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Single-Atom-Thick Active Layers Realized in Nanolaminated Ti$_3$(Al$_x$Cu$_{1-x}$)C$_2$ and Its Artificial Enzyme Behavior

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ABSTRACT

A Ti$_3$(Al$_x$Cu$_{1-x}$)C$_2$ phase with Cu atoms with a degree of ordering in the A plane is synthesized through A-site-replacement reaction in CuCl$_2$ molten salt. The weakly bonded single-atom-thick Cu layers in Ti$_3$(Al$_x$Cu$_{1-x}$)C$_2$ MAX phase provide actives sites for catalysis chemistry. As-synthesized Ti$_3$(Al$_x$Cu$_{1-x}$)C$_2$ presents unusual peroxidase-like catalytic activity similar to natural enzymes. A fabricated Ti$_3$(Al$_x$Cu$_{1-x}$)C$_2$/chitosan/Glassy carbon electrodes (GCE) biosensor prototype also exhibits a low detection limit in electrochemical sensing of H$_2$O$_2$. These results have broad implications for property tailoring in nanolaminated MAX phase by replacing the A
site by late transition elements.

**KEYWORDS:** nanolaminate, MAX phase, copper, catalysis, replacement reaction

The $M_{n+1}AX_n$ phases are a family of nanolaminated compounds with hexagonal crystal structure. The crystal structure of $M_{n+1}AX_n$ phases are comprised of MX slabs interleaved by single-atom-thick A layers (where M is an early transition metal, A is an element mostly from groups 13 or 14, X is C and/or N, and n = 1-3). Generally, that the mixed covalent and ionic M-X bond in MAX phases contributes to their high electrical/thermal conductivities and ceramic-like properties such as super elastic stiffness. The comparatively weak M-A bond renders the MAX phases resistant to thermal shock and even irradiation damage. Therefore, MAX phases have been investigated as promising structural materials in the environments of neutron radiation, severe corrosion, high temperature oxidation, tribological, and high-power electrical contacts. However, up-to-now the exploration of the functional application of MAX phases was much limited. Recently, noble-metal-containing MAX phases ($Ti_3AuC_2$ and $Ti_3IrC_2$) were synthesized by a substitution reaction through annealing. These results indicate that highly stable Au and Ir atoms at the A-site contribute to much improved electron transportation behavior of the MAX phases, resulting in excellent ohmic contact with SiC substrate. In our recent study, a series of MAX phases with Zn at the A-site were synthesized through an element replacement reaction approach from traditional MAX phase in Lewis acidic molten salt, i.e. $ZnCl_2$. Since Ir, Au, and Zn belong to late transition metal elements (groups 9, 11 and 12, respectively), their outmost $d$-orbital electrons would expand the chemical space for tailoring the properties and functionality of MAX phases.

In the present communication, we have used a replacement reaction between $Ti_3AlC_2$ and $CuCl_2$ molten salt to synthesize a MAX phase where Cu atoms in the A-layer show a degree of in-plane ordering. The alloying of Cu atoms in the Al sublayers

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in Ti$_3$AlC$_2$ follows a reaction that can be predicted thermodynamically from the Cu-Al phase diagram. The Cu atoms are theoretically predicted to weakly bonded to the MX sublayers, thus weakly bonded single-atom-thick Cu layers in Ti$_3$(Al$_x$Cu$_{1-x}$)C$_2$ MAX phase providing reactive sites for potential catalysis chemistry. In fact, the as-synthesized Ti$_3$(Al$_x$Cu$_{1-x}$)C$_2$ phase exhibits unusual peroxidase-like catalytic activity, similar to natural enzymes. Moreover, a MAX/chitosan/Glassy carbon electrodes (GCE) biosensor prototype also exhibited a very sensitive detection capability of H$_2$O$_2$.

