Oxidative Peeling of Carbon Black Nanoparticles

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Oxidative Peeling of Carbon Black Nanoparticles

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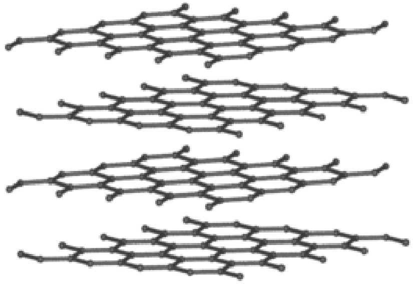
Historically ...

Brodie

Solution oxidation of 3D graphite

1859

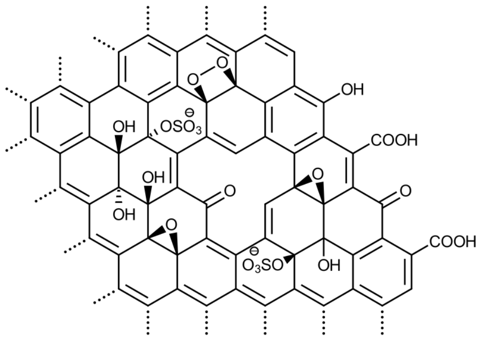


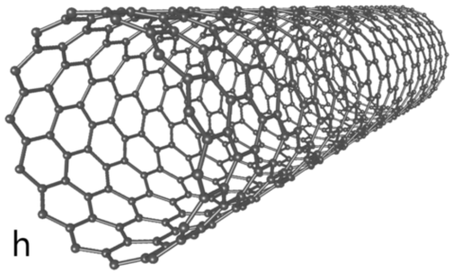
Hummers and Offeman

Results in 2D material known as graphene oxide (GO)

Potassium permanganate and sulfuric acid $KMnO_4/H_2SO_4$

1958





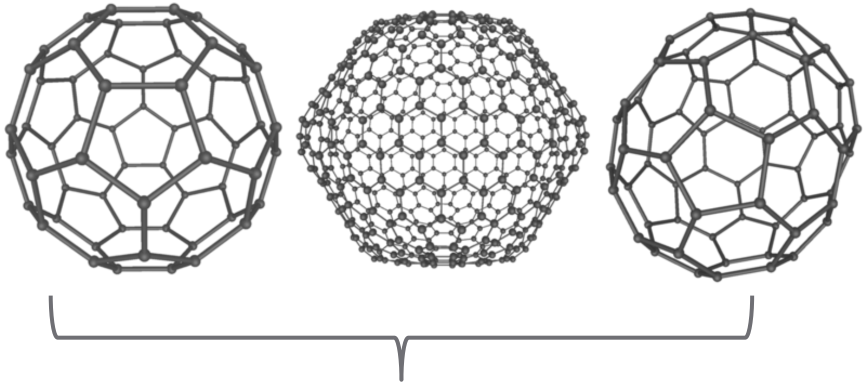
Tours et al

$KMnO_4/H_2SO_4$ was used to “unzip” carbono nanotubes (CNTs) thus converting to 1D graphene oxide nanoribbons

2009

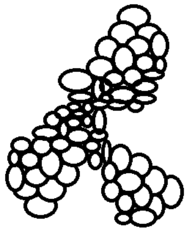
About 0D materials

Carbon nano-onions (CNOs)



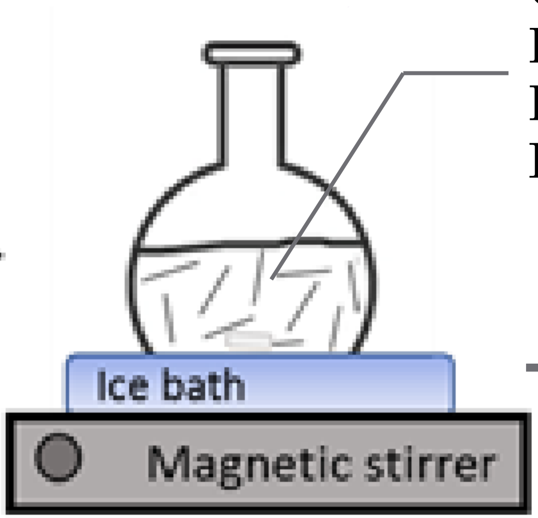
Fullerenes

Carbon Black nanoparticles (CBNPs)



Oxidation of this materials has been studied to the syntesis of graphene quantum dots.

The synthesis



CBNP (25 mg)
H_2SO_4 (6.7 mL)
H_3PO_4 (1.26 g)
$KMnO_4$ (0.295 g)

→ Sonicated for 24 hours → 48 hours in room temperature → The reaction was stoped with 3% hydrogen peroxide →

Centrifuged at 7000 rpm for 30 min → Separated
- precipitade
- supernatant

→ Supernatant was centrifuged at 14000 rpm for 1 h → Precipitade was resuspended in aqueous solution

After oxidation: high solubility in water.
Oxidation introduced oxygen funcionalities.

