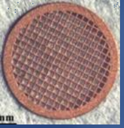

Graphene Oxide: Structural Analysis and Application as a Highly Transparent Support for Electron Microscopy

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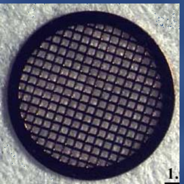

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Introduction

- The extra ordinary electrical and mechanical properties of grpahene and plausible applications.
- Bulk synthesis, GO and bulk graphitic oxide.
- Structure of GO.
- Recent reports suggests that GO is amorphous or semi-amorphous.

In This Paper……

Use of TEM imaging and diffraction to study the structure of GO.

GO is highly electron transparent due to its low atomic number and two-dimensional nature. Here it is demonstrated that GO is an extremely effective ultrathin TEM support film: it is stable in the electron beam, gives low background in both imaging and diffraction modes, and can also serve as its own calibration standard.

Experimental Section

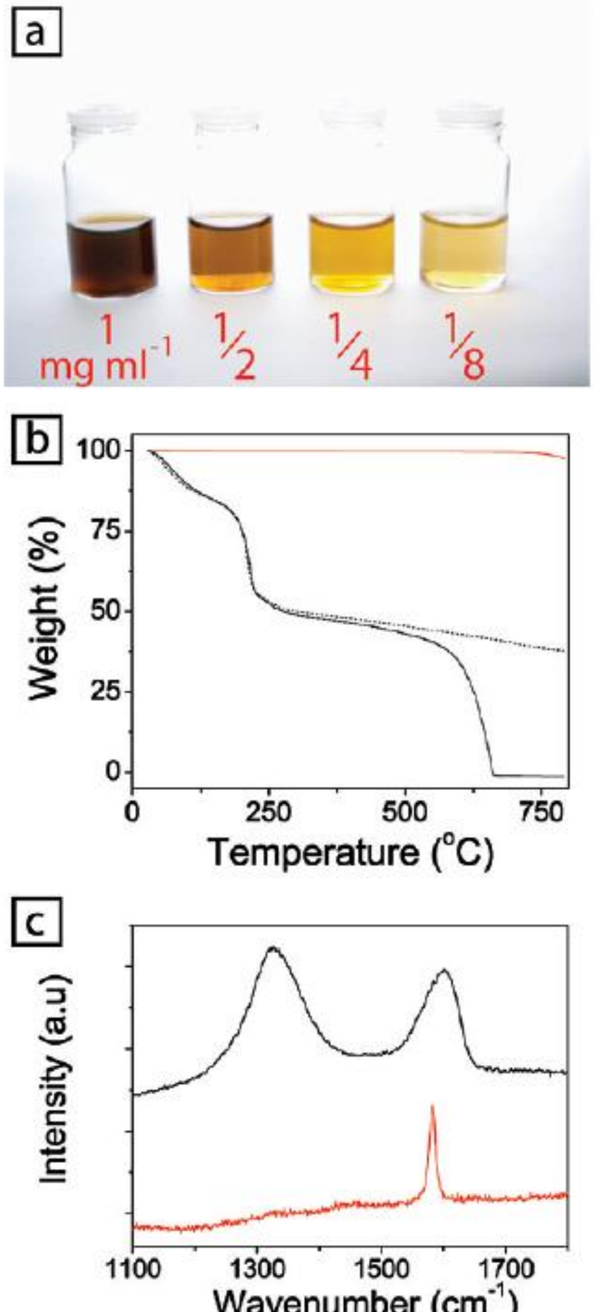
GO and FLG Preparation

- GO was prepared from graphite powder *via a modified Hummers method.*
- Few-layer graphite samples were made using the method described by Hernandez *et al. Graphite powder was exfoliated* by sonication in 1-methyl-2-pyrrolidinone; the dispersion was used immediately after sonication.
- Monolayer graphene samples for micro-Raman analysis were prepared by mechanical exfoliation onto silicon oxide as described by Geim *et al.*
- *Monolayer GO samples were prepared* by spin-coating GO from a 1 mg mL1 suspension onto silicon oxide.