RESULTS AND DISCUSSION

The Ti$_3$(Al$_x$Cu$_{1-x}$)C$_2$ phase was synthesized by replacement reaction between Ti$_3$AlC$_2$ and CuCl$_2$ molten salt with a mole ratio of 1:1.5 at 700°C. The X-ray diffraction peaks of the products are very close to that of Ti$_3$AlC$_2$, as shown in Fig.1a. Several specific peaks of the resulting phase, e.g., (103), (104), and (105) peaks, are shifted towards lower angles, indicating an expanded crystal lattice caused by the replacement of Al atoms with larger Cu atoms.$^{16}$ The (002) peak is almost vanished and the (006) peak becomes strong, indicating a change in periodic symmetry along c axis and corresponding structure factor. Fig.1b shows a SEM image of Ti$_3$(Al$_x$Cu$_{1-x}$)C$_2$. The morphology of product powders become less sharp in edges when compared with typical layered microstructure of the Ti$_3$AlC$_2$ materials (Fig. S1a) and other MAX phases.$^{17}$ The atomic ratio of Ti:(Al+Cu):C can be semi-quantitatively estimated from energy-dispersive X-ray spectroscopy (EDS) results (Fig.S1b) of powders and is close to 3:1:2, the stoichiometry of Ti$_3$AlC$_2$. Moreover, the relative atomic ratio of Al:Cu is about 1:2 (Table S1), which indicates that the as-synthesized MAX phase may have a chemical formula of Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$. 


The atomic structure and chemical analysis of the Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ were further identified by a high-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and a lattice resolved energy dispersive X-ray (EDX) spectroscopy, as shown in Fig. 2. A low magnification of STEM image of Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ clearly show an in-plan ordering phenomenon, some bright dots appear and have somehow periodic spacing between each other (Fig. 2a). The exact atomic positions along to [110] and [1 0 0] orientations are shown in Fig. 2b-2c, respectively. The Ti$_3$C$_2$ sub-layers in new-fabricated MAX phase preserve the zig-zag pattern with respect to each other and separated by layers of A element, brighter than Ti element.\(^{15}\) Since the brightness of the atom is dependent on its mass (intensity~$Z^2$), it can be confirmed that the Cu atoms have replaced Al atoms in the A layers (Fig. 2a and 2b). The Cu atoms appear to exhibit a degree of ordering, in contrast to the Au and Zn cases where the A element is completely replaced.\(^{15,18,19}\) A lattice-resolved EDS map and a line scan that reveal the elemental distribution of Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ are shown in Fig. 2d-2e, respectively. The relative atomic ratio of Al to Cu is about 1:2 as identified by STEM-EDS (Table S2). The continuous bright line shown in STEM image along [1 1 0] further indicates that the Cu atoms occupy the A atomic layer but is difficult to resolve atomically, similar to Zn-containing MAX phases.\(^{15}\)

The formation of a Cu-Al layer with short-distance ordering in the MAX phase is intriguing when compared with the complete replacement of MAX phases by Zn and Au atoms.\(^{15,18}\) It should follow a similar chemical reaction, that molten CuCl$_2$
thermodynamically reacts with Al atoms in Ti$_3$AlC$_2$ and generates both Cu and AlCl$_3$ in the initial stage. AlCl$_3$ quickly evaporates due to its low boiling point (~180°C), which will allow Cu atoms to occupy the lattice vacancies left by Al. This will initially occur on the Ti$_3$AlC$_2$ surface, to maintain the structural integrity and to form the substitutional defect Cu$_{\text{Al}}$. The continuous Cu substitution at the basal plane attributes to two reasons. First, at a synthesis temperature of 700°C, the trigonal prism space between two neighboring MX sublayers expands enough for movement of thermally activated Al and Cu atoms. Secondly, in the binary phase diagram, Al and Cu (lower than 40 at.% of Cu) can form a liquid solution since their lowest eutectic point is 548°C (Fig.S2), meaning the mutual diffusion of Al and Cu atoms is favorable. Thus, both kinetic and thermodynamic factors are satisfied for the in-diffusion of Cu atoms and the out-diffusion of Al atoms in MAX phase. When inner Al atoms diffuse to the surface, they will be soon oxidized by Lewis acid Cu$^{2+}$ and form gaseous AlCl$_3$ until the composition of Al-Cu in A layer reach the solid phase zone. According to the Al-Cu phase diagram, when the concentration of Cu in the Al layer reaches 40 at.%, solid intermetallic phases are formed. In the Zn-Al and Au-Si binary phase diagram, there are two metal endmembers that have limited dissolution with each other below a low solidus line, which explains why nearly pure MAX (A=Zn and Au) phases$^{14,15,20}$ are achieved if Al atoms can be fully driven out. In the case of the Cu-Al binary system, there are intermediate alloy phases between these two metal endmembers. The nucleation of intermediate Cu-Al alloy phases at high concentration of Cu in Al would solidify the liquid alloy. It can also be determined from the Cu-Al phase diagram that
the Cu atomic percentage of $\varepsilon$ phase at 700°C is about 56.7 at.%, close to the experiment result of 66 at.% of Cu in A site of Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$. The above explanation is reasonable when Cu and Al atoms stay in a weakly-bonding space that resembles the three-dimensional alloying condition. However, the bonding strength between the M and A elements will also influence the alloying behavior of atoms in A layer.

