

Fabrication and Properties of A Free-standing Two-dimensional Titania

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Abstract

The synthesis of two-dimensional (2-D) Titania with band gap near the visible light range presents complex challenges to synthetic chemists. Here we report a free-standing 2-D TiO₂ sheet synthesized via a one-step solvothermal methodology. Field emission-scanning electron microscopy, transmission electron microscopy and scanning tunneling microscopy together reveal that the TiO₂ is composed of free-standing 2-D monolayers of micron length scales, with a crumpled morphology but exhibiting short-range lattice order. The Raman spectrum of these sheets is significantly different from that of bulk TiO₂, but closely resembles that computed for a monolayer of lepidocrocite TiO₂. Using first principles calculations in combination with experiment, we propose that the as-formed 2-D TiO₂ sheets are layers of the lepidocrocite TiO₂ structure, but with large non-uniform strains consistent with its crumpled morphology. These strains result in a significant change in the quasiparticle band structure and optical absorption spectra, resulting in large absorption in the visible light range, with a measured optical onset at ~1.84 eV. This narrow band gap 2-D TiO₂ can catalyze the formation of singlet oxygen under visible/near-IR light absorption. Our work demonstrates that lattice strains intrinsic to 2-D materials, especially its crumpled, free-standing forms, can result in new and useful properties, which are applicable in environmental and medical research with the reported 2-D TiO₂.

Introduction

The study of two-dimensional (2-D) materials is a burgeoning field of research with wide applications ranging from electronics to energy storage, owing to their low-dimensional nature and unprecedented properties.^{1, 2, 3, 4} The 2-D nature of these materials results in enhanced electron-electron interactions^{5, 6} and quantum confinement effects.^{7, 8,}⁹ On the other hand, Mermin and Wagner had pointed out that strictly two-dimensional crystals cannot exist.¹⁰ Elasticity theories predict that free-standing 2-D membranes will suffer severe buckling at finite temperatures.¹¹ These theories have been verified experimentally, with buckling and rippling observed in suspended 2-D materials, such as MoS₂ and graphene.^{11, 12} The buckling of such free-standing 2-D materials is expected to lead to substantial strain and opens up the possibility of new properties that are different from the ideal unstrained structures.¹³ 2-D materials can sustain significant strains of up to 20%,¹⁴ as well as lattice distortions involving shearing forces.¹⁵ Changes in the band gap have also been observed due to lattice strain.^{16, 17}

In addition to graphene and transition metal dichalcogenides, such as MoS₂, several transition metal oxides also have layered host crystals. These include MnO₂, MoO₃, and lepidocrocite-phase TiO₂, which can be made 2-D by exfoliation, bottom-up, or top-down methods.^{2, 15, 18, 19} Titania (TiO₂), in its more common 3-D anatase and rutile phases, has been widely studied for its applications in photocatalysis,²⁰ photovoltaics,²¹ and lithium batteries,²² mainly because of its superior electronic properties and photochemical stability. Thus far, surfactants, ions, or substrates have been employed to enable the fabrication of 2-D TiO₂ nanosheets via several methodologies: exfoliation,^{23, 24} ion sputtering,¹⁹ and pulsed laser deposition.² Yet, these methods have some drawbacks

associated with the employment of solid substrates/stabilizers (surfactants or polymers) and inhomogeneity.^{2, 19, 25} Exploring free-standing 2-D TiO₂ to make it free from substrate/surfactant effects remains challenging. The unique properties of 2-D TiO₂ stemming from free-standing structure particularly have yet to be demonstrated.

Here, we report free-standing and homogeneous 2-D TiO₂ single layers synthesized via a solvent-engineering route. The Raman spectrum of the as-synthesized 2-D TiO₂ is very different from 3-D bulk pristine TiO₂ (Degussa, P25), but closely resembles that computed for lepidocrocite phase TiO₂, which is a layered TiO₂ structure.^{18, 26, 27, 28} Similar to suspended graphene and MoS₂,^{11, 12} we found that as predicted by Mermin and Wagner,¹⁰ the free-standing 2-D TiO₂ is far from flat, and has a morphology resembling crumpled sheets of paper. Local lattice periodicity was observed, but with non-uniform strains and lattice distortions across different parts of the sample. Remarkably, such free-standing 2-D TiO₂ presents a narrow optical band gap (~1.84 eV), in comparison with that of 3-D bulk pristine TiO₂ (Degussa, P25) (~3.3 eV). First principles calculations show that this narrow optical band gap arises from the large lattice strains observed in the as-synthesized TiO₂. This work creates new opportunities for TiO₂ in many applications, and demonstrates that new material properties can be realized by the large strains that are intrinsic to the buckled/crumpled free-standing forms of 2-D materials.