For TEM analysis a drop of GO/FLG suspension was deposited on a lacey carbon support grid and allowed to dry in air (“drop-casting”). For accurate quantitative analysis of the GO/FLG lattice spacing, the supporting lacey carbon was sputter coated with Au (thickness 1 to 5 nm) prior to the drop-casting of GO.

To test the efficacy of GO as a support grid, horse spleen ferritin (Sigma-Aldrich) was diluted 100:1 in water, and a single drop added to a preprepared GO-coated grid.

Results and discussion



(a) Photograph of aqueous graphene oxide suspensions of decreasing concentration from left to right as marked.

(b) TGA of graphite powder in air (red line), graphene oxide in air (solid black line), and graphene oxide in Ar/H2 (dashed line).

(c) Raman spectra of monolayer graphene oxide (black line) and monolayer graphene (red line).

Structural Analysis of GO.

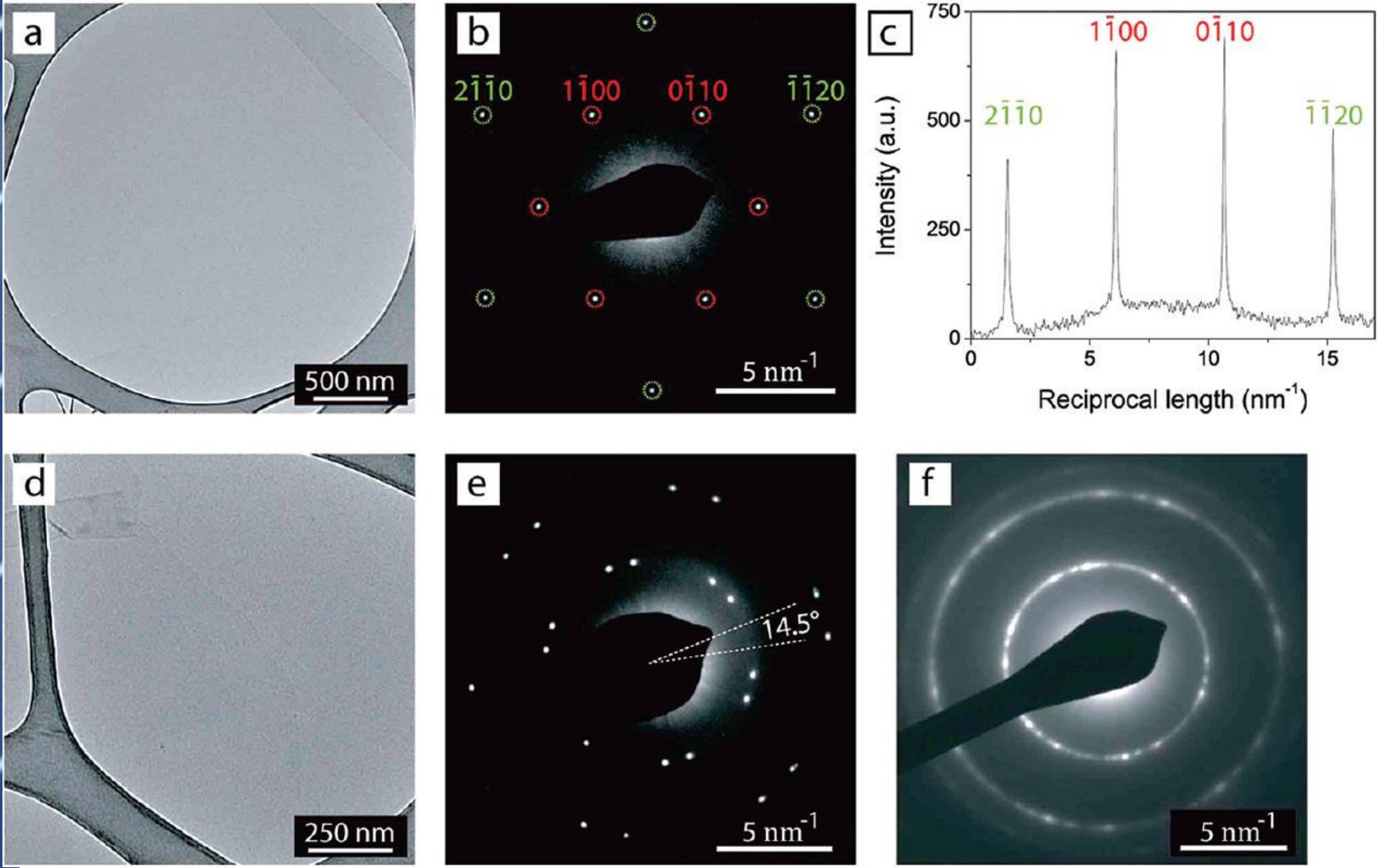


Figure 2. (a) TEM image of a single GO sheet on a lacey carbon support; a double fold is visible in the top right corner. (b) SAED of the center of the region shown in panel a, the diffraction spots are labeled with Miller−Bravais indices. (c) Intensity profile through the diffraction spots labeled in panel b. (d) TEM image with two overlapping GO sheets; a SAED pattern from the double sheet region (lower left side) is given in panel e. (f) Electron diffraction pattern from a thin film of GO *ca.* 15−20 layers thick.

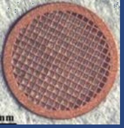
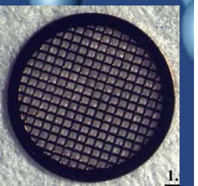
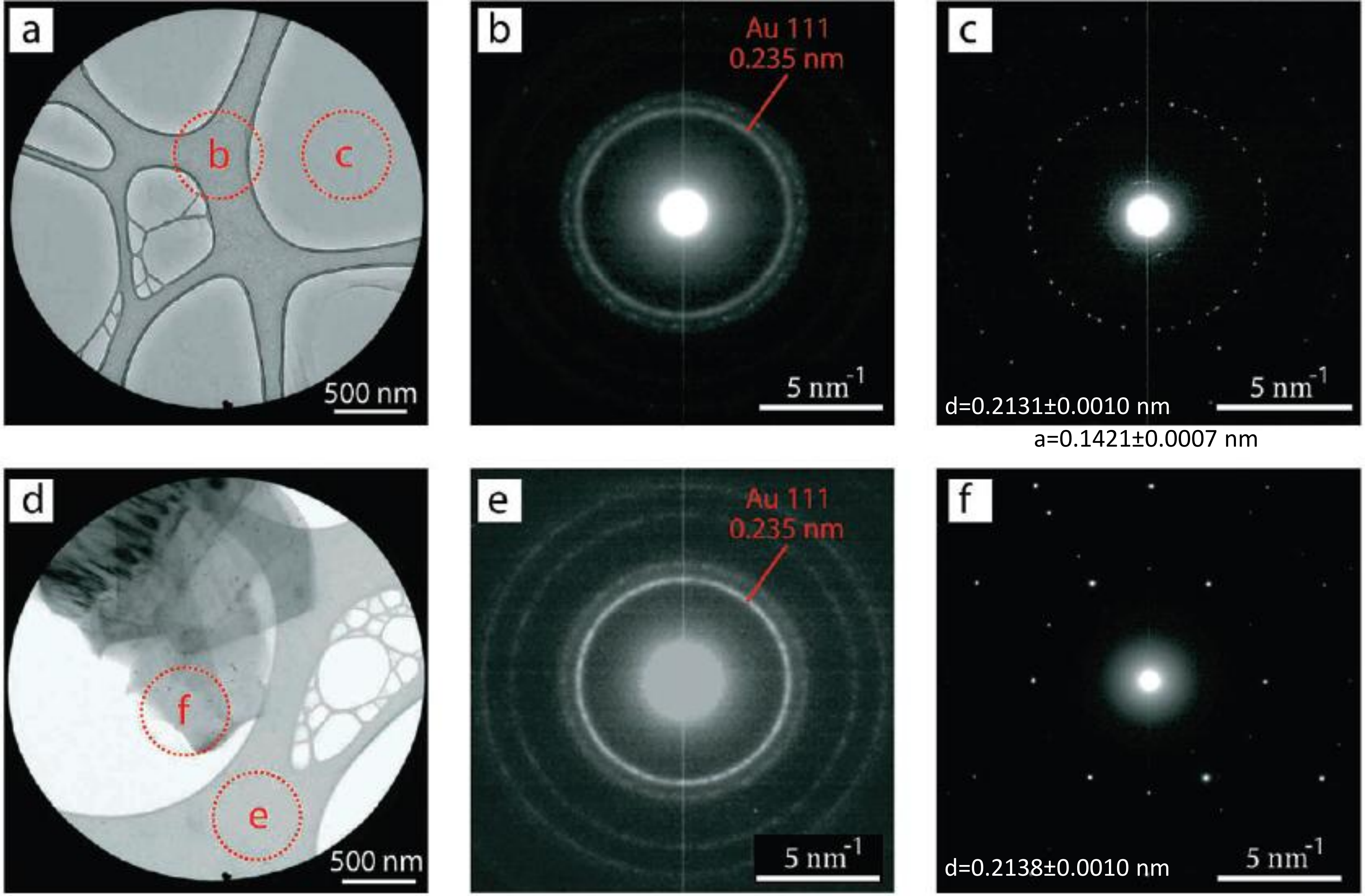