First-principles density functional calculations were performed in order to investigate the structure of Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ and its stability. A lattice-symmetry-preserved structure model formed by simply replacing two-third Al of Ti$_3$AlC$_2$ by Cu was found to be unstable since evident imaginary frequencies are appeared (Fig. S3). Instead, Figure 3a shows a stable configuration was achieved by allowing the symmetry to be broken. It should be stressed that this proposed lattice structure is approximation of the observed ordering of the Cu and Al in the A layer. Interestingly, in such stable Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ configuration, the Cu(Al) site deviates from the original A-site (0, 0, 1/4) and towards to the rectangle center of the neighboring four Ti atoms. The corresponding total energy of this configuration shows 0.39 eV lower energy than in the hypothetical structure where Cu precisely stays at the original Al sites. The front-, side- and top-views of this configuration are presented in Figure 3a. The deviation of A site element is consistent with symmetry reduction in Ti$_3$(Al$_{1-\delta}$Cu$_\delta$)C$_2$ MAX phase reported previously, and it also explains the blurred Cu atom distribution as shown in STEM image (Fig. 2c). Figure 3b and 3c shows the corresponding phonon dispersion and projected density of states (PDOS) of this configuration. The structure is
dynamically stable, since no imaginary frequencies are observed in the phonon dispersion. From the partial DOS, the conductive behavior of Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ is metallic, and the DOS in the vicinity of Fermi level is mainly contributed by the Ti-\textit{d}, Cu-\textit{p} and Al-\textit{p} orbitals (Fig. S4). The calculated structure parameters are also presented in Table S3. The elastic parameters in Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ are much lower than those in Ti$_3$AlC$_2$, and the cleavage energy of 1.528 J/m$^2$ between Ti-Cu(Al) interface is much lower than that of 1.934 J/m$^2$ for the Ti-Al surface in Ti$_3$AlC$_2$. The decreased elastic constants and cleavage energy of Cu-substituted configuration also explain the symmetry reduction along the \textit{c} axis (Fig. 1a). In Ti$_3$AlC$_2$, the Al atom is six-coordinated, and the bond length of Ti-Al is calculated to be 2.890 Å. However, due to the four-coordination in Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$, the nearest bond length of Ti-Cu is calculated as 2.753 Å, and the next-nearest Ti-Cu(Al) bond length is larger than 3.279 Å, which make Cu atoms more free than in six-coordinated site. Since Cu has more outmost \textit{d} orbital valence electrons than Al, the Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ could provide many active atoms for further chemical reaction, such as catalysis.