Are uniform nearly spherical particles d ≈ 20 – 40 nm.

Nearly spherical but smaller

Nanosheets

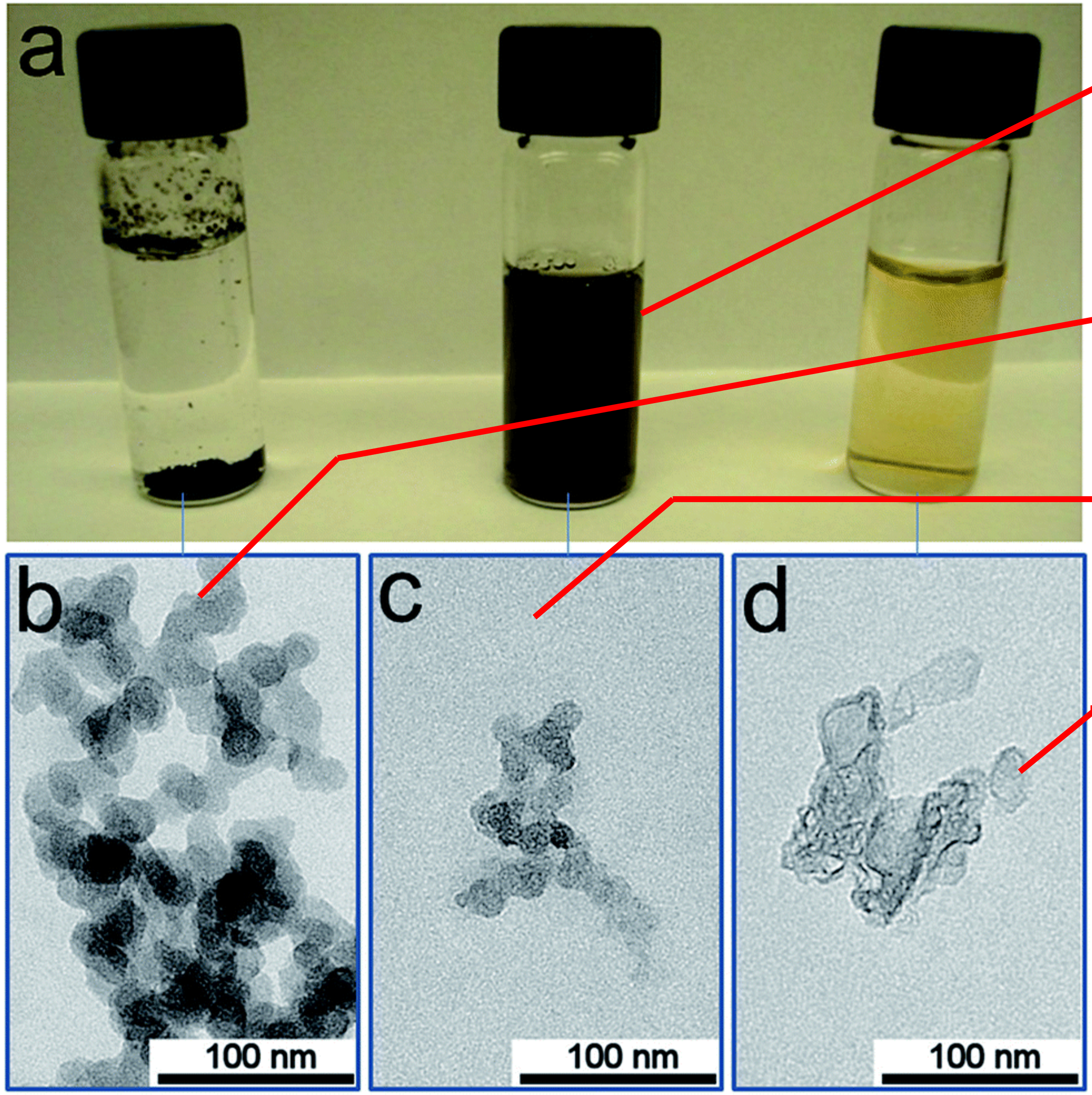
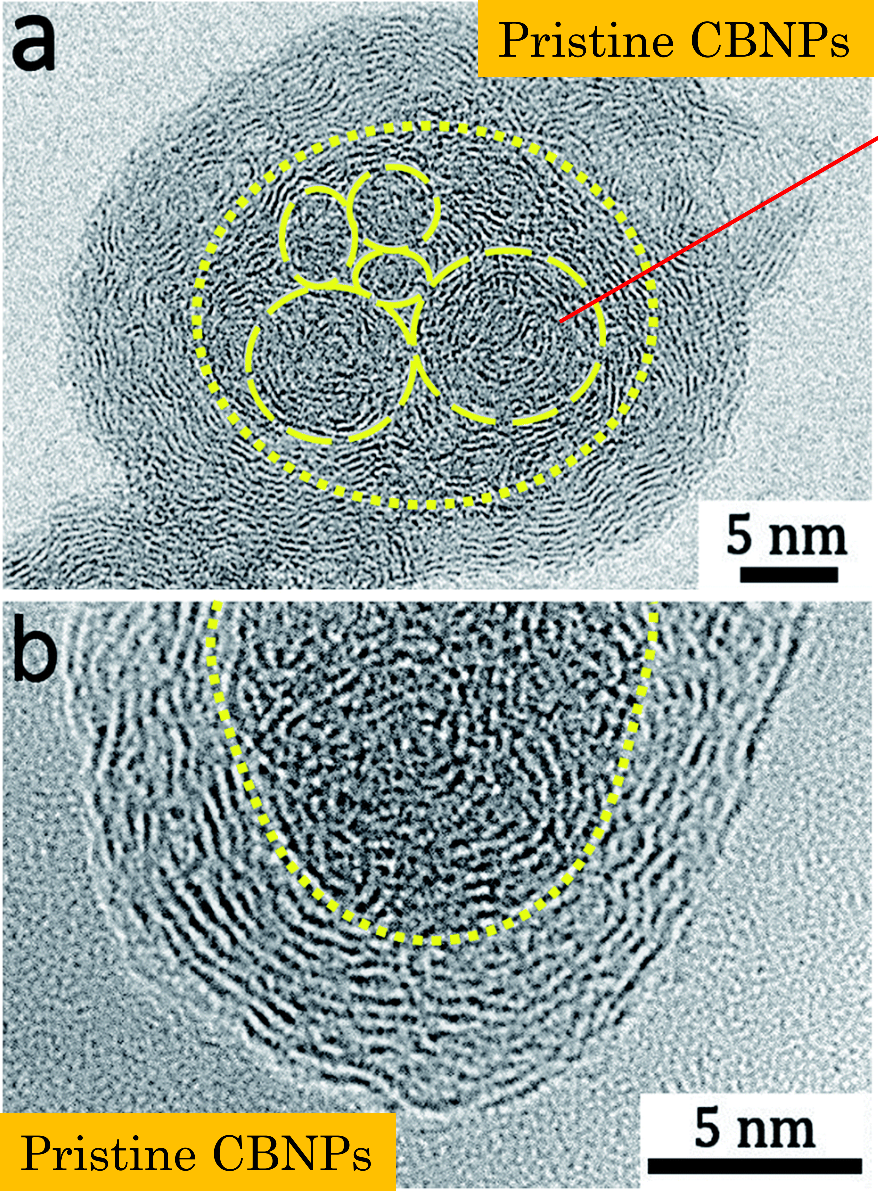
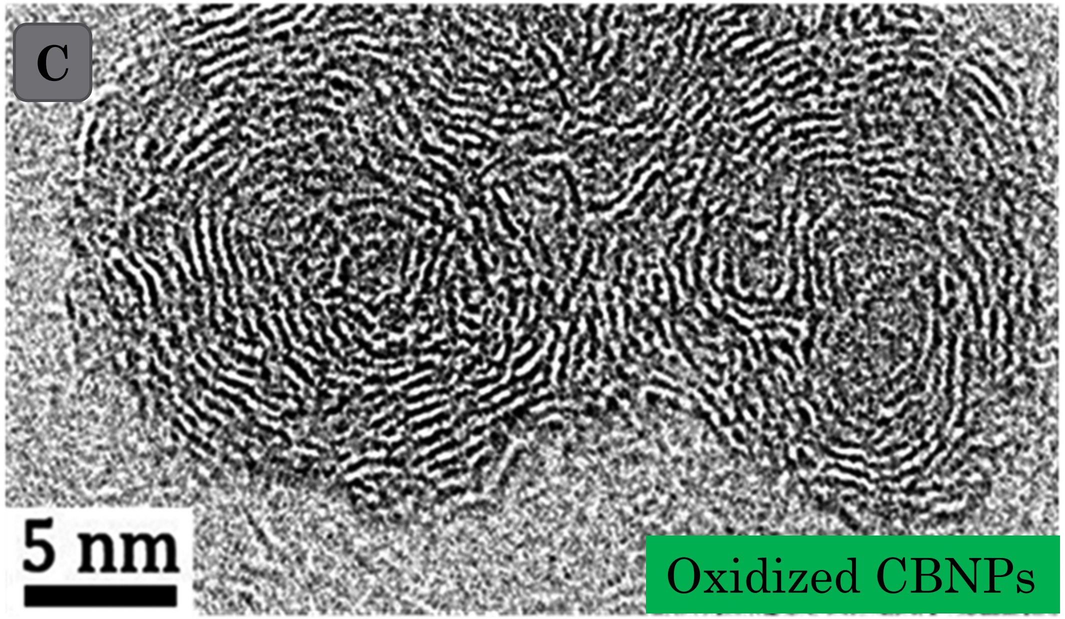


Fig. 1 (a) Optical photograph of the CBNPs and the reaction products dispersed in water. From left to right, the pristine CBNPs, oxidized CBNPs, and byproduct of oxidation. **(b-d)** TEM images of (b) pristine CBNPs, (c) oxidized CBNPs, and (d) byproduct of oxidation (nanosheets).