Results

Synthesis and microscopy characterizations of 2-D TiO₂ sheet. The titania in this work was synthesized from isopropyl titanate, oleylamine, and 1, 2- ethanedithiol using a one-step solvothermal methodology. Unlike the conventional bulk TiO₂ material with white colour, such synthesized TiO₂ is red in color (Figure 1a). Field emission-scanning

electron microscopy (FE-SEM) and transmission electron microscopy (TEM) (Figures 1b and c, respectively) of the as-prepared TiO₂ show that the TiO₂ consists of free-standing sheets at least a few square microns in area. These sheets exhibit a crumpled morphology with severe folds and bends appearing on different length scales. High-resolution TEM (HR-TEM) images (Figures 1d-f) further reveal that locally, the lattice is ordered and periodic, but with different lattice parameters for different parts of the sheet, as expected for a crumpled morphology. The lattice parameters in Figures 1d-f differ not only in the lengths of the lattice vectors, but also in the angles between lattice vectors (1d: |OA| = 0.238 nm, |OB| = 0.233 nm, Angle A-O-B=90°; 1e: |OA| = 0.364 nm, |OB| = 0.378 nm, Angle A-O-B=71.8°; 1f: |OA| = 0.374 nm, |OB| = 0.487 nm, Angle A-O-B=66°). Renormalization group calculations have previously shown that membranes with crystalline order will have a finite temperature crumpling transition.²⁹ The tendency to crumple is expected to be larger for larger sheets.¹¹ Based on these theories, the micrometer length scales of the 2-D sheets, their free-standing nature, and the local crystalline order are all consistent with the large non-uniform lattice strains and severe folds exhibited by the as-synthesized 2-D sheet, which we take to be in its crumpled, finite temperature phase.²⁹

Atomic and electronic structures and band gap of 2-D TiO₂ sheet. The 2-D TiO₂ sheet was further characterized by scanning tunneling microscopy (STM). The 2-D TiO₂ was dispersed in hexane and then loaded onto a Au (111) surface. After annealing at 200 °C for 2 hours, the STM image was measured in vacuum at 77 K. The height profile obtained along the black line in the image (Figure 2a) clearly shows that the 2-D TiO₂ is a single layer, with an apparent height of $\sim 1 \pm 0.1$ nm (Figure 2b). This height is consistent

with other reports on TiO₂ single layers.²³ The atomic resolution STM image in Figure 2c shows again the local crystalline order of the TiO₂.

To identify the exact chemical components of the 2-D TiO₂ sample, we carry out X-ray photoelectron spectroscopy (XPS), which is a surface-sensitive quantitative spectroscopic technique that can measure the elemental composition and electronic state of the elements that exist within the material. In Figure 3a, it is clear that there are no reduced Ti charge states in the 2-D TiO₂ material, such as Ti³⁺ or Ti²⁺ species. Figure 3b shows XPS valence band (VB) photoemission spectra of 2-D and bulk pristine TiO₂ (Degussa P25). The Fermi Energy (E_F) level of the sample and substrate is set at 0 eV. The edge of the VB energy for the P25 is located at ~2.88 eV, while that of the 2-D TiO₂ system is at ~1.49 eV, indicating ~1.4 eV upward-shift of VB level in 2-D TiO₂ compared to that of bulk. Additionally, X-ray absorption spectra (XAS) (Figure 3c) show that the peak corresponding to the edge of conduction band (CB) down-shifts about 0.1 eV and becomes broadened in 2-D TiO₂. Taken together, we can conclude that the quasiparticle gap for the free-standing 2-D TiO₂ is about 1.5 eV smaller than that for P25.