It is expected that the exposed Cu atoms on the surface of as-synthesized Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ MAX phase (Fig. 4a and 4b) could provide active sites of single-atom-thick Cu layers for catalysis. The STEM image indicates the particles have a clean surface without amorphous phase (Fig. 4a and 4b). Thus, the single-atom Cu should expose to environment as illustrated in a simulated surface atomic configuration (Fig. 4c). Actually, the as-synthesized Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ MAX phase can strongly accelerate H$_2$O$_2$ solution and release O$_2$ while the control Ti$_3$AlC$_2$ MAX phase show no such phenomenon (Video material in the SI). The peroxidase-like activity of
Ti$_3$AlC$_2$ was further tested in terms of oxidations of chromogenic 3,3',5,5'-Tetramethylbenzidine (TMB). It was revealed that Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ is able to oxidize TMB in the presence of H$_2$O$_2$ in a manner similar to peroxidative ability of horseradish peroxidase (HRP), resulting in a blue-colored solution with a maximum absorbance at 652 nm, like other enzyme catalytic materials. Fig. 4d shows the time dependent absorbance evolution at 652 nm of blank solution, Ti$_3$AlC$_2$ and Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ for TMB oxidation. Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ demonstrated tremendous increasing absorbance value with reaction time which is similar to that of HRP (Fig. S5), while Ti$_3$AlC$_2$ and blank sample shows no obvious peroxidase-like catalytic activity even after 20 min. Cu-MAX also demonstrated higher temperature stability in comparison to HRP. Following 20 mins of reaction at 80°C, Cu-MAX showed significant lesser decreased in absorbance value as compared to HRP (Fig. S6). In addition, Cu-MAX also demonstrated good catalytic stability and able to maintain 98.03 ± 0.26 % of its initial catalytic activity after 5 consecutive reactions (Fig. S7). The steady-state kinetic parameters for both HRP and Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ were examined and Lineweaver-Burk plots showed good linear relationship with parallel lines (Fig. S8) indicating characteristic of a ping-pong mechanism similar to that of the natural HRP enzyme or Fe$_3$O$_4$ artificial enzyme. A comparison of the HRP and Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ kinetic parameters obtained from the Michaelis-Menten and Lineweaver-Burk plots are shown in Table S4. $K_m$ values are an indication of enzyme affinity towards substrates. A small $K_m$ value indicates high affinity between the enzyme and the substrates and vice versa. The observed $K_m$ (0.512 mM) value of Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ with H$_2$O$_2$ substrate is found to be smaller than that of the HRP enzyme (1.611 mM), suggesting Cu-MAX phase possess higher affinity of the catalyst for H$_2$O$_2$. It is possible that Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ possesses more active sites on the surface; whereas HRP has only one active site per molecule. Regarding the catalase behavior observed in Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$, H$_2$O$_2$ must adsorb on the surface of Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ particles, and the O-O bond of H$_2$O$_2$ can be broken up into double hydroxyl radical (\(^{\cdot}\)OH) radical by exposed surface Cu atom layers in MAX phase. Electron spin resonance (ESR) spectra results suggesting that the decomposition of H$_2$O$_2$ with concomitant formation of \(^{\cdot}\)OH in the presence of...
Ti₃(Al₁/₃Cu₂/₃)C₂ (Fig.S9), and the phase composition of Ti₃(Al₁/₃Cu₂/₃)C₂ is unchanged after reaction with H₂O₂ (Fig.S10). In addition, X-ray photoelectron spectra (XPS) results implying the presence of an unfilled Cu 3d⁹ shell and thus confirms the existence of Cu²⁺ on the sample surface (Fig.S11). Thus, we supposed that the catalytic ability of Ti₃(Al₁/₃Cu₂/₃)C₂ might be attributed to oxidation of surface exposed Cu atoms by H₂O₂. These ’OH are generated in the reaction between H₂O₂ and surface oxidation Cu atom layers in Ti₃(Al₁/₃Cu₂/₃)C₂, and released ’OH oxidized TMB to form blue color TMB⁺, like Cu nanoclusters. It is well known that copper is soluble in concentrated nitric acid, compared to artificial nanozyme of Cu nanoclusters, bulk Ti₃(Al₁/₃Cu₂/₃)C₂ MAX phase with particle size of several micrometers (about 2 μm) is employed (Fig.S12 and Table S5), which shows structure stability in acid corrosive environment (e.g. concentrated nitric acid (Fig.1a), concentrated hydrochloric acid (Fig.S13), etc.).

The peroxidase-like catalytic activity of Ti₃(Al₁/₃Cu₂/₃)C₂ may find application in detection of H₂O₂ in food, biology, medicine and the environment fields. Fig. 4e shows the amperometric responses of Ti₃(Al₁/₃Cu₂/₃)C₂/chitosan/GCE and Ti₃AlC₂/chitosan/GCE following successive additions of H₂O₂ to phosphate buffer. Unlike chitosan/GCE and Ti₃AlC₂/chitosan/GCE, Ti₃(Al₁/₃Cu₂/₃)C₂ /chitosan/GCE yielded an obvious step-like response of current following successive additions of H₂O₂ to phosphate buffer, showing linear regression behavior in the concentration range from 0.06 to 11.25 μM (Fig. S14). A low limit of detection (LOD) of 0.06 μM was achieved, which is much lower than that of CuO, Cu NCs, Au NPs, Pt, Ag NPs and Pd (Table S6). Moreover, the catalysis activity of nanoparticles gradually deteriorates due to Ostwald ripening. However, in Ti₃(Al₁/₃Cu₂/₃)C₂ MAX phase, active Cu atoms isolated by MX sublayers should avoid such poisoning grain-growth, which
also explains the micrometer-size particles of MAX phase still preserve the catalytic activity.