Smaller spherical particles that ar made by concentric graphitic layers.
This is explain by the combustion of etylene – grow over a nucleus.



The core are wrapped smaller number of outer layers

Fig. 2 TEM **(Transmission electron microscopy)** images of CBNPs. The yellow dotted lines mark the boundaries between the conformal graphitic layers that form the outer shells of CBNPs and the more disordered cores of the CBNPs. Dashed yellow circles in panel **(a-b)** show small aggregated CBNPs that likely served as a nucleus for the bigger CBNP. **(c)** Oxidized CBNPs.

Size distribution

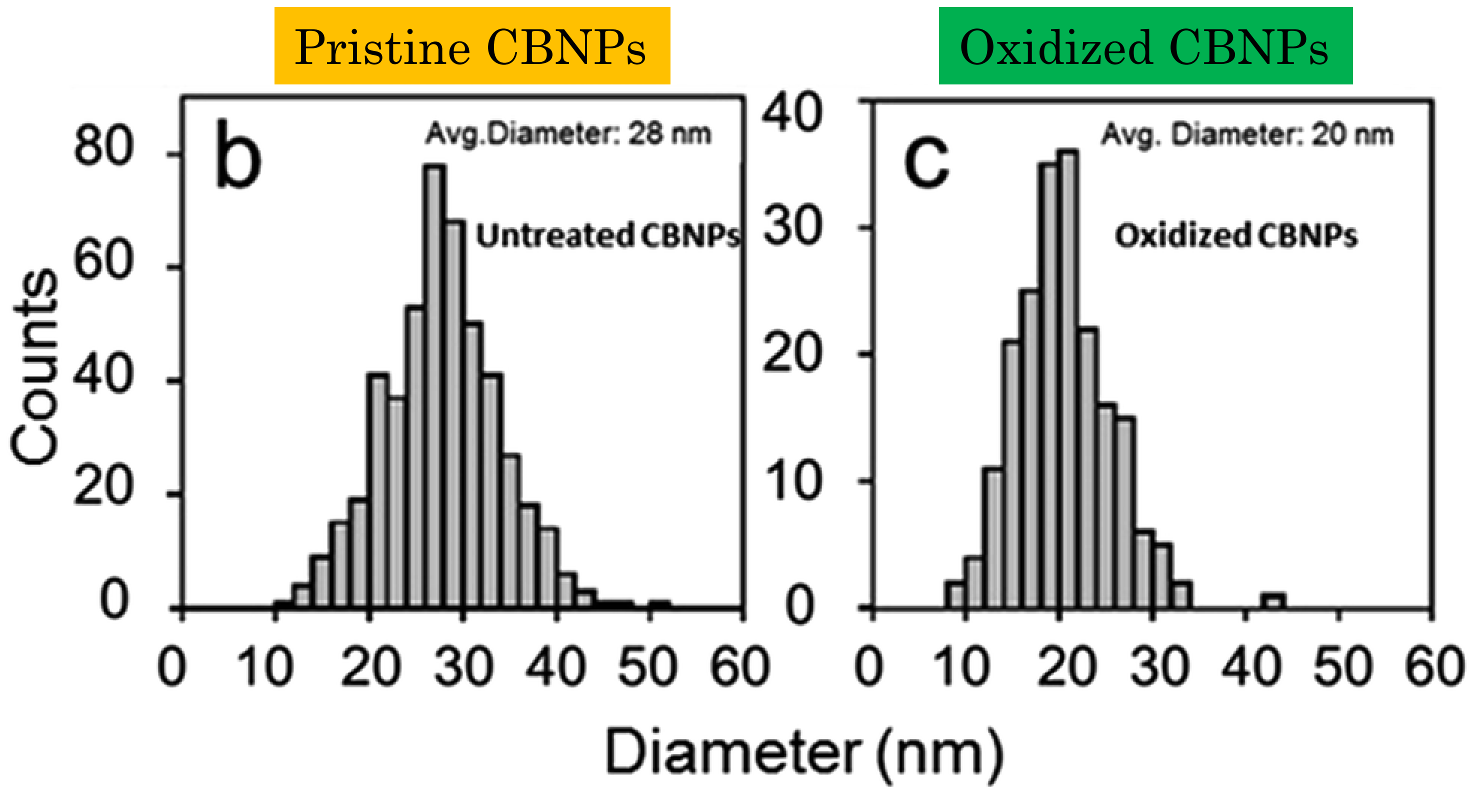
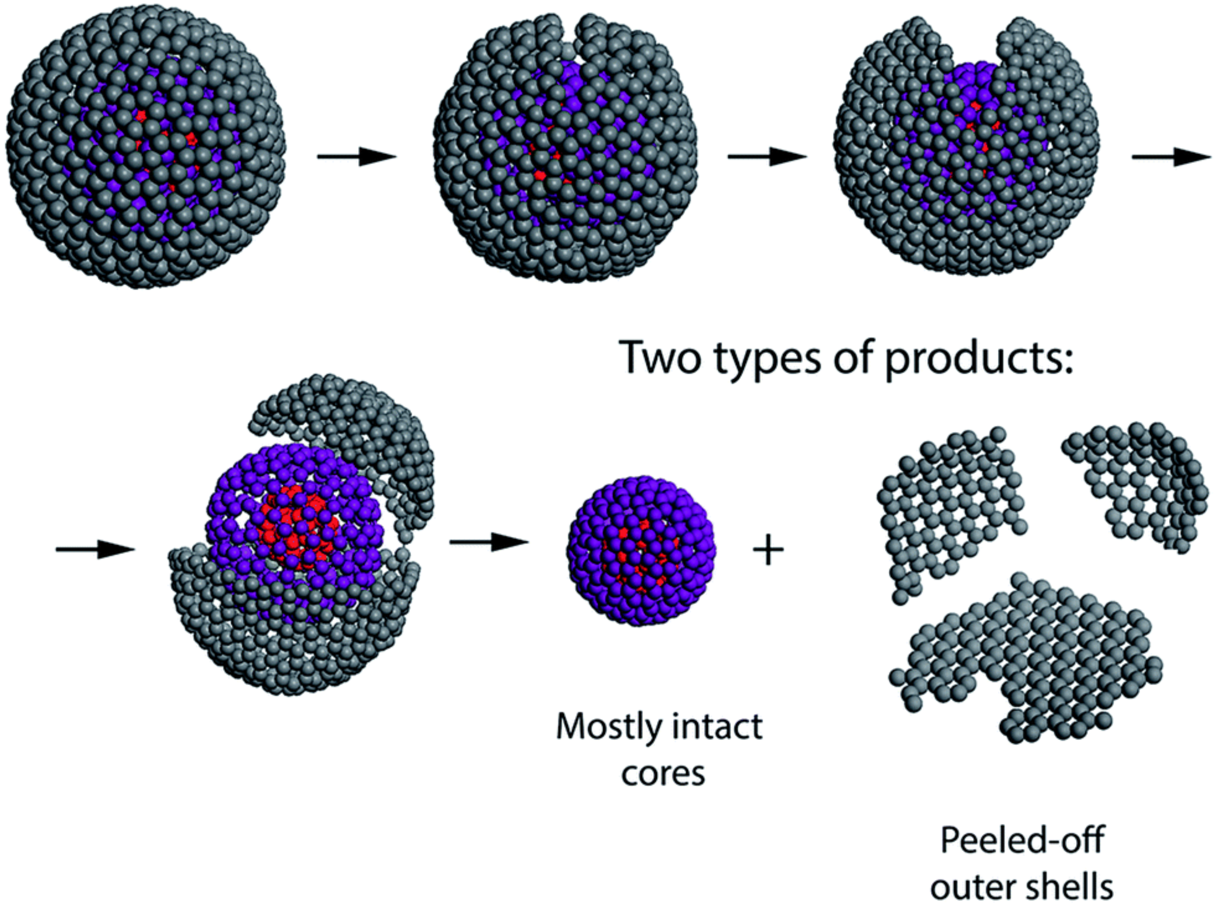