The sheet structure of the free-standing TiO₂ strongly suggests that this 2-D TiO₂ material is not directly related with the 3-D bulk P25. The Raman spectrum of a material is often used as a fingerprint to determine its atomic order and symmetry. We measured the Raman spectra of the as-synthesized 2-D TiO₂ (Figure 4b), and found that it is very different from that measured for 3-D bulk TiO₂ (anatase) (Figure S1). To identify the atomic structure from the Raman spectra, we used first principles density functional theory (DFT) calculations. Calculations on the bulk anatase phase give a Raman spectrum in good agreement with experiments (Figure S1). For the unknown 2-D TiO₂

phase, besides the three major peaks at 282, 444 and 700 cm^{-1} in Figure 4b, smaller Raman peaks were observed, as summarized in Table S1. Among the existing phases of TiO_2 , lepidocrocite TiO_2 is a layered compound with Ti^{4+} states.^{18, 23, 26, 27, 28} Each layer has six atomic planes and has a thickness of ~ 0.7 nm (Figure 4a). The calculated Raman frequencies of a monolayer from the lepidocrocite phase compare remarkably well with those measured for the unknown 2-D TiO_2 , even for the smaller Raman peaks (Figure 4b and Table S1). These Raman studies thus strongly suggest that the free-standing 2-D TiO_2 nanosheets consist of monolayers of the lepidocrocite TiO_2 phase. The significant broadening in the experimental Raman spectra is compatible with the large nonuniform strains in the sample. The stability of the lepidocrocite phase in monolayer form can be confirmed by the fact that it has no imaginary phonon frequencies (Figures 4c and S4a). We have also considered an alternative TiO_2 monolayer structure based on the T phase of hexagonal transition metal dichalcogenides. Here, we found that the system is unstable and would prefer a larger unit cell. The simulated Raman frequencies also differ significantly from the measured spectra (See Figure S2). Additionally, the XRD patterns of the as-prepared 2-D TiO_2 match reasonably well with the simulated XRD of the bulk lepidocrocite TiO_2 , except for the peak near 13 degrees circled in Figure S3, which corresponds to the out-of-plane (001) diffraction direction of the bulk and is missing in the 2-D sample. We thus conclude that the 2-D TiO_2 sheets are single sheets of lepidocrocite TiO_2 , but with a crumpled morphology.

It is instructive to compare the atomic structures of bulk anatase and bulk lepidocrocite TiO_2 . The major differences between the two structures can be found in the shaded area, as shown in Figure 4a. If the atoms in the shaded area of anatase TiO_2 move half a unit

cell length along the b axis, and the whole structure is stretched along the c axis, one obtains the lepidocrocite phase. We found that the anatase phase is about 1 eV/unit cell more stable than the lepidocrocite phase in the bulk (Figure S4b). However, a TiO₂ monolayer would favour the layered lepidocrocite phase due to the absence of surface dangling bonds. In particular, the interlayer binding energy in lepidocrocite TiO₂ is very small (0.005eV/layer/Å²), compared with other layered materials such as black phosphorus (0.02eV/layer/Å²) and MoS₂ (0.015eV/layer/Å²), thus indicating that lepidocrocite TiO₂ can exist in its monolayer form. Previous DFT calculations had also found that single-layer lepidocrocite TiO₂ has very high flexibility along the sheet normal, consistent with the large degree of buckling seen in these sheets.²⁸

As discussed above, the micron-sized, free-standing sheets exhibit a crumpled morphology with non-uniform lattice strains. To understand the effect of these large strains on the electronic structure of the monolayer, we first investigated systematically the effect of uniaxial and biaxial strains on the DFT band gap of the lepidocrocite monolayer, computed within the local density approximation (LDA) for the exchange-correlation functional (Figure 5b). These calculations show that the LDA band gap can be tuned from 3.1eV (unstrained) to 0.8 eV (under 20% compressive strain).

We also investigated the effects of lattice distortions (in addition to lattice strain) by using a lattice that is consistent with the STM image in Figure 2c. This corresponds to a distorted lepidocrocite TiO₂ structure with 4% and 20% compressive strain along the a and b axes, respectively, together with a distortion in the angle between the a and b axes, from 90° to 116° (Figure 5a). After relaxing the internal coordinates, we simulated the STM image and found excellent agreement with the experimental STM image, with Ti

atoms closest to the surface layer appearing as bright spots (Figure 2d). The DFT LDA band gap of this strained TiO₂ monolayer is 0.96 eV, much smaller than that for the unstrained layer. While the trends in band gaps can be predicted reasonably well with DFT LDA, it is known that LDA can underestimate band gaps significantly. Many-electron GW calculations^{30, 31, 32} were performed on the distorted, strained monolayer as well as the unstrained lepidocrocite layer. The resulting quasiparticle gaps were 5.97 eV and 2.86 eV for the unstrained and strained lepidocrocite layers, respectively. In comparison, the reported GW gap for bulk anatase TiO₂ is ~3.73-4.05 eV,³³ ~0.9-1.2 eV larger than that computed for the strained lepidocrocite monolayer.