Figure 3. (a) TEM image of multiple GO sheets on a gold-coated lacey carbon support; (b,c) SAED patterns from the regions marked accordingly in panel a. The dominant features in panel b are rings characteristic of polycrystalline gold, which are used to calibrate the GO pattern (*ca.* 7 overlapping sheets) in panel c. (d) TEM image of few-layer graphite on a gold coated lacey carbon support; (e,f) SAED patterns from the regions marked accordingly in panel d. The gold diffraction pattern in panel e is used to calibrate the pattern due to few-layer graphite in panel f.

HR-TEM of GO.

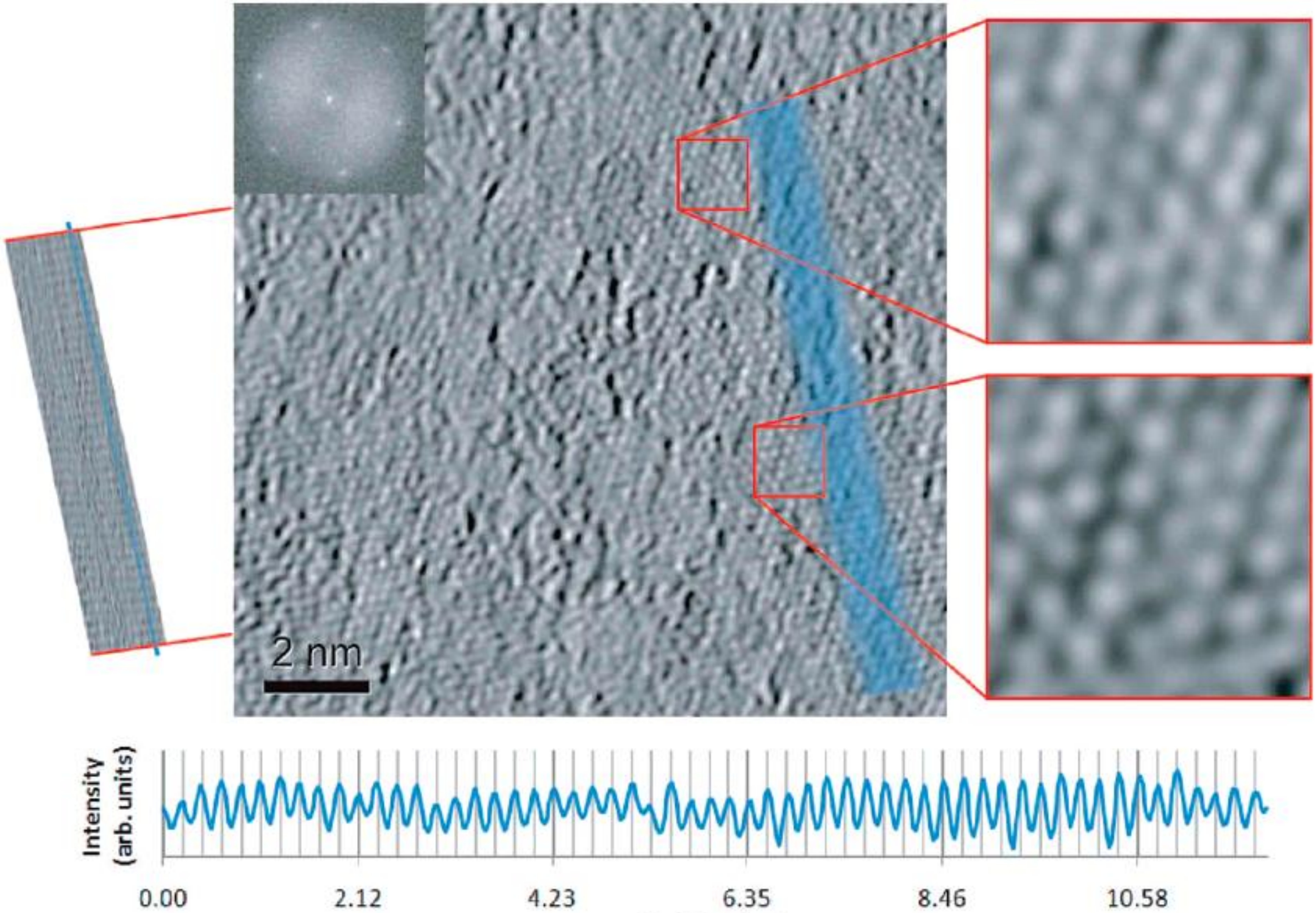


Figure 4. (Main panel) HR-TEM of a single sheet of GO, with an FFT of the image (inset top left); (right) enlargements as marked, showing the GO crystalline lattice; (left) digital compression of a portion of the image (to 10% of its width) along the direction marked by the red lines, the clearly visible parallel lines demonstrate the regular period of the lattice planes; (below) line plot of the average intensity along the blue line (marked on both compressed and original images), the gray lines are guides to the eye.

Conclusions on the Structural Analysis of GO.

- ❖ Maintains the hexagonal symmetry and order of an unmodified graphene sheet
- ❖ Has an average in-plane carbon-carbon spacing of 0.1421±0.0007 nm
- ❖ Has no regular ordering of the functional groups
- ❖ Underlying carbon lattice has hexagonal order on the length-scale of the coherence of the electron beam (a few nm), evident from diffraction patterns; a graphene-like lattice with crystalline order on length-scales 10 nm as visible by atomic-resolution HR-TEM; and long-range orientational order over the entire (typically micrometer size) GO sheet, as evident in the SAED patterns.
- ❖ Has no preferential stacking arrangement between adjacent sheets when deposited by drop-casting.

TEM investigations also demonstrate that GO is highly electron transparent and stable in the electron beam