CONCLUSIONS

In summary, a Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ MAX phase, where Cu atoms partially occupy the A layer with a degree of ordering, was synthesized through a replacement approach. Due to the outmost $d$-orbital electrons of Cu, the bulk Ti$_3$(Al$_{1/3}$Cu$_{2/3}$)C$_2$ phase provides a large amount of catalytically active sites in single-atom layers, resulting in unusual peroxidase-like catalytic activity similar to natural enzymes. An electrochemical biosensor with wide linear range and low limit of detection was fabricated in a MAX/chitosan/GCE prototype electrode. The active sites of Cu atoms and conductive MX sublayers account for the high detection capability. It is thus expected that other transition element atoms (such as Pt, Ag, Au, etc.) can similarly occupy A layer sites and form other types of active single-atom-thick layers in MAX phases and enable tailoring of chemical properties and functionality.

METHODS

Preparation of Cu-MAX phase. The Ti$_3$AlC$_2$ powders were synthesized by a molten salt method, as in our previous work.$^{15}$ The Ti$_3$AlC$_2$ powders were mixed with CuCl$_2$ in stoichiometric molar ratios of 2:3. Then, the mixed powders were put into an aluminum oxide boat and heated to 700°C during 2 h with a heating rate of 10°C/min under an argon atmosphere. After the end of the reaction, the surplus Cu was removed...
by immersing in nitric acid for about 15 min. Finally, the product was filtered, washed, and dried at 40°C in vacuum.

**Peroxidase-like catalytic activity of Cu-MAX.** Peroxidase-like activity Cu-MAX was evaluated in terms of its ability to oxidize typical horseradish peroxidase (HRP) substrate 3,3',5,5'-Tetramethylbenzidine (TMB) in the presence of H₂O₂. The reaction was carried out at 37°C and 80°C by using 4 µg/mL HRP or Cu-MAX in 10.0 ml reaction substrates containing 496.5 uM TMB and 0.38 M H₂O₂. The blue color that developed as the reaction proceeded was monitored in time scan mode at 652 nm using Infinite 200 PRO multimode plate reader (Tecan, Switzerland). Control experiments were conducted in the absence of HRP or Cu-MAX. The steady-state kinetics were conducted using standard reaction conditions as described above by varying concentrations of TMB at a fixed concentration of H₂O₂ or vice versa. Kinetics parameters were determined by fitting reaction data to the Michaelis–Menten (Eq. (1)) and Lineweaver-Burk (Eq. (2)) equations.

\[
\frac{1}{V} = \frac{K_m}{V_{max}} \times \frac{1}{[S]} + \frac{1}{V_{max}} \tag{1}
\]

\[
V = V_{max} \times \frac{[S]}{[S] + K_m} \tag{2}
\]

Where V is the reaction velocity, \(V_{max}\) is the maximal reaction velocity, [S] is the substrate concentration (H₂O₂ or TMB) and \(K_m\) is the Michaelis-Menten constant.

**Fabrication of the Cu-MAX/chitosan/Glassy carbon electrodes (GCE) and Ti₃AlC₂/chitosan/GCE electrochemical sensor.** Glassy carbon electrodes (GCE, 3 mm) was polished using alumina oxide powder (1.0, 0.3, 0.05 µm), cleaned by ethanol and water, and dried under gentle N₂ stream. Three hundred microliters of Cu-MAX or
Ti₃AlC₂ aqueous solution (30 mg/ml) was mixed with 100 μl chitosan solution (6 mg/ml) for 5 min. Five microliter of the Ti₃(Al₁/₃Cu₂/₃)C₂/chitosan or Ti₃AlC₂/chitosan mixture solution was dropped cast onto the GCE surface.

