GRAPHENE AND 2DM VIRTUAL CONFERENCE & EXPO

10 ANNIVERSARY

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Graphene chemical derivatives: from synthesis to applications

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Graphene chemical derivatives: point of interest

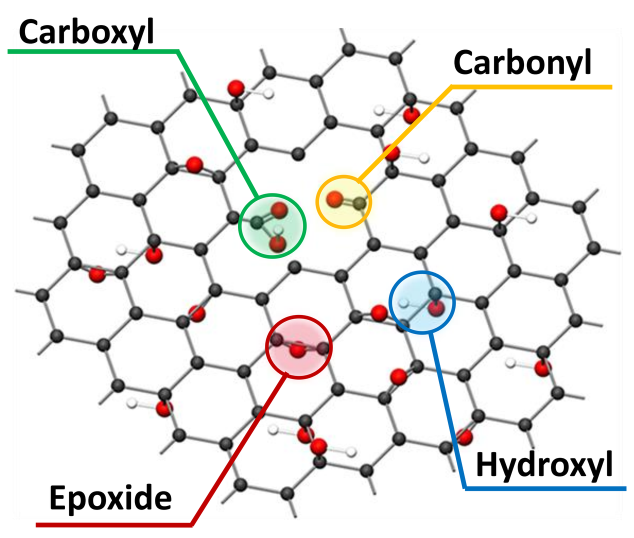
Graphene oxide (GO):

- ○ Inefficient for the graphene production (introduction of defects & contaminants during the GO reduction)
- ✓ versatile platform for the synthesis of graphene layers with the intended composition of organic groups

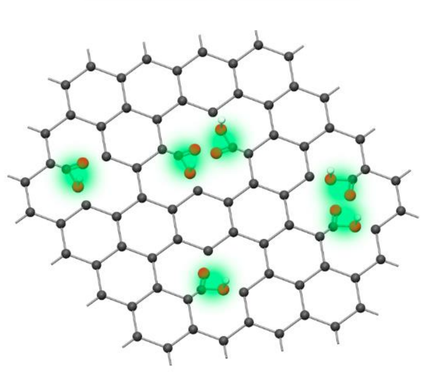
Graphene derivatization provides:

- Tunable electronic structure, charge transport and optical properties
- Variable chemical reactivity
- Easiness of the subsequent grafting

Graphene Oxide

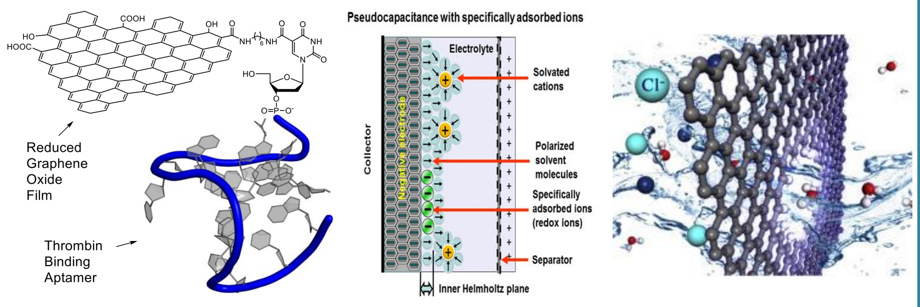


✓ Carboxylated

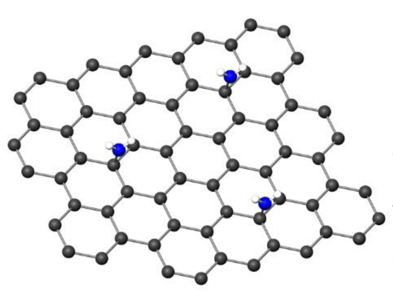


Applications:

(a) Graphene-based aptasensors with high selectivity and sensitivity;
(b) Pseudocapacitors with high power density;
(c) Membranes for water purification & desalination



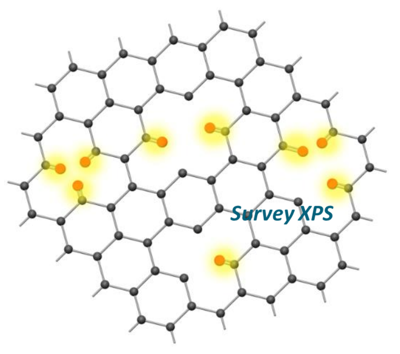
✓ Aminated



Applications:

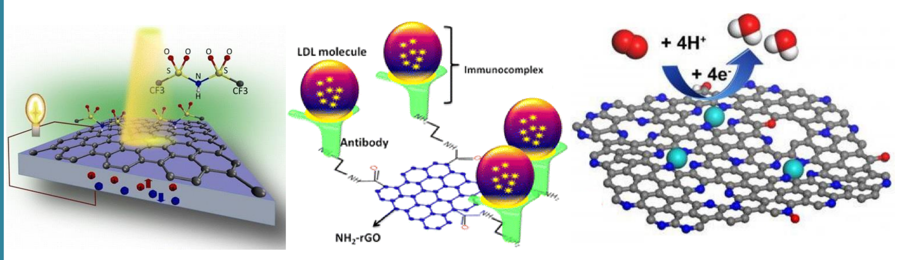
(a) Electrodes for photovoltaic devices;
(b) Label-free electrochemiluminescent sensors;
(c) Heterogeneous catalysts

✓ Carbonylated



Applications:

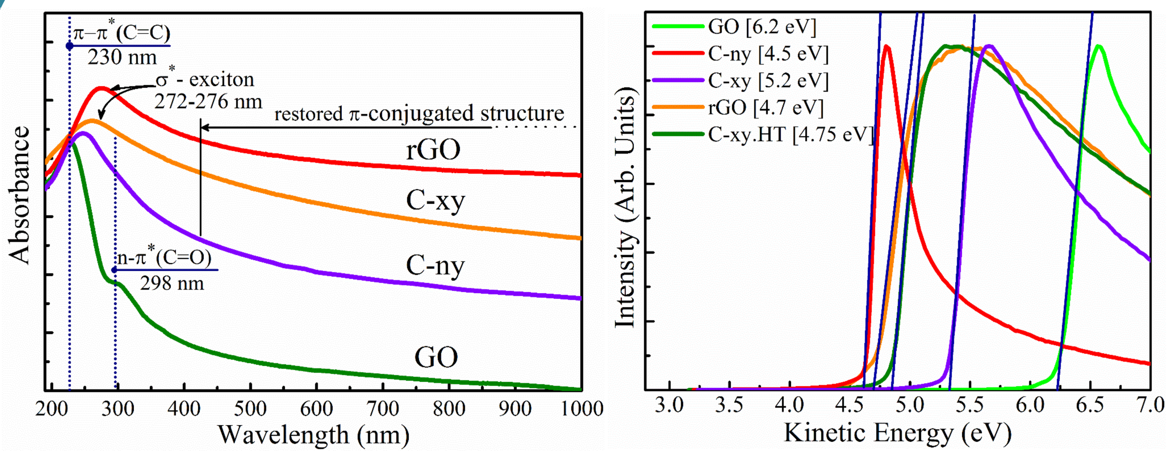
(a) Graphene-based gas sensors and multielectrode chips with tunable selectivity;
(b) Graphene-based E-inks;
(c) Organic light-emitting coatings



How to obtain?

The effect of derivatization?

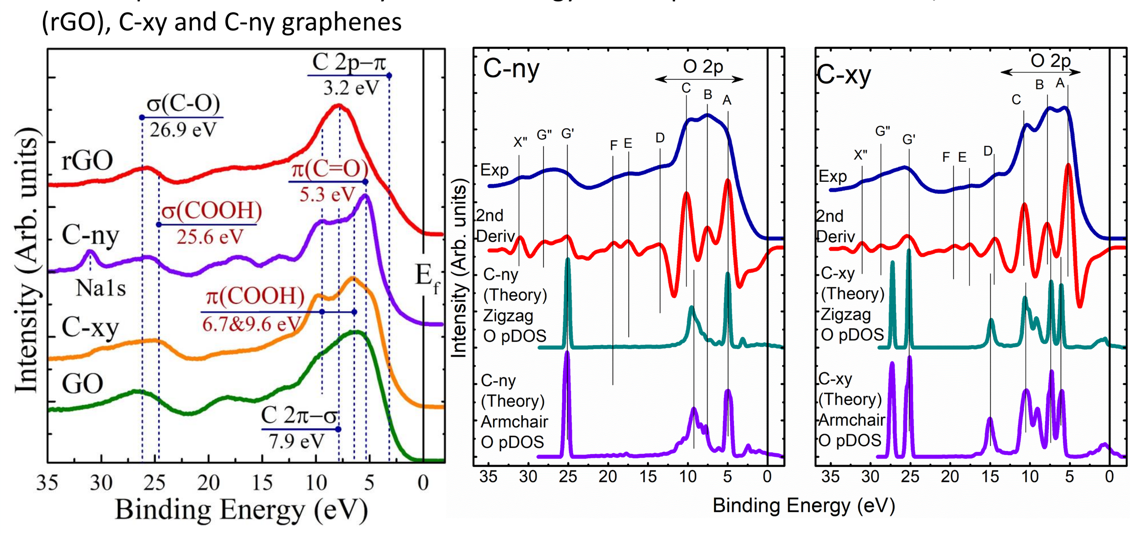
Carboxylated (C-xy) & Carbonylated (C-ny) graphenes:



UV-Vis spectra and secondary electron energy cutoff spectra of the initial GO, reduced GO (rGO), C-xy and C-ny graphenes

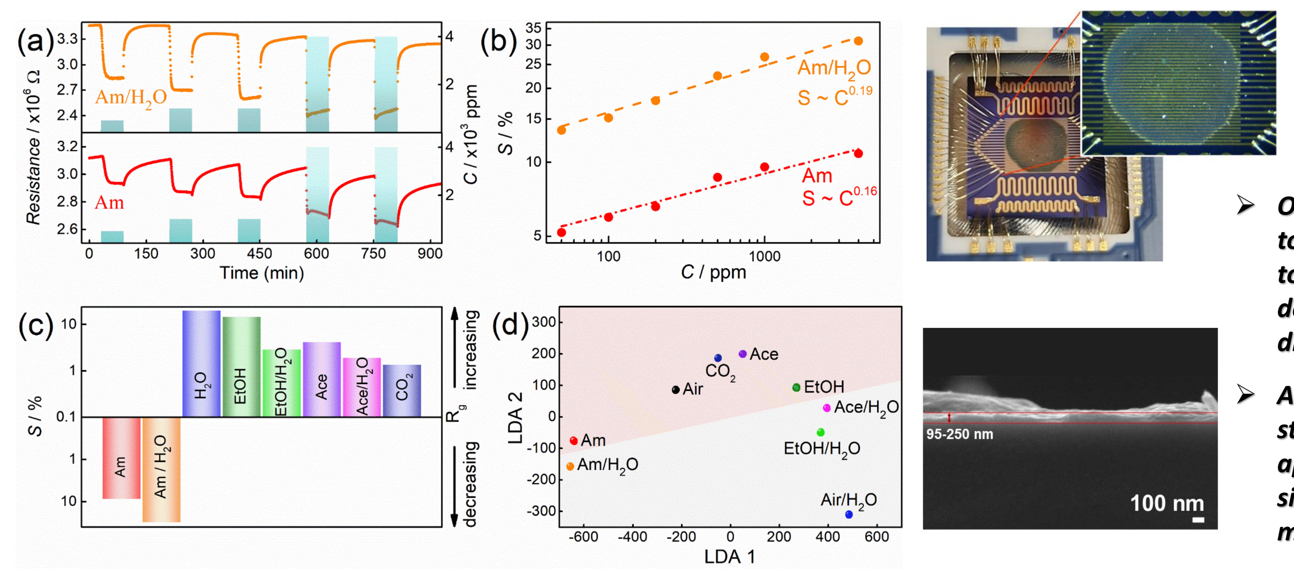
Type	Resistance, kΩ/□	Conductivity, S/m
GO	$> 10^9$	$< 10^{-12}$
C-xy	1-1.4	180
C-ny	1000-5000	0.4-3
rGO	0.3-0.6	220

Sheet resistance and the corresponding conductivity values for the studied materials



(left) XPS valence band spectra of pristine GO, rGO, carboxylated, and carbonylated graphene. (right) Experimental graph, its 2[nd] derivative and theoretically calculated Valence band spectra of the C-xy and C-ny graphene

