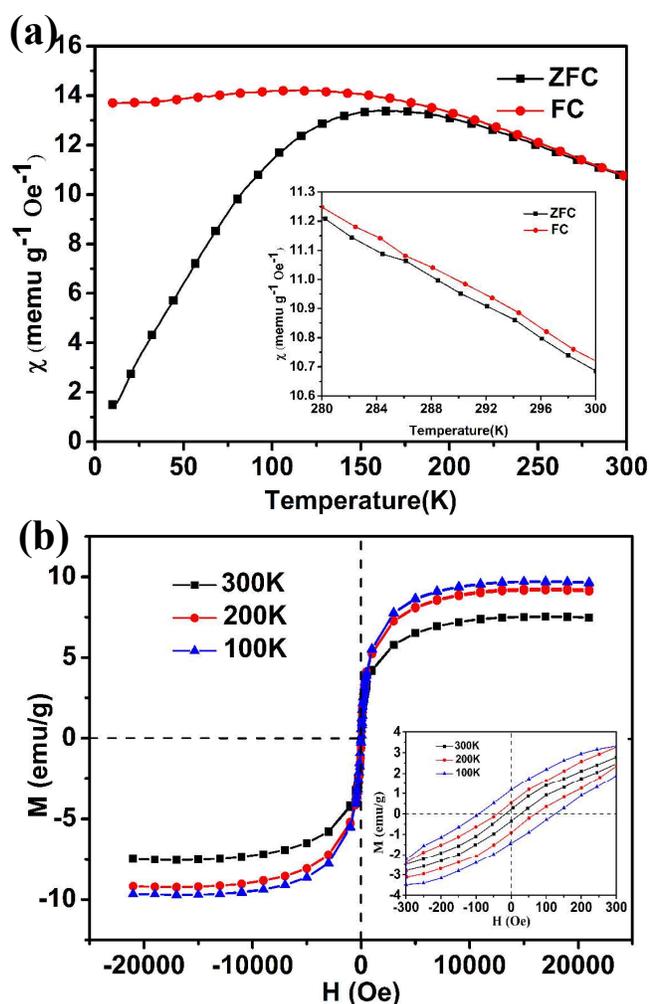


Figure 4. (a) Temperature dependence of ZFC and FC magnetization of as-synthetic δ -FeOOH ultrathin nanosheets. Inset: the magnified part for ZFC and FC curves at temperature range from 280 K to 300 K. (b) M-H curves for the as-synthetic δ -FeOOH ultrathin nanosheets measured at different temperatures. Inset: the enlarged M-H section in the low applied field.

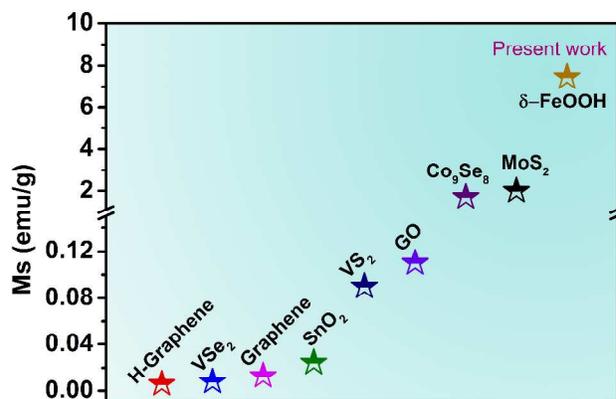


Figure 5. Comparison of saturation magnetization of the reported ferromagnetic nanosheets including H-graphene,³⁰ VSe₂,²² graphene,³¹ SnO₂,³² VS₂,³³ graphene oxide (GO)³⁴ and Co₉Se₈,²³ MoS₂³⁵ etc.

