Graphene nanoflakes functionalized with cobalt/cobalt oxides formation during cobalt organic framework carbonization

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Supplementary information

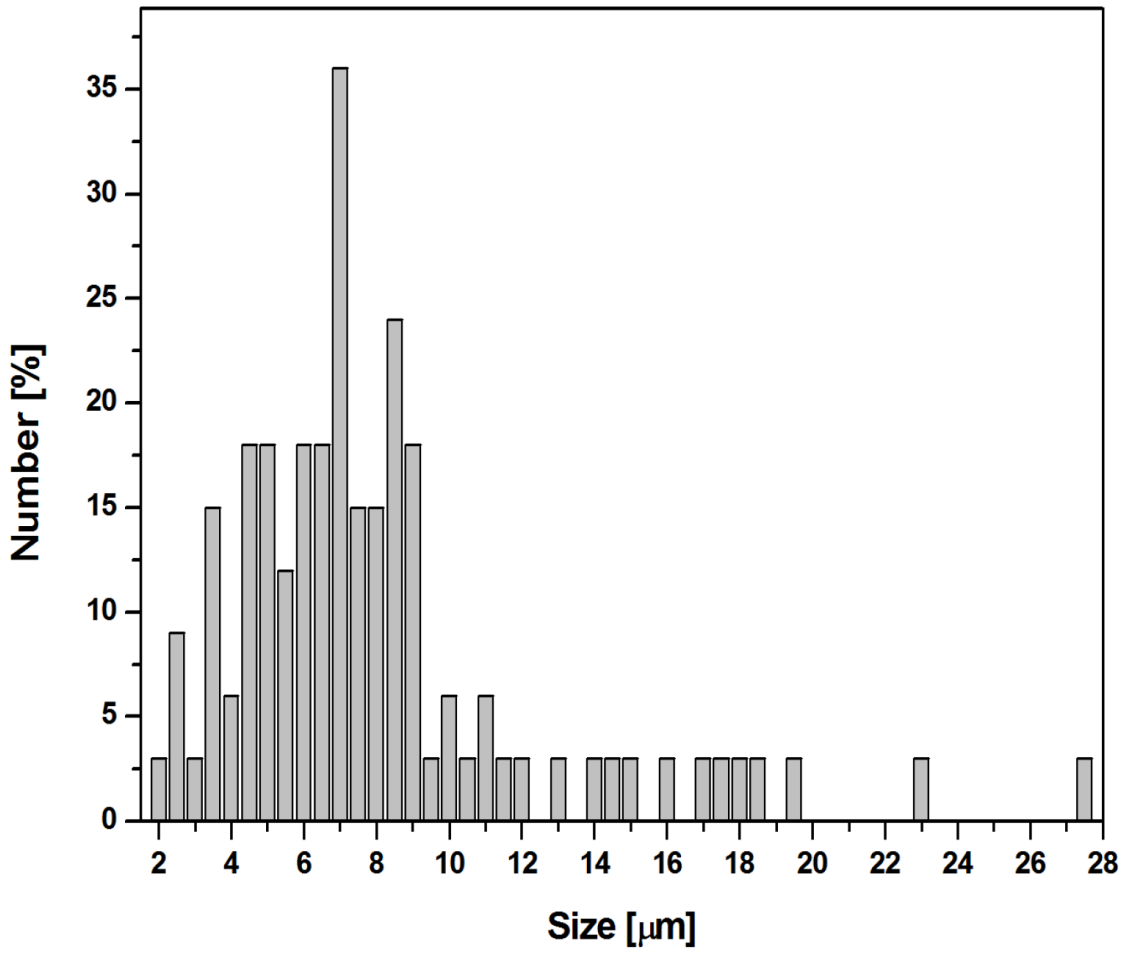

Figure 1s. Metal Organic framework size distribution.