- ➢ ***UV-Vis spectra demonstrate almost complete restoration of π-conjugated structure in C-xy and only partial – in C-ny, although both are perforated***
- ➢ ***Despite C-ny terminated by electron-withdrawing C=O groups – it has the lowest Work Function value in graphene derivatives***
- ➢ ***Carboxylation and carbonylation leads to formation of new localized electronic states in the valence band of the graphene layer***
- ➢ ***New electronic states arise from the molecular orbitals localized on the introduced carboxyl and carbonyl groups as is verified by DFT calculations***



The gas-sensing performance of C-ny graphene layer. (a) The resistance transient of the exemplary sensor exposed to NH_3 in humid (upper curve) and dry (lower curve) air. (b) The dependence of median chemiresistive response of sensors in the on-chip multisensor array on the concentration of NH_3 in humid and dry air. (c) The values of median chemiresistive response of sensors in the on-chip multisensor array to various analyte VOCs: water (H_2O), NH_3 in dry and humid air (Am and Am/H_2O)), ethyl alcohol in dry and humid air (EtOH and EtOH/H_2O), acetone in dry and humid air (Ace and Ace/H_2O), and CO_2. (d) The results of the recognition of the studied analyte VOCs using LDA the red-highlighted zone indicate a location of analytes in dry air background.

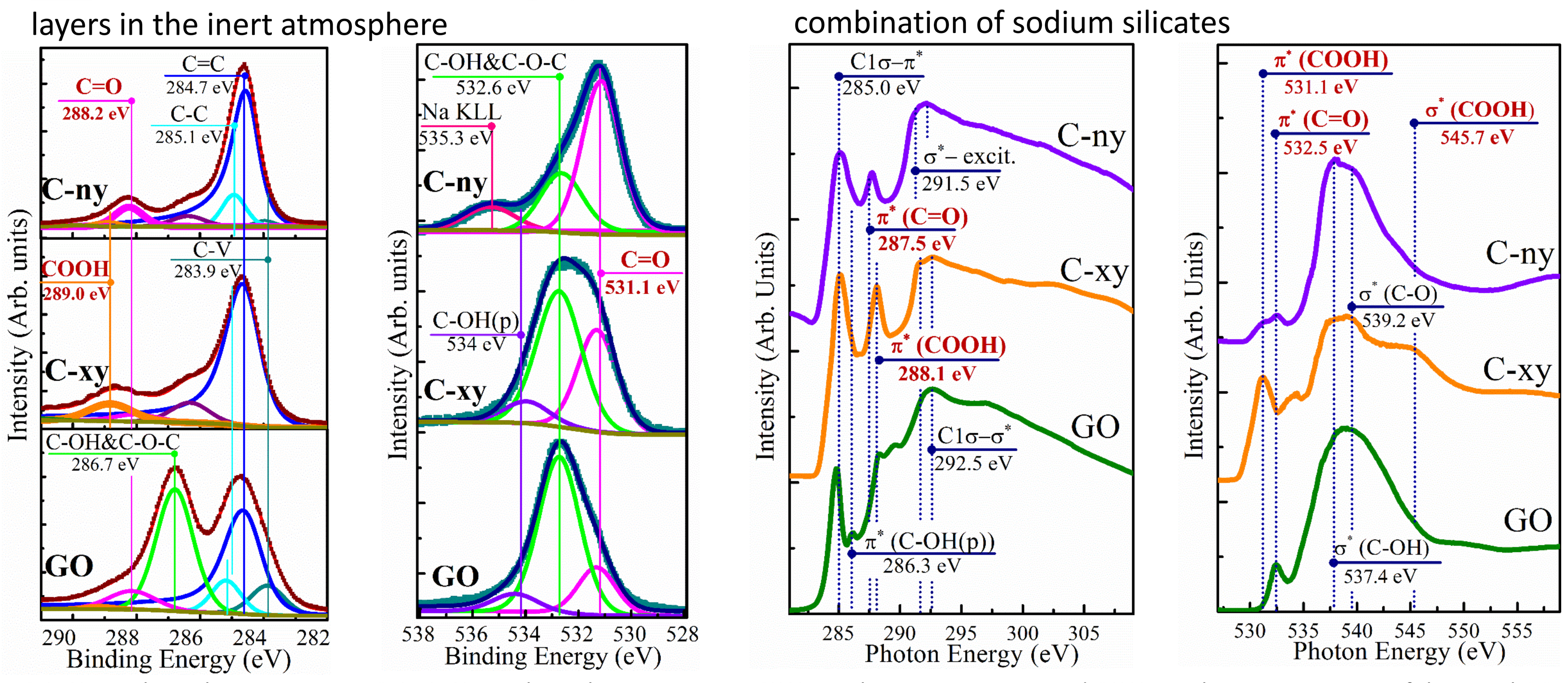
- ➢ ***Opposite chemiresistive response towards ammonia when compared to ethanol, acetone, and CO_2 is demonstrated both in humid and dry air background***
- ➢ ***A selective discriminating all of the studied analytes is further approached by employing a vector signal generated by C-ny multielectrode chip***