**Electrochemical sensing of H₂O₂ by Cu-MAX/chitosan/GCE and Ti₃AlC₂/chitosan/GCE.** Electrochemical sensing of H₂O₂ by Cu-MAX/chitosan/GCE and Ti₃AlC₂/chitosan/GCE was carried out using CHI760E electrochemical workstation (Chenhua, Shanghai) with GCE (Cu-MAX/chitosan/GCE or Ti₃AlC₂/chitosan/GCE) as working electrode, platinum wire as counter electrode and saturated calomel electrode (SCE) as reference electrode. Amperometric current-time curves for H₂O₂ were carried out to construct a calibration curve of current response at different H₂O₂ concentration. Measurements were performed in 10 mL of stirred 0.1M PBS (pH = 7.0) with successive addition of H₂O₂ at room temperature under an applied peak potential value of -0.9 V.

The limit of detection (LOD) was determined according to the following equation:

\[
\text{LOD} = 3\text{SD}/K
\]

whereby SD refers to the standard deviation of the control measurement and K refers to the slope of the calibration curve.

**DFT Calculations.** All the structural, electronic and mechanical properties of the MAX phases investigated in our work were calculated in the plane-wave CASTEP³⁶,³⁷ software. The ultrasoft pseudopotential with a plane wave cutoff energy of 500 eV was adopted. The generalized gradient approximation (GGA) of the Perdew-Breke-Ernzerhof (PBE) scheme was employed for the exchange-correlation functional.³⁸-⁴¹
All the structures were relaxed until the total energy change was smaller than $5 \times 10^{-6}$ eV/atom, and the force on each atom was below 0.001 eV/Å. A k-points mesh of $13 \times 13 \times 2$ was utilized for the until cell of MAX phase, and an approximately equivalent k-point density was adopted for the Cu-substituted Ti$_3$(Cu$_{2/3}$Al$_{1/3}$)C$_2$ state. Both relaxations with keeping structure symmetry and without symmetry were considered. To test the structural dynamical stability, phonon dispersions were calculated based on the finite displacement approach. Elastic constants were calculated based on the stress-strain relationship, and then the shear (G) and Young’s modulus (E) were obtained from the Voigt-Reuss-Hill approximation. In order to investigate the adhesive strengths between the M-A sublayers of MAX phases before and after Cu substituted, the cleavage energies were calculated. The definition of cleavage energy is $E = (E_{\text{broken}} - E_{\text{bulk}})/A$, where $E_{\text{bulk}}$ is the total energy of bulk MAX phase after optimization, and $E_{\text{broken}}$ denotes the corresponding total energy of a configuration with a vacuum separation of 10 Å between the M and A atomic layers in the previous bulk MAX, $A$ is the surface area of the cleavage surface.

Characterization. The phase composition of the samples was analyzed by X-ray diffraction (XRD, D8 Advance, Bruker AXS, Germany) with Cu Kα radiation. The microstructure and chemical composition were observed by scanning electron microscopy (SEM, QUANTA 250 FEG, FEI, USA) coupled with an energy-dispersive spectrometer (EDS). The chemical state of the materials before and after exfoliation was analyzed by X-ray photoelectron spectroscopy, XPS (AXISUltro DLD, Kratos, Japan). The ESR measurements were carried out using a Bruker EMX ESR (ESR, A300-
10/12, Sigma, Germany) spectrometer operating at 9.853 GHz (microwave powder: 19.27 mW, modulation frequency: 100 KHz, modulation amplitude: 1.00 G, receiver gain 1.00 x 10^3) with DMPO as the capturer in dark condition (room temperature). The particles size of the Ti3(Al1/3Cu2/3)C2 was determined by a particle size analyzer (Microtrac, S3500-special, USA). Structural and chemical analysis was carried out by high-resolution STEM high angle annular dark field (HRSTEM-HAADF) imaging and STEM affiliated energy dispersive X-ray spectroscopy (EDS) within Linköping’s double-C_s corrected FEI Titan3 60-300 microscope operated at 300 kV, and STEM-EDX was recorded with the embedded high sensitivity Super-X EDX detector.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge on the ACS Publications website at DOI: xxx/xxx.

The SEM image of Ti3AlC2, EDS analysis results of Ti3(Al1/3Cu2/3)C2, the average chemical composition, Cu-Al binary phase diagram, phonon dispersion and crystal model of Ti3(Al1/3Cu2/3)C2 (I), PDOS analysis of Ti3(Al1/3Cu2/3)C2 (II), absorbance evolution of HRP, steady-state kinetic assays of the HRP and Ti3(Al1/3Cu2/3)C2, absorbance evolution of HRP Ti3(Al1/3Cu2/3)C2 at 80°C, electron spin resonance (ESR) spectra, relative catalytic activity of Cu-MAX phase, XRD patterns of Ti3(Al1/3Cu2/3)C2 before and after the reaction with H2O2, X-ray photoelectron spectra (XPS) of Ti3(Al1/3Cu2/3)C2, particle size distribution of the Ti3(Al1/3Cu2/3)C2, the XRD patterns of Ti3(Al1/3Cu2/3)C2 before and after the reaction with concentrated hydrochloric acid, calibration curve of amperometric responses, and other materials detection limit for H2O2 are provided.