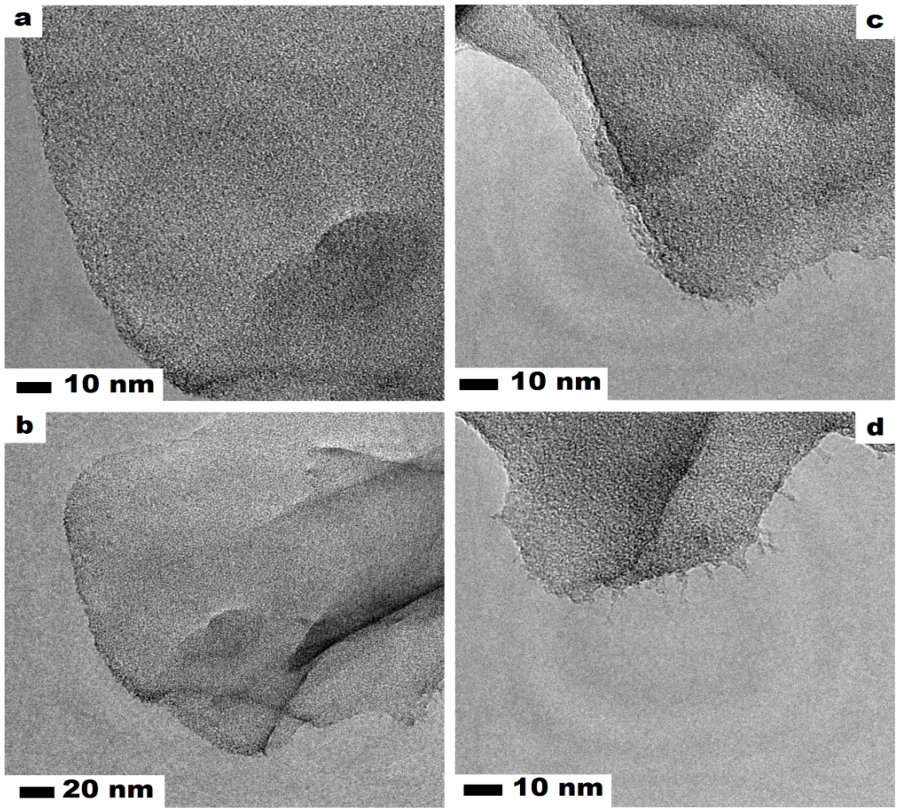

Figure 2s. TEM micrographs of cobalt organic framework (CoOF) before (a-b) and after (c-d) exposition to the electron beam.