M. K. Rabchinskii et al. Carbon, 2020, ***DOI: 10.1016/j.carbon.2020.09.087***

Carboxylated (C-xy) & Carbonylated (C-ny) graphenes:

C-xy: Photoinduced reduction of graphene oxide layers in the inert atmosphere

C-ny: Liquid-phase graphene oxide reduction using combination of sodium silicates



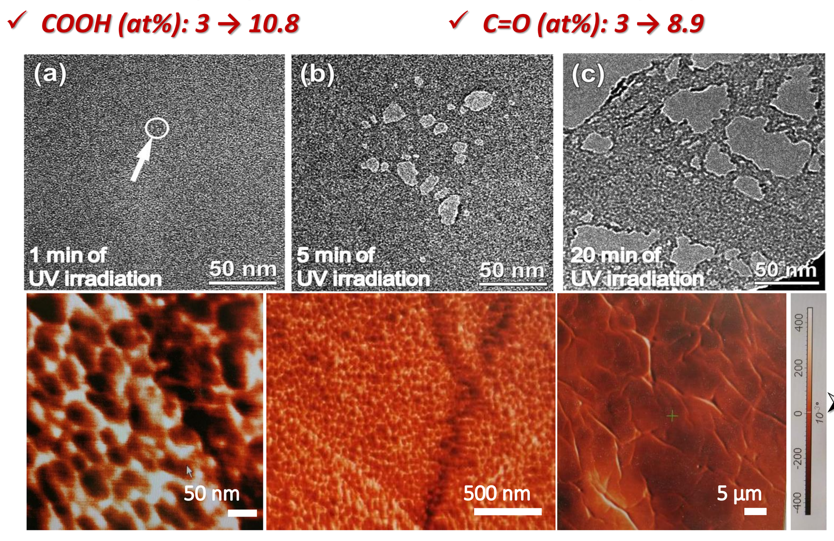
C 1s X-ray photoelectron spectra, O 1s 1s X-ray photoelectron spectra, CK X-ray absorption spectra and OK X-ray absorption spectra of the initial GO, carboxylated graphene and carbonylated graphene

Carboxylated graphene:

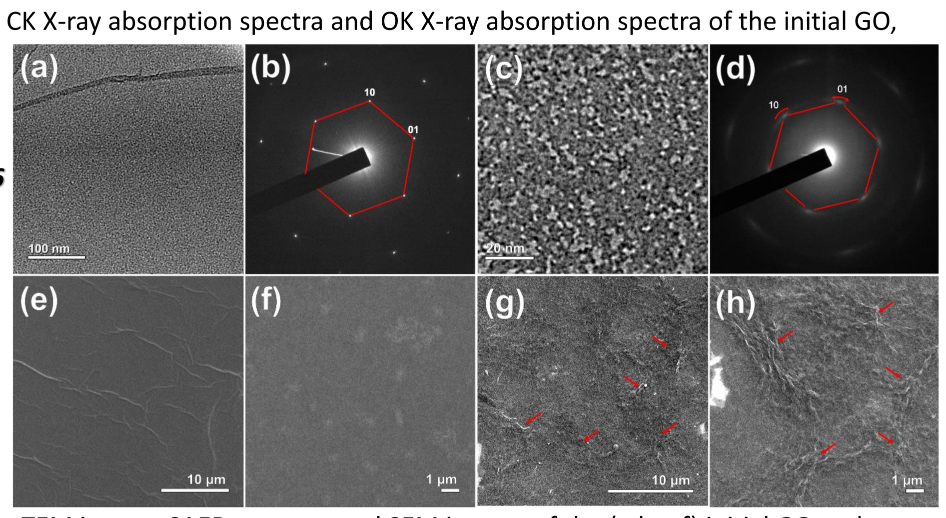
- ✓ *C/O ratio: 1.68 → 7.41*
- ✓ *C-OH&C-O-C (at%): 53.2 → 2.3*
- ✓ *COOH (at%): 3 → 10.8*