Fig. 3 Size distribution chart of pristine CBNPs **(b)** and oxidized CBNPs **(c)** .

Reaction mechanism



The unfurling of the outer shells is likely driven by steric forces between the sheets caused by the swelling of the intersheet distances incurred upon addition of oxygen functionalities to the edges and basal planes of the outer shells.

Fig. 4 A simplified scheme of the proposed mechanism of the oxidative peeling of CBNPs resulting in peeled graphene-oxide-like sheets from the outer shells and lightly oxidized cores. Note that **irregularities** in the structure of the CBNPs and the products, such as **discontinuity** of the shells and presence of the **oxygen functional groups**, **are omitted.**

OXIDATIVE DEGRADATION OF CARBON BLACKS WITH NITRIC ACID (I)—CHANGES IN PORE AND CRYSTALLOGRAPHIC STRUCTURES

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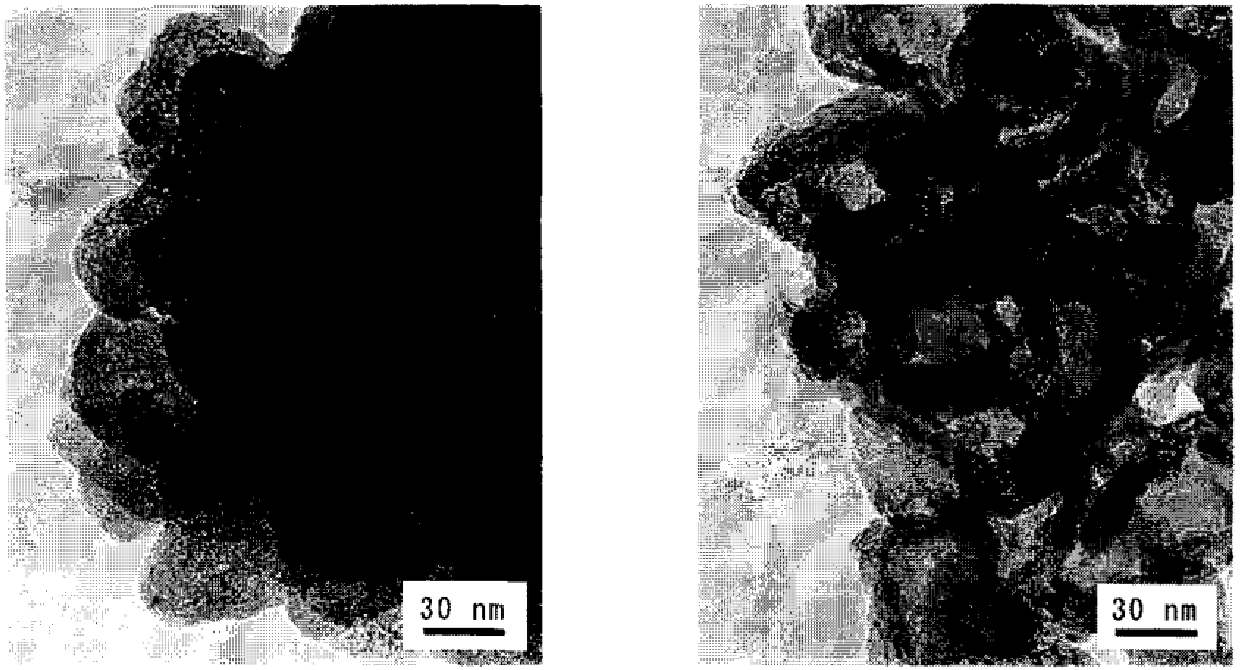
(*Received* 29 *September* 1997; *accepted in revised form* 7 *November* 1997)

Reported an experiment in which acetylene-derived CBNPs were treated by concentrated nitric acid at 100 $_{o}$C for 1000 h.c

Oxidative degradation of carbon blacks with nitric acid (I)



(a) (b)

Fig. 6. TEM images of (a) F-black oxidized for 20 hours (F20AI) and (b) A-black oxidized for 1000 hours (A1000AI).

Disordered cores of CBNPs were completely eliminated, resulting in hollow particles of more stable outer shells of CBNPs