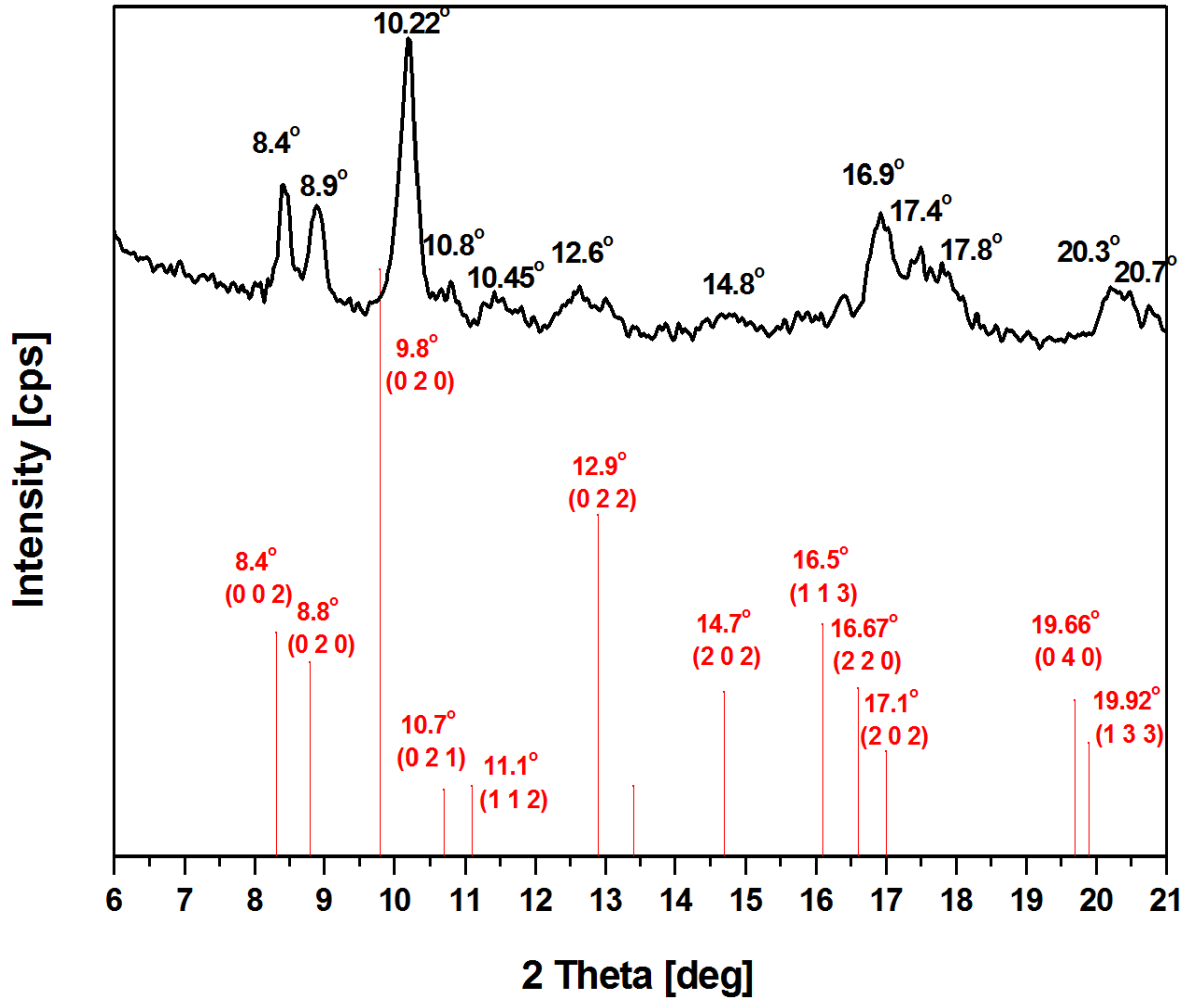

Figure Xs. XRD pattern of obtained MOF structure (black) and simulated (red) peaks positions and intensity according to thestandard card CCDC – 639913.

X-ray analysis shows similar pattern to the isostructural coordination polymers of the cobalt(II) and 2,6-naphthalenedicarboxylate. Fig. 3s shows powder X-ray diffraction (XRD) patterns of the CoOF and isostructural coordination polymer of the cobalt(II) and 2,6-naphthalenedicarboxylate[1]. The reference pattern was obtained from the Cambridge Crystallographic Data Centre (CCDC Nos. 639913). Copies of the data can be obtained, free of charge, on application to the CCDC. The XRD pattern of pristine CoOF shows distinctive reflections at (2θ angle) 8.4° (8.4°), 8.9° (8.8°), 10.22° (9.6°), 10.8º (10.7º), 12.6° (12.9°), 14.8° (14.7°), 16.0° (16.1°), 17.4 (16.6°), 17.8º (17.0º), 18.1º (17.7°), 20.3° (19.7º), 20.7º (20.1º), corresponding to the planes (0 0 2), (1 1 1), (0 2 0), (0 2 1), (0 2 2), (2 0 2), (1 1 3), (2 2 0), (2 0 2), (2 2 2) (0 4 0), and (1 1 4), respectively. The value in the round brackets next to the peak position, shows the reference pattern angle and hkl planes reported in the standard card CCDC – 639913. The measured peak position in the correlation to the reference pattern shows the maximum deviations ~0.8°. This indicates that obtained CoOF consists of linear trimeric Co_3 clusters building block

units. This block units are linked via six carboxylate groups of the BDC ligands to form a three-dimensional network. These building units along a-axis, resembles the hexagonal shape of the obtained CoOF structure[1]. The central metal atom is coordinated octahedrally by six carboxylate oxygen atoms. The other two metal atoms on both sides of the inversion center are coordinated by four carboxylate oxygen atoms and two DMF molecules. Carboxylate groups of BDC ligands adopt bidentate and tridentate coordination modes to bridge metal atoms, similar to the NDC ligands reported by the B. Liu et al. The crosslinking of the building units via the organic ligands results in a three-dimensional network. The organic–inorganic layers can be observed along the c-axis[1]. The coordinated DMF molecules can be removed during heating, creating the unsaturated metal sites. As reported previously by B. Liu et al., MOF after the DMF molecules removing, exhibit different diffraction peaks. Changes made in the structure are reversible after MOF introduction in to the DMF solution[1].