Carbonylated graphene:

- ✓ *C/O ratio: 1.68 → 5.4*
- ✓ *C-OH&C-O-C (at%): 53.2 → 5.6*
- ✓ *C=O (at%): 3 → 8.9*



TEM (upper row) and AFM (lower row) images of the C-xy graphene

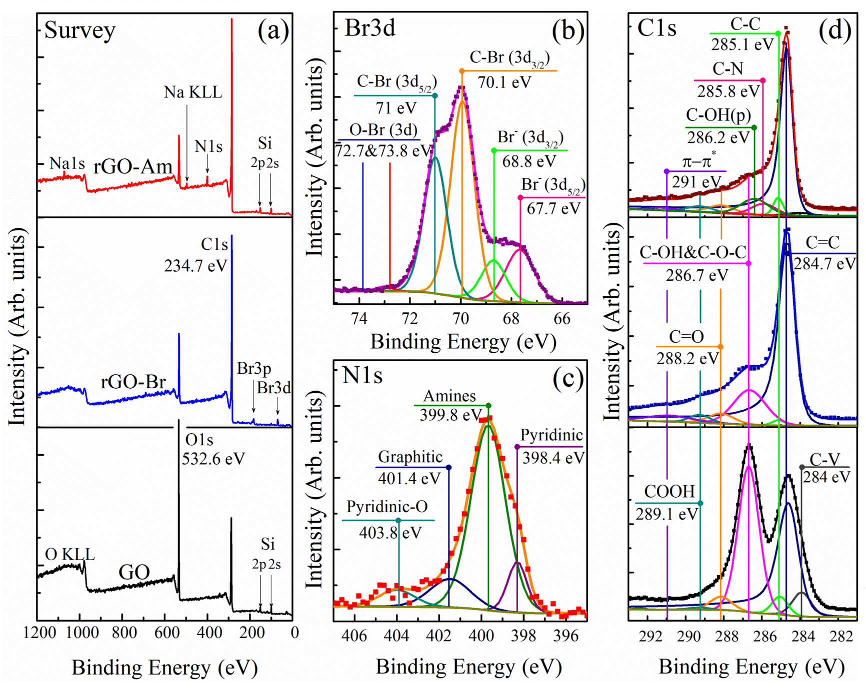


TEM images,SAED patterns and SEM images of the (a,b,e,f) initial GO and (c,d,g,h) C-ny graphene;

- ➢ ***Carboxylation results in perforation of graphene layers (20-100 nm holes)***
- ➢ ***Carbonylation leads to holey and corrugated structure of graphene layer***
- ➢ ***The obtained films preserve intact structure, containing massive arrays of holes***

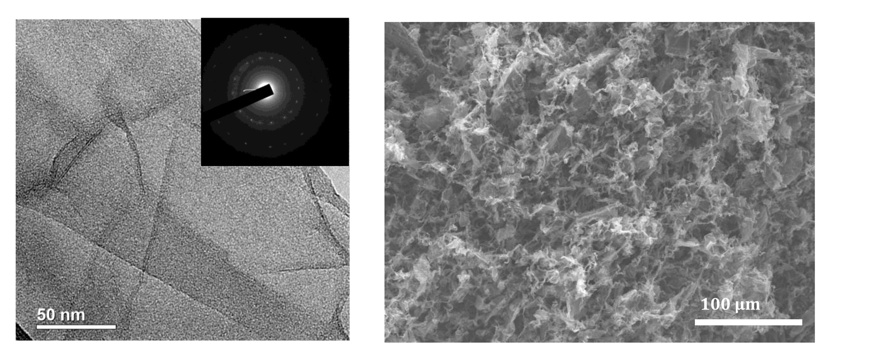
M. K. Rabchinskii et al. J. Phys. Chem. C, 2016, 120, 28261–28269 ***DOI: 10.1021/acs.jpcc.6b08758***