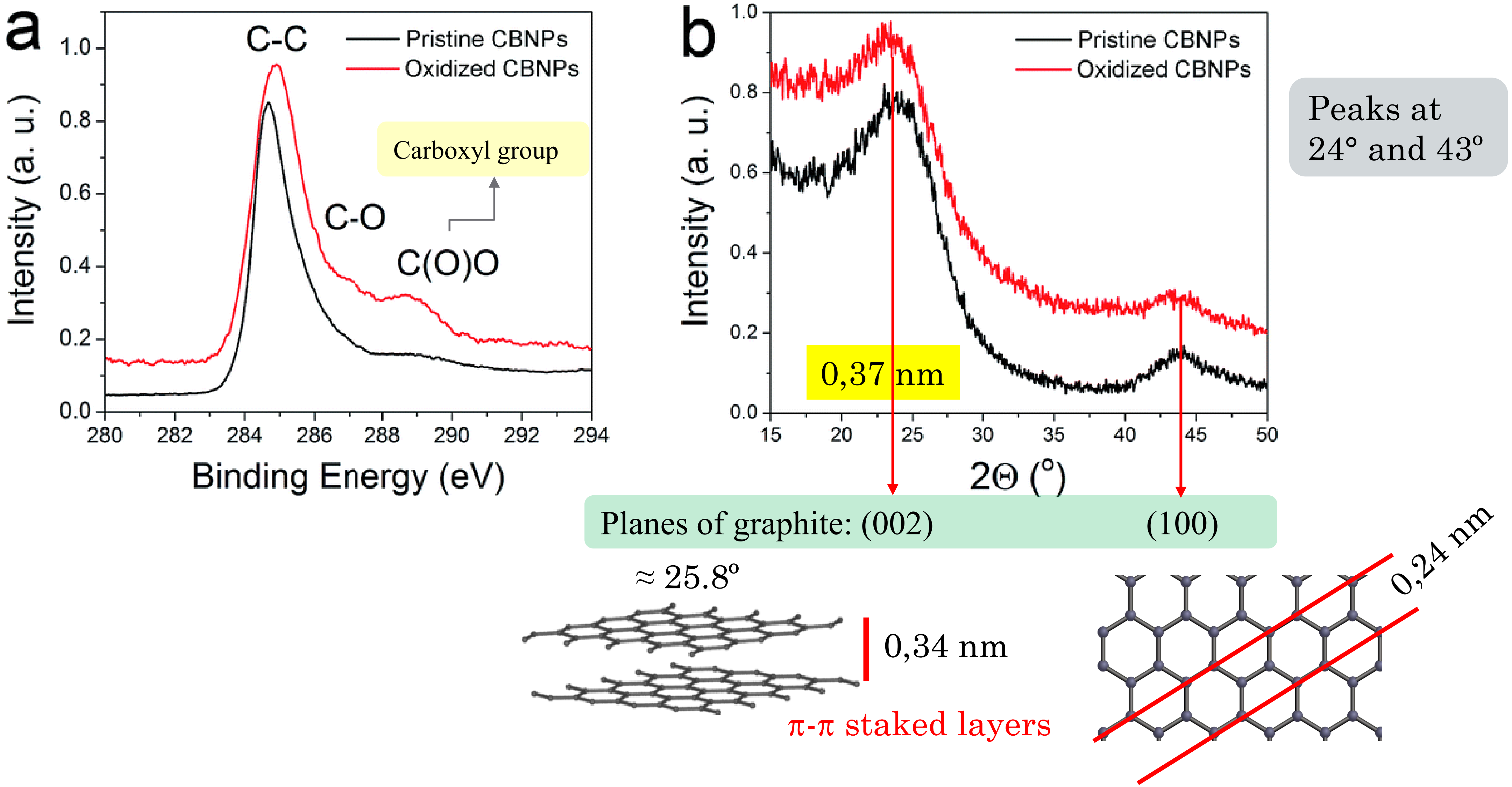
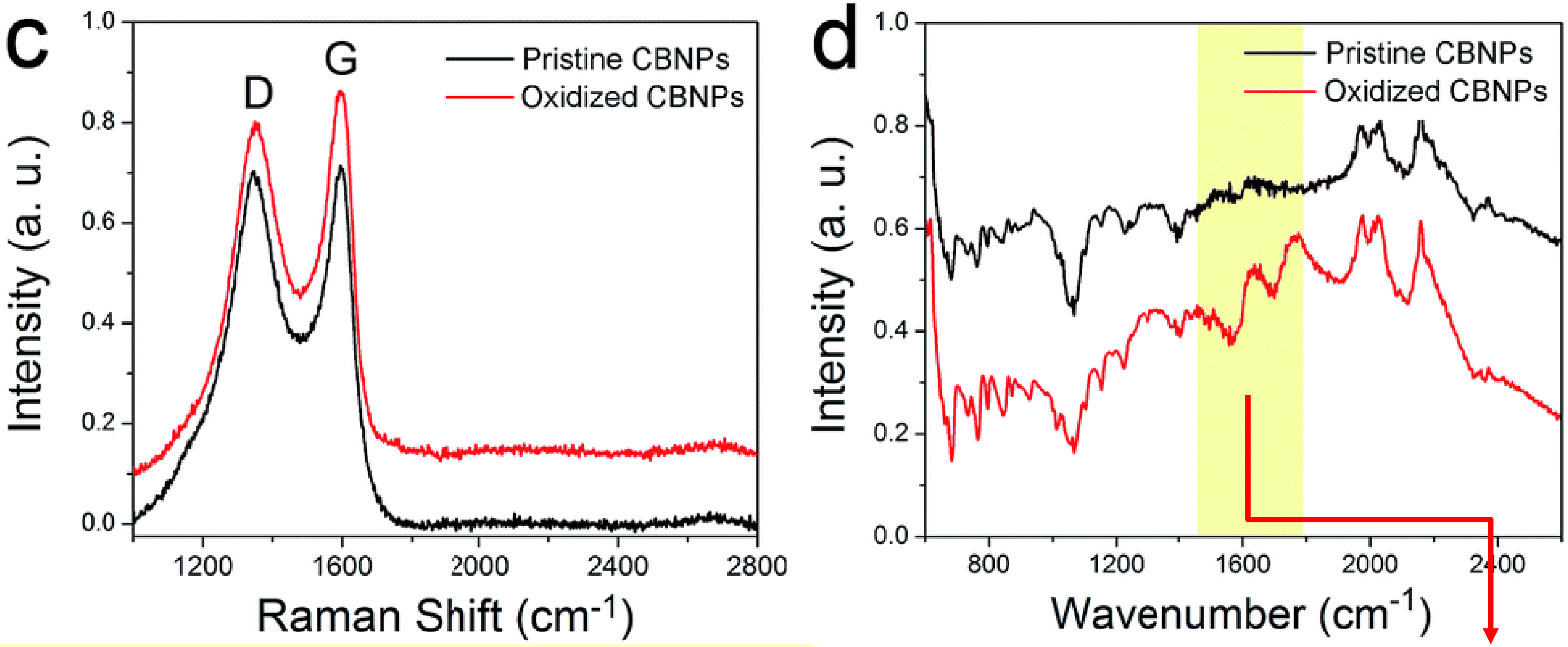


Fig. 5 Spectroscopic characterization of pristine and oxidized CBNPs. **(a)** C1s XPS **(X-ray photoemission spectra)** spectra of pristine and oxidized CBNPs. **(b)** XRD **(X-ray diffraction)** patterns of pristine and oxidized CBNPs.