GO as a Support Film: Diffraction and Imaging of Ferritin

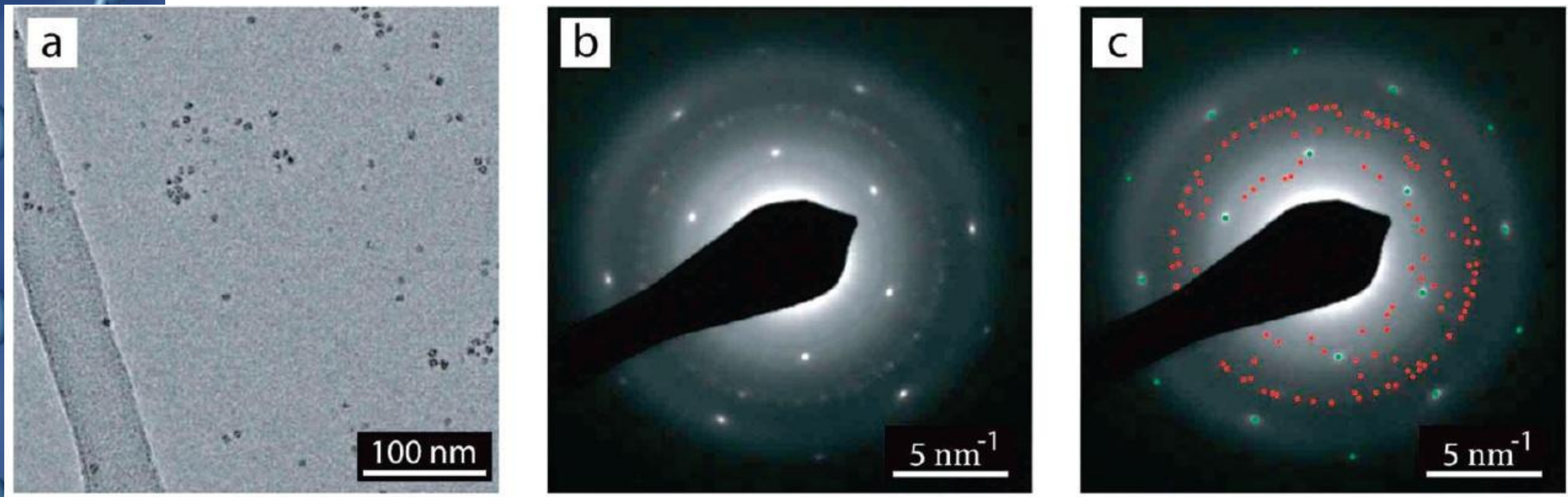


Figure 5. (a) TEM image of ferritin (dark particles) on GO. The lacey carbon support can be seen to the lower left. (b,c) SAED of a region containing *ca. 500 particles on a single sheet of GO. More than 100 ferritin diffraction spots are visible, these are* marked in panel c in red, with the spots due to GO marked in green.