Our results show that lattice strains and distortions in monolayers of lepidocrocite TiO₂ result in quasiparticle band gaps that are smaller than that in bulk anatase TiO₂. This is consistent with the experimental findings of a reduction in quasiparticle band gap in the as-synthesized, crumpled 2-D TiO₂ compared to bulk TiO₂ (Figure 3). The small quasiparticle gaps in these TiO₂ monolayers suggest that we may be able to get optical absorption in the visible range, a long sought-after goal for TiO₂. Indeed, from UV-Vis diffuse reflectance spectroscopic studies (UV-vis DRS), we found that the free-standing 2-D TiO₂ shows a remarkably enhanced absorption in the visible and even near-infrared (NIR) light regions compared to pristine bulk P25 (Figure S5a). Analysis using the Kubelka-Munk function, $F(R) = (1-R)^2/2R$, $A = \log(1/R)$ (A , the absorbance of sample; R , the reflectance of sample), gives an estimated optical band gap of 1.84 eV for the free-standing 2-D TiO₂ nanosheets, compared with 3.3 eV for P25 (see Figure S5b). In Figure 6a, we compare the experimental optical spectrum with that computed using GW-BSE^{34, 35} calculations for the strained lattice taken from the STM image. These calculations take

into account both electron self-energy effects in the quasiparticle spectrum and electron-hole interactions in the exciton. The optical gap calculated for the unstrained TiO₂ monolayer is very close to the experimental value (4.7 eV) for nanosheet and bulk lepidocrocite TiO₂,^{36, 37} while the optical gap of the strained lepidocrocite TiO₂ monolayer is computed to be ~ 1.80 eV (Figure 6b, Table 1), much smaller than the unstrained lepidocrocite phase but close to the experimental measurements (1.84 eV). The difference between the GW gap and the optical gap is the exciton binding energy in isolated 2-D TiO₂ layers. This exciton binding energy (~1.06 eV) is large, similar to that found in other 2-D materials.^{4, 6} We note that the optical gaps in different parts of the sample would vary depending on the degree of local strain. However, the measured optical onset is dominated by regions of the sample with the smallest optical gaps.

Performance of photocatalytic activities. Since the free-standing 2-D TiO₂ can absorb visible and even near-IR light, this material exhibits great potential as a photocatalyst. Figure 6c shows that the time-dependent photocurrent densities over the 2-D TiO₂, characterized under the various light irradiation ranging from 450 up to 800 ± 5 nm. The optical spectra of the filters used in photocatalytic activities have also been indicated in Figure S6. The photocurrent signal at each given wavelength presented no obvious decrease with increasing irradiation time, suggesting photo-stability of 2-D TiO₂. We used the synthesized 2-D TiO₂ as a photocatalyst for decomposing the dye rhodamine B, a prototypical organic dye pollutant in waste water. Figure 6d shows that 2-D TiO₂ exhibited excellent performance in the decomposition of rhodamine B under light irradiation from 450-800 nm, in comparison with the bulk TiO₂ (P25). In addition to environmental treatment, photodynamic therapy is a promising method for minimally

invasive cancer treatment with singlet oxygen. Thus, we further evaluated the performance of 2-D TiO₂ catalyst to produce singlet oxygen (O₂¹). Here, we used 9, 10-anthracenediyl-bis (methylene) dimalonic acid (ABDA) molecule as a probe to monitor O₂¹ production efficiency.³⁸ The ABDA can react with O₂¹ to yield an endoperoxide, thus leading to a reduction in absorption intensity of ABDA.³⁸ We found that under laser irradiation at 532 nm and 750 nm, the ABDA concentration decreased over time in the presence of 2-D TiO₂ (Figure 6f). In contrast, the control experiment without 2-D TiO₂ showed no obvious reduction in absorption intensity of ABDA. Overall, the free-standing 2-D TiO₂ can catalyze the redox of organic dye and production of O₂¹ by using low-energy photons (visible and NIR light). These measurements show that the 2-D TiO₂ nanosheets have potential for environmental treatment, energy, or even biological applications using solar light.