Aminated graphene: GO treatment with hydrobromic acid & ammonia solutions



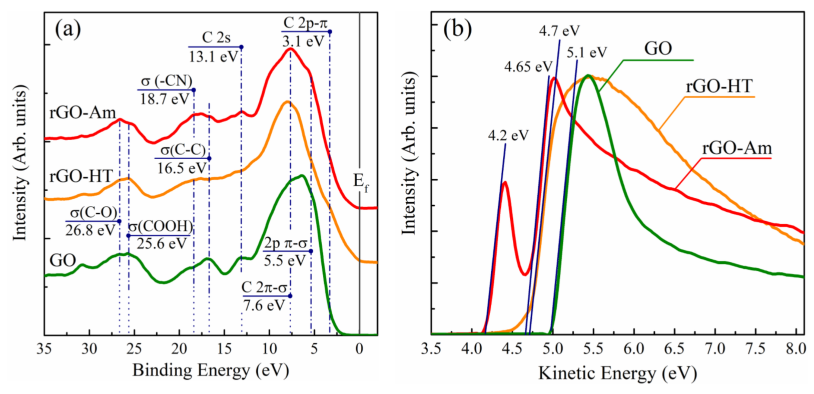
XPS characterization of the initial GO, brominated graphene (rGO-Br) and aminated graphene (rGO-Am)

- ➢ ***C/O ratio: 1.68 → 19.41***
- ➢ ***C-OH&C-O-C (at%): 53.2 → 1.8***
- ➢ ***NH_2 (at%): 4.87***



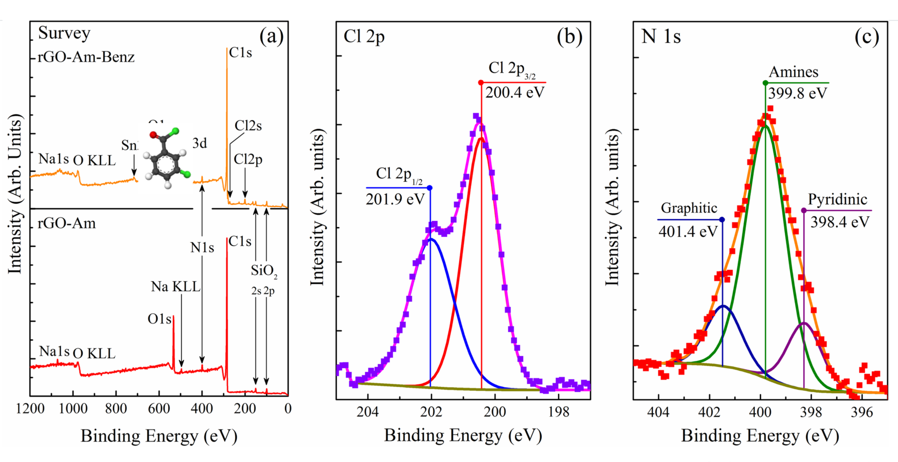
(Left) TEM image and the corresponding SAED pattern of the individual layer of aminated graphene; (Right) SEM image of the aminated graphene film

- ✓ ***Aminated graphene exhibits defect-free structure***
- ✓ ***Owing to the presence of amines – Am graphene layers demonstrates tendency to corrugate and roll***



XPS valence band spectra of the initial GO, rGO and aminated graphene

- ✓ ***Amines has little effect on the Valence band structure***
- ✓ ***Local areas with reduced work function value due to the introduction of amines are formed within the graphene layer***



XPS characterization of the aminated graphene after its grafting with 3-chlorobenzoic anhydride

The mixture of CuCl and HCl wih (left flask) and without (right flask) the aminated graphene

- ✓ ***The chemical reactivity of the synthesized aminated graphene was verified by i) successful grafting with 3-chlorobenzoic anhydride and ii) the test reaction between the amines on graphene layer and Cl- ions with formation of tetraamine copper hydroxide complex (indicated by blue color)***

M. K. Rabchinskii et al. Sci. Rep., 2020, 10, 6902 ***DOI: 10.1038/s41598-020-63935-3***

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Presented materials (Graphene Oxide & Functionalized Graphenes) are commercially available.

See: https://graphtechrus.com/products/

ACKNOWLEDGMENTS

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