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Author contributions

Q. H. conceived and initiated the work. Y. B. Li. synthesized the materials. J. Lu performed and analyzed the STEM results. P. O. Å. Persson, L. Hultman and P. Eklund contributed to the discussion of STEM results. B. K. Ma, Z. P. Wang, Q. G. Wang, and L. Z. Cheong performed the peroxidase-like catalytic activity, electrochemical sensing of H$_2$O$_2$ measurement. K. Luo, X. H. Zha and S. Y. Du performed the theoretical calculation. M. Li, K. Chen, C. Shen, J. M. Xue, Z. R. Huang and Z. F. Chai contributed to the scientific discussion.

Conflict of interest: The authors declare no competing financial interests.

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REFERENCES


Figure captions

Figure 1. (a) The XRD patterns of Ti₃AlC₂ and Ti₃(AlₓCu₁₋ₓ)C₂. (b) SEM image of the Ti₃(AlₓCu₁₋ₓ)C₂.

Figure 2. (a) The High-resolution (HR)-STEM image of Ti₃(Al₁/₃Cu₂/₃)C₂. (b) Corresponding partial magnification from (a) and showing atomic positions along [11̅20] direction. (c) HR-STEM image of Ti₃(Al₁/₃Cu₁₋ₓ)C₂ along [1̅100] direction. The EDS mapping and line-scan of Ti-Kα (red), Cu-Kα (green) and Al-Kα (blue) signals of Ti₃(Al₁/₃Cu₁₋ₓ)C₂ along [11̅20] (d) and [1̅100] (e).

Figure 3. (a) The crystal model of Ti₃(Al₁/₃Cu₂/₃)C₂ along and [1̅100], [11̅20] and [0001] direction. (b) The phonon dispersion of Ti₃(Al₁/₃Cu₂/₃)C₂. (c) The projected density of states (PDOS) of Ti₃(Al₁/₃Cu₂/₃)C₂.

Figure 4. (a) STEM image of Ti₃(AlₓCu₁₋ₓ)C₂ along [1̅100] orientation showing the exposed Cu atoms (bright lines) and (b) the enlarged STEM image near the surface of particle. (c) simulated surface atomic configuration for peroxidase-like catalysis. (d) Time dependent absorbance evolution at 652 nm of blank solution, Ti₃AlC₂ and Cu-MAX catalyzed TMB oxidation. The insert show the optical photographs of TMB solution following oxidation by Ti₃AlC₂, Cu-MAX and HRP, the reaction temperature is 37°C. (e) Amperometric responses of Chit/GCE, Cu-MAX/Chit/GCE and Ti₃AlC₂/Chit/GCE at -0.9 V upon successive additions of 1.25 mM H₂O₂ in a stirred 0.1 M PBS (pH = 7.0).
Figure 1. (a) The XRD patterns of Ti3AlC2 and Ti3(AlxCu1-x)C2. (b) SEM image of the Ti3(AlxCu1-x)C2.
Figure 2. (a) The High-resolution (HR)-STEM image of Ti3(AlxCu1-x)C2. (b) Corresponding partial magnification from (a) and showing atomic positions along [112(_0)0] direction. (c) HR-STEM image of Ti3(AlxCu1-x)C2 along [11(_0)00] direction. The EDS mapping and line-scan of Ti-Kα (red), Cu-Kα (green) and Al-Kα (blue) signals of Ti3(AlxCu1-x)C2 along [112(_0)0] (d) and [11(_0)00] (e).
Figure 3. (a) The crystal model of Ti3(Al1/3Cu2/3)C2 along and [1100], [1120] and [0001] direction. (b) The phonon dispersion of Ti3(Al1/3Cu2/3)C2. (c) The projected density of states (PDOS) of Ti3(Al1/3Cu2/3)C2.