Discussion

In this work, we reported the synthesis and electronic properties of a free-standing 2-D TiO₂ that can absorb visible and near-IR light. Due to the free-standing, 2-D nature of the material, as well as the micron length scales achieved in the synthesis process, the 2-D TiO₂ exhibits a crumpled morphology with severe folds and buckling. The crumpled morphology is consistent with previous theories investigating the properties of free-standing 2-D membranes.^{10, 11, 29} Raman measurements show that the 2-D TiO₂ is from the lepidocrocite TiO₂ phase, while single layers are clearly seen in our STM images. The small optical and quasiparticle gaps of this material are attributed to the large strain in the crumpled, free-standing layer. Our work demonstrates that the intrinsic strain present in crumpled, free-standing 2-D materials can result in new and exciting properties, such as

improved photocatalytic performance of TiO₂. The challenge is on to find ways to synthesize other free-standing 2-D materials, which theory predicts to exhibit crumpled morphology at finite temperatures.²⁹

Methods

Fabrication of free-standing 2-D TiO₂. 5 mL of 1, 2-ethanedithiol was added into oleylamine (5 mL) under magnetic stirring at room temperature. The red colour could be immediately seen after dropping 1 mL of tetrabutyl titanate into the mixed solution. The resulting mixture was transferred to a 50 mL autoclave for solvothermal reaction at 200 °C for 24 h. Upon completion, the autoclave was cooled down to room temperature and the as-prepared free-standing 2-D TiO₂ was collected after washing with hexane, ethanol, and acetone, and then freeze drying in vacuum chamber.

Photocurrent densities measurement. A three-electrode system was used to measure the photocurrent. The working electrode is the synthesized 2-D TiO₂ sample coated on ITO (1 × 0.5 cm). Platinum gauze and Ag/AgCl serve as the counter and reference electrodes, respectively. The NaOH aqueous solution (1M) is the electrolyte in a quartz reaction cell. A 500 W xenon lamp provides the simulated sunlight. Light with a specific wavelength was obtained by mounting an appropriate filter on the lamp. The light transmittance ratios of filters used have also been identified by optical spectroscopy. The chronoamperometric measurement of 2-D TiO₂ material was obtained at 0V while the simulator was switched on and off every 10 seconds manually using a shutter to record the change of photocurrent. We tested photocurrent response densities of the 2-D TiO₂ material under light irradiation with various wavelengths, including 450, 475, 500, 600, 700, and 800 nm.

Degradation of rhodamine B (RhB). 20 mg of 2-D TiO₂ was added into RhB aqueous solution (20 ml, 25 mg/L) followed by ultrasonication for 10 min. Under magnetic stirring, this solution was kept in darkness for 4 hours at room temperature for saturated adsorption of RhB. A 500 W xenon lamp fixed with one filter was used as light source. After light irradiation for four hours, 5 mL of the reactive solution was sampled. The supernatant solution with RhB molecules left was obtained by centrifuging and removing the 2-D TiO₂ catalyst precipitate. Thus, the concentration of the remaining RhB was measured using UV-vis absorption spectrophotometer. Based on this procedure, we conducted the degradation of RhB at different wavelengths (450, 500, 550, 600, 700, 800 nm). For comparison, we also tested the degradation of RhB over the bulk TiO₂ (Degussa P25).

Detection of Singlet Oxygen (¹O₂) Generation. The generation of singlet ¹O₂ species under light excitation was monitored by chemical oxidation of 9, 10-anthracenediyl-bis (methylene) dimalonic acid (ABDA) molecules. Note that ABDA reacts irreversibly with ¹O₂, leading to the decrease in the absorption of ABDA at 377 nm. The aqueous solution prepared by mixing 2-D TiO₂ catalyst (0.2 mg) with ABDA (10 mL) solution was saturated with oxygen for 1 min followed by sealing with parafilm. Continuous wave (CW) laser was used as light source. The above solution was irradiated with 532 nm and 750 nm CW laser. Absorbance of the solution at 377 nm was recorded at 1 min intervals using a UV-vis spectrometer. For comparison, the control experiments without light/catalysts were also performed with the same procedure.