Decrease in the I_D/I_G ratio is due to the shrinking of the hexagonal sp^2 hybridized domain.

Indicative of the addition of C=O in carboxylic acid

Formation of oxidized regions of carbon which break the sp^2 hybridization.

Tearing of the outer layers of the CBNPs due to the curvature induced strain.

Fig. 5 Spectroscopic characterization of pristine and oxidized CBNPs. **(c)** Raman spectra of pristine and oxidized CBNPs. **(d)** FT-IR spectra of pristine and oxidized CBNPs. In all panels spectra of pristine CBNPs are shown in black, while spectra of oxidized CBNPs are shown in black.

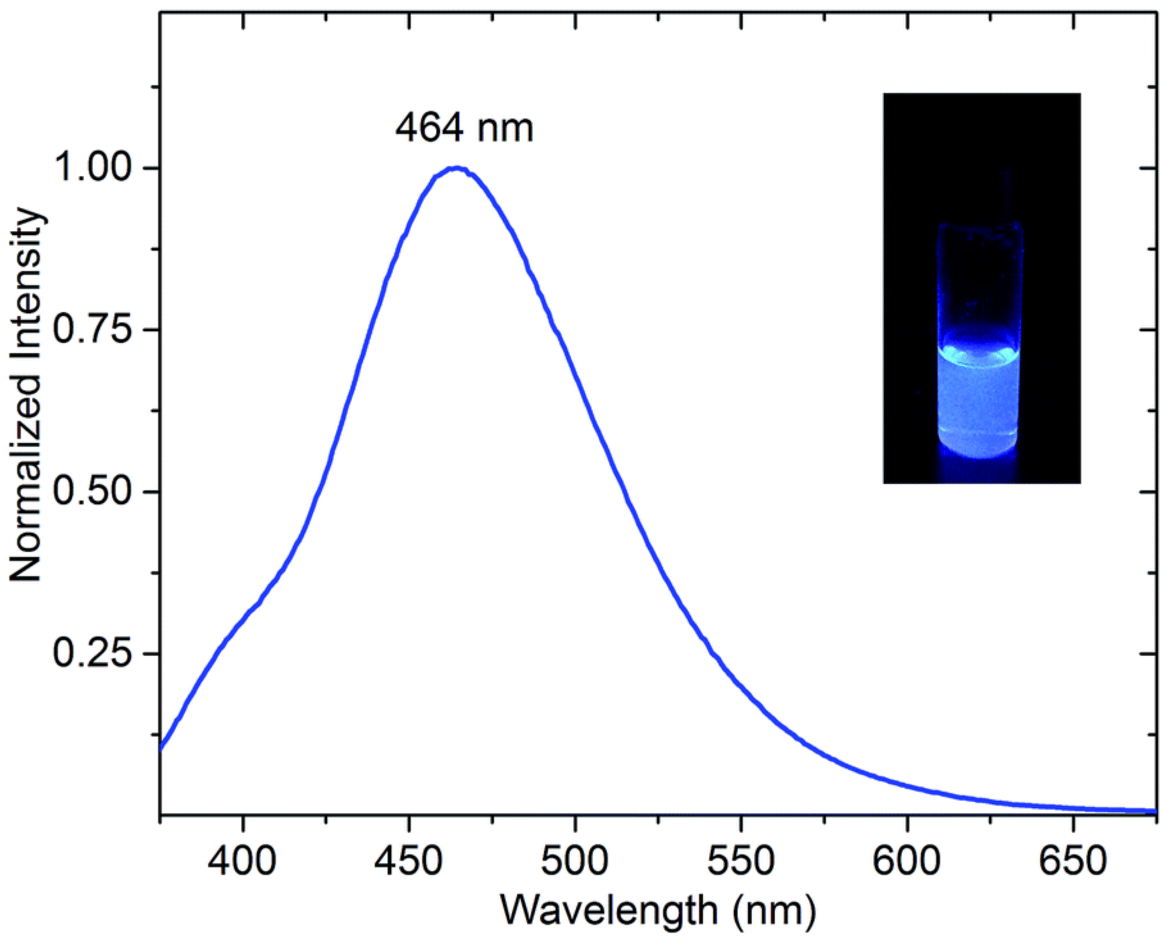


Fig. 6 Photoluminesce spectrum recorded for the aqueous solution of byproduct material with a 350 excitation. The inset shows photograph of photoluminescence from the same solution under a 365 nm UV lamp.

THANK YOU!