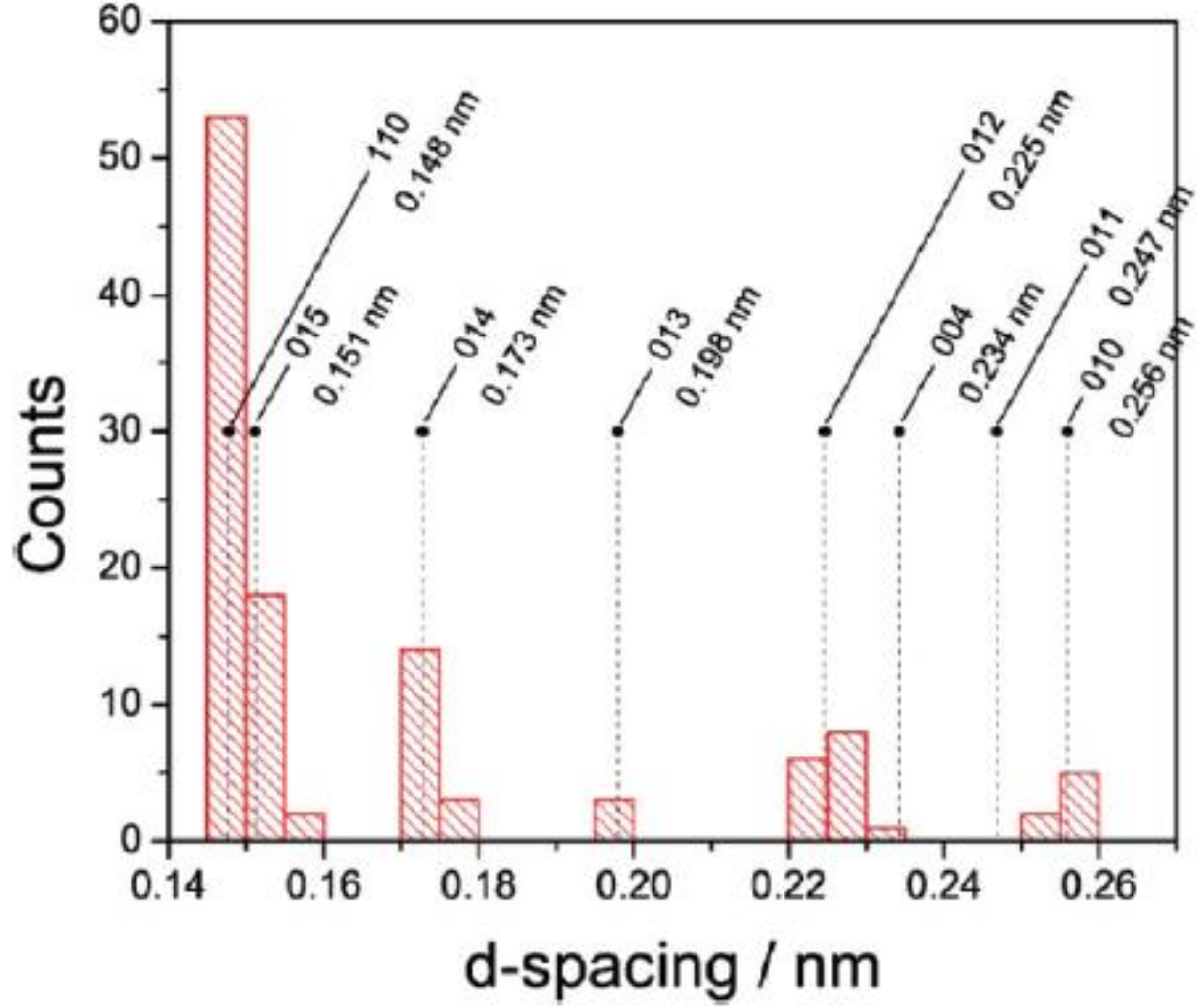
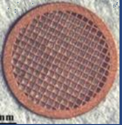


Figure 6. Histogram of the *d*-spacing of the ferritin diffraction peaks marked in Figure 5c after calibration. The dotted lines and labels (*hkl* and *d*-spacing) correspond to the peaks predicted for "six-line" ferrihydrite.