Characterization. Transmission electron microscopy (TEM) and high-resolution transmission electron Microscopy (HR-TEM) were carried out using JEOL 2010

Scanning TEM. The X-Ray Diffraction (XRD) pattern was recorded on Bruker D8 High-Resolution XRD featuring a four-bounce Ge (022) incident beam monochromator and highly monochromatic X-rays with Cu radiation (Cu $K\alpha = 0.15406$ nm). X-Ray photoelectron spectroscopy (XPS) measurements were conducted using a UHV vacuum generators VG ESCALAB 220I-XL system with a monochromatic Mg- $K\alpha$ source. Before XPS measurement, the as-prepared sample was treated at 200 °C for 4 hours in oven to remove any adsorbed species. All the binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon. The Raman data was collected on the Thermo Scientific DXR Raman microscope system and Renishaw Invia system with laser excitation of 532 nm and 780 nm, respectively. The UV-vis absorbance data was obtained on a Shimadzu UV-2600 UV-visible spectrometer. We conducted the X-ray absorbance spectroscopic investigation (XAS) at Singapore synchrotron radiation center. The STM measurement was performed on a Unisoku low temperature STM housed in an ultrahigh vacuum chamber with a base pressure better than 1×10^{-10} Torr. The polycrystalline tungsten wires were electrochemically etched to STM tips. The STM image was recorded in constant current mode at 77 K. The tunneling parameters used for STM imaging was sample bias and 20-100 pA (tunneling current). WSxM software was used for the STM image data processing and analysis.

DFT calculations. First principles calculations were performed with the plane-wave code VASP,³⁹ using projected augmented wave (PAW) potentials with the local density approximation (LDA)⁴⁰ to the exchange-correlation functional. The PAW potential of Ti has 12 electrons in valence ($3s^2, 3p^6, 3d2, 4s^2$). The monolayer is simulated by adding a vacuum thickness of 20 Å of vacuum to prevent interactions between periodic image

slabs. An energy cut-off of 500 eV is used for the plane wave basis set. Increasing the cutoff energy to 550 eV gives similar results. The structures are considered as relaxed when the maximum component of the Hellmann–Feynman force acting on each ion is less than $0.01 \text{ eV}\cdot\text{\AA}^{-1}$. The phonon band structure was computed using a $4\times 5\times 1$ supercell,⁴¹ where atoms are displaced to get the force constants that can build the dynamical matrix. The Raman frequencies and intensities of zone centre (Γ -point) phonons are calculated within density functional perturbation theory (DFPT)⁴² as implemented in the Quantum Espresso Package.⁴³ The DFT simulated Raman spectra of anatase and lepidocrocite phase is obtained with an artificial Lorentzian broadening based on the calculated non-resonant Raman intensity. GW calculations are performed using the one-shot (G_0W_0) approach.^{30, 31, 32} 288 bands (where 24 bands are occupied) are used in the GW calculation (decreasing this number to 240 changed the quasiparticle gap by only 0.02 eV). Using these GW energies, the Bethe-Salpeter equation (BSE)^{34, 35} (including the effect of electron-hole interaction) is solved to obtain the optical absorption spectra (288 bands were used in this calculation as well). Monkhorst-Pack k-point meshes of $9\times 11\times 1$ and $9\times 13\times 1$ are used to sample the Brillouin Zones for the perfect and stained TiO_2 monolayers. The calculated GW gaps are converged with respect to these k-point meshes (Table S2), and the major peak positions of the optical absorption spectra do not change significantly with the different k-point meshes used (Figure S7).

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Author contributions

Under G.Q.X.'s supervision, S.L.W. planned the project, conceived the experiments, performed fabrication and measurements, and analyzed the experimental data. X.L. and S.Y.Q. proposed the atomic structure for the 2-D layers, and X.L. performed all the theoretical calculations under S.Y.Q.'s supervision. X. Z. performed STM measurement. X. C. helped to test XAS spectra. Y. Z. conducted the HR-TEM measurement. The manuscript was written by S.L.W., L.X., S.Y.Q. and G.Q.X., with comments from all authors.

Acknowledgements

S.L.W. and G.Q.X. acknowledge the financial support from Singapore Ministry of Education program R-143-000-636-112 for chemical experiments and characterizations. Y.Z. acknowledges the Hong Kong Polytechnic University grant (project No: 1-ZE6G). Y.Z. thanks Dr. Lu Wei for optimizing the JEOL JEM-2100F microscope. X.L. and S.Y.Q. acknowledge support from the Singapore National Research Foundation under grant NRF-NRFF2013-07. Computations were performed on the NUS Graphene Research Centre cluster. We acknowledge support from the Singapore National Research Foundation, Prime Minister's Office, under its medium-sized centre program.

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