flexible mechanical properties. As expected, a layer-by-layer assembled thin film of δ -FeOOH ultrathin nanosheets could easily be obtained by vacuum filtration method and transferred to a flexible plastic substrate, taking on excellent flexibility and structural integrity (**Figure S7**). In fact, thin film of the δ -FeOOH ultrathin nanosheets could be transferred to any substrates such as silicon, quartz, copper and so on. Also, the thickness of the δ -FeOOH ultrathin nanosheets thin film could be tuned by controlling the dosage of δ -FeOOH nanosheet solution used. It is amazing that the δ -FeOOH ultrathin nanosheets/PET hybrid thin film could be readily gripped by a magnet, revealing the as-synthesized δ -FeOOH ultrathin nanosheets are robust ferromagnetic materials at room-temperature. The flexible mechanical properties provide promising for this robust ferromagnetic material to be utilized in flexible magnetic device. In order to understand the intrinsic room-temperature ferromagnetism of the as-synthesized δ -FeOOH ultrathin nanosheets in details, a SQUID magnetometer was performed to measure the temperature-dependent magnetization of zero-field-cooled (ZFC) and field-cooled (FC) processes. The obtained temperature-dependent magnetic susceptibility (M-T) curves are shown in **Figure 4a**, which reveals high magnetic susceptibility and obvious divergence between FC and ZFC even as high as 300 K, indicating intrinsic room-temperature ferromagnetism of δ -FeOOH ultrathin nanosheets and the Curie temperature of the sample far over 300 K. The magnetic-field dependence of magnetization (M-H) curves for the δ -FeOOH ultrathin nanosheets measured at different temperature are displayed in **Figure 4b**, which shows a coercivity (H_c) of 30 Oe for δ -FeOOH ultrathin nanosheets at 300 K and the coercivity gradually increases with the temperature decreasing from 300 K to 100 K. Moreover, the saturation magnetization (M_s) reaches up to 7.5 emu/g at 300 K, which is higher than that of various 2D ferromagnetic materials (**Figure 5 and Table S1**), confirming the room-temperature robust ferromagnetism of the synthesized δ -FeOOH ultrathin nanosheets. More importantly, UV-vis spectrum of the δ -FeOOH ultrathin nanosheets (**Figure S8**) clearly manifests that it is a semiconductor with a direct band gap of 2.2 eV. As is well known, the 2D ferromagnetic semiconductor ultrathin nanosheet is a promising candidate for the design of

next-generation spintronics. The coexistence of both intrinsic robust ferromagnetic characteristics and a band gap in 2D materials will offer the opportunity for simultaneous regulation of spin and charge, while guarantee the enhanced utilization efficiency for spin-dependent devices and enriching them with novel functions in the future.³⁶

Conclusions

In conclusion, δ -FeOOH ultrathin nanosheets as the new two-dimensional material were successfully obtained by a facile topochemical transformation strategy for the first time. The FeOOH ultrathin nanosheets achieved an unprecedentedly high saturation magnetization value of 7.5 emu/g at room temperature, which is the highest value among the graphene and graphene analogues. Realizing robust room temperature ferromagnetism and semiconductor behavior in a single 2D material is of great importance for constructing next generation spintronic device. We anticipate that this work not only trigger more scientific interest in new types of 2D ferromagnetic materials, but also provides a highly promising candidate 2D ferromagnetic semiconductor material for constructing next generation spintronic devices.

Experimental section

Preparation of δ -FeOOH ultrathin nanosheets. The Fe(OH)₂ precursor nanosheets were synthesized using a modification of the method proposed by Ma et al.³⁷ In a typical procedure, 0.5 g NaOH was added into 5 ml distilled water under vigorous stirring, and then 25 ml ethylene glycol (EG) was added to form a homogeneous solution A. Next, 100mg FeSO₄·7H₂O was dissolved into 6 ml 0.01 M H₂SO₄ to obtain the solution B and then the two solutions were bubbled with nitrogen under stirring respectively. After bubbling for about 1h, the solution B was injected into solution A at a constant rate and sealed for stirring another 3h. The obtained product was then collected by centrifuging the mixture solution, washed with distilled water and absolute ethanol for several times to remove NaOH completely. Next, the collected precipitation was dispersed by 10ml ethanol-water mixture solution to form a suspension, and then 40ml 3wt% hydrogen peroxide solution was dropped into the suspension at ambient temperature for 8h. Finally, the δ -FeOOH ultrathin nanosheets could readily collected through magnetic decantation, after washing with distilled water and absolute ethanol for several times, the obtained products was dried in vacuum overnight for further characterization.

Characterizations. X-ray powder diffraction (XRD) was performed by using a Philips X'Pert Pro Super diffractometer with Cu K α radiation ($\lambda=1.54178$ Å). The field emission scanning electron microscopy (FE-SEM) images were taken on a JEOL JSM-6700F SEM. The transmission electron microscopy (TEM), high-resolution TEM (HR-TEM) were performed on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 KV. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and

EDS mapping images were taken on a JEOL JEM-ARF200F atomic resolution analytical microscope. X-ray photoelectron spectra (XPS) were obtained on an ESCALAB MK II X-ray photoelectron spectrometer with Mg K α as the excitation source. The binding energies achieved in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.5eV. Raman spectra were recorded at ambient temperature with LABRAM-HR Confocal Laser Micro Raman Spectrometer 750K with a laser power of 0.5mW. The Fourier transform infrared (FT-IR) experiment was operated on a Magna-IR 750 FT-IR spectrometer in a KBr pellet, scanning from 4000 to 400 cm⁻¹ at room temperature. Atomic force microscopy (AFM) images were carried out on a DI Innova scanning probe microscope. The magnetic measurement was carried out with a superconducting quantum interference device magnetometer (SQUID, quantum design MPMS XL-7).

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