HR-TEM of Ferritin on GO



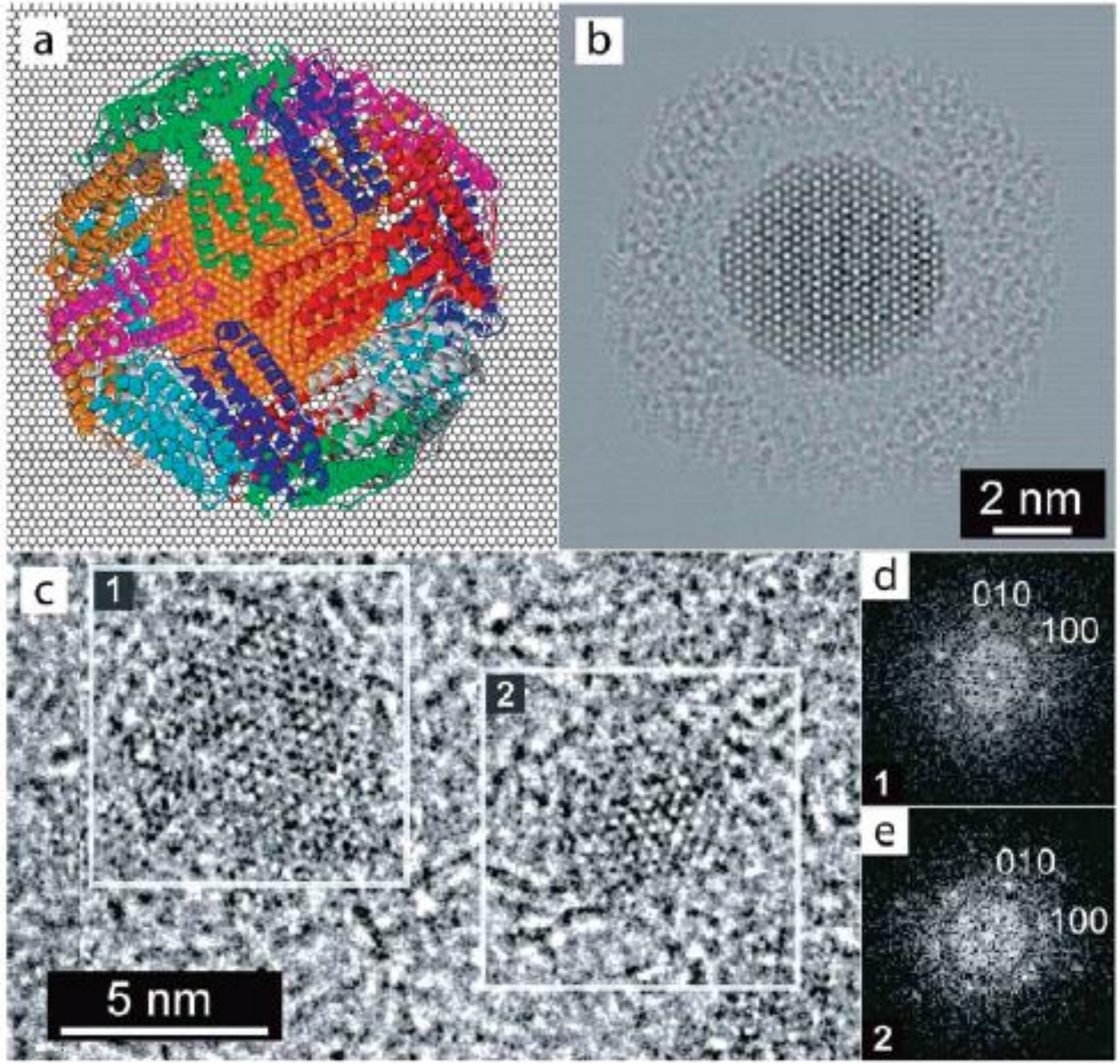
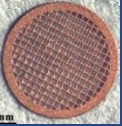


Figure 7. (a) Schematic model of ferritin on a graphene sheet. Ferritin consists of a protein shell (multicolored ribbons) containing a ferrihydrite core (Fe atoms indicated by orange spheres, O by red spheres) which here is oriented along [001] relative to the bulk crystal structure. (b) HRTEM image simulation of the structure in panel a. (c) 300 kV HRTEM image of ferritin on a single sheet graphene oxide support; (d,e) FFTs obtained from the marked regions 1 and 2, respectively, in panel c.

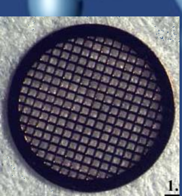
Summary of structural investigation of Ferrtin on GO support

- Allowed the identification of the predominant core composition by electron diffraction
- Identification of the core composition, and orientation by HR-TEM
- Observation of the degraded protein shell.
- The ability to use the GO to accurately calibrate the diffraction pattern, without obscuring the pattern due to the nanoparticles.
- In contrast to other ultrathin films, these GO support films are simple and quick to make



Conclusions

- Applied electron microscopy to the structural analysis of graphene oxide.
- The carbon substructure of graphene oxide is found on average to maintain the hexagonal symmetry, order, and carbon-carbon bond length of an unmodified graphene sheet.
- Owing to its high electron transparency and stability under the electron beam, graphene oxide is also a very promising support film for high resolution structural analysis of macromolecules and nanoparticles by TEM.
- Demonstrated this through the analysis of physiological ferritin, both by electron diffraction and high resolution imaging.
- GO TEM grids are simple, cheap, and quick to fabricate in any laboratory



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