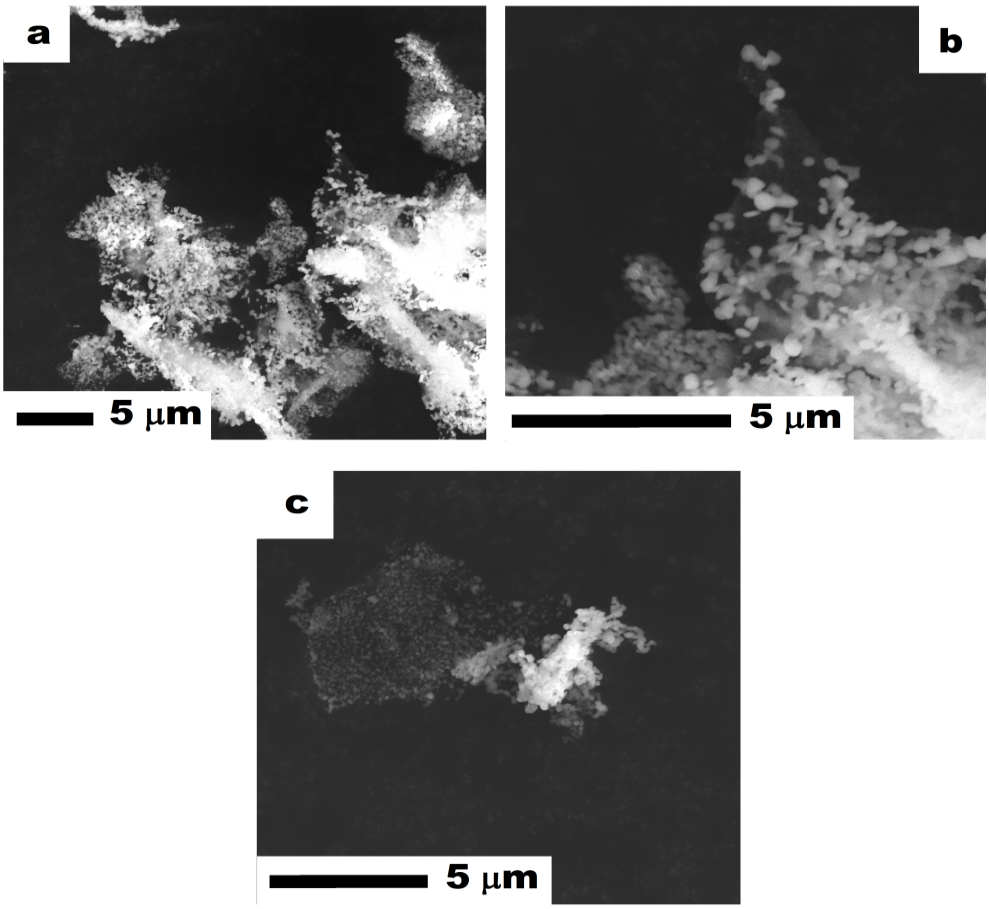

Figure 4s. SEM images of the carbonized cobalt organic framework (CoOF) with cobalt oxides arranged in the shape of the derived carbon structure.

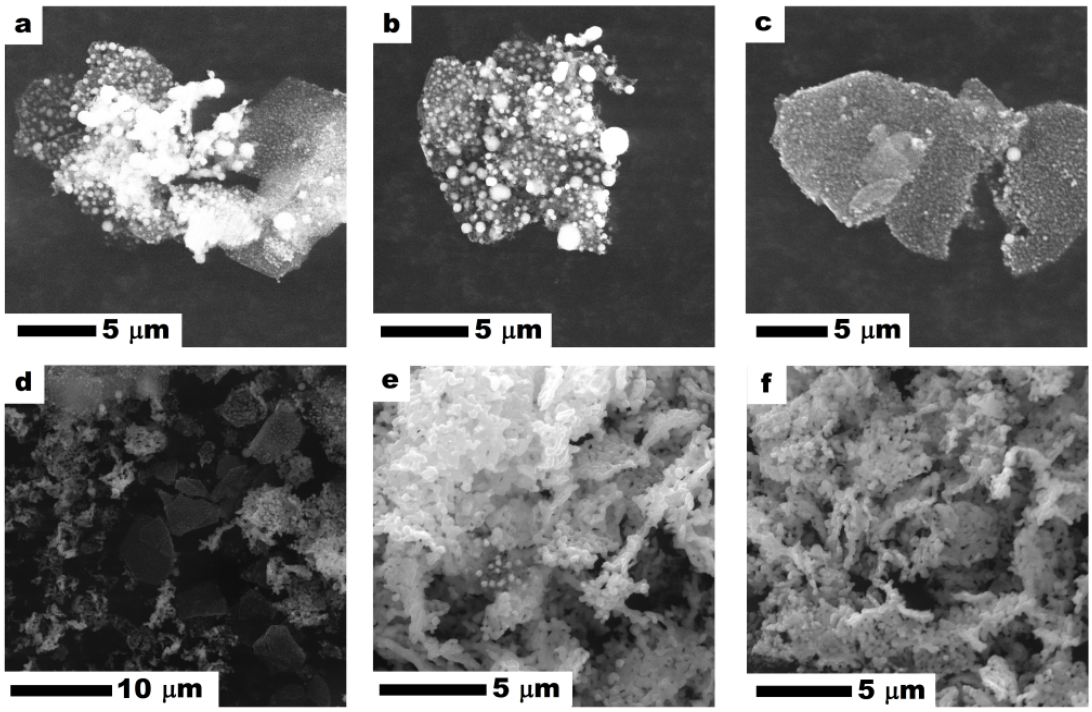

Figure 5s. SEM images of the carbonized cobalt organic framework (CoOF) with cobalt oxides agglomerate and cavities around them (a-b), cracked carbonized framework (c) and cobalt oxides agglomerates detached from the carbonized frameworks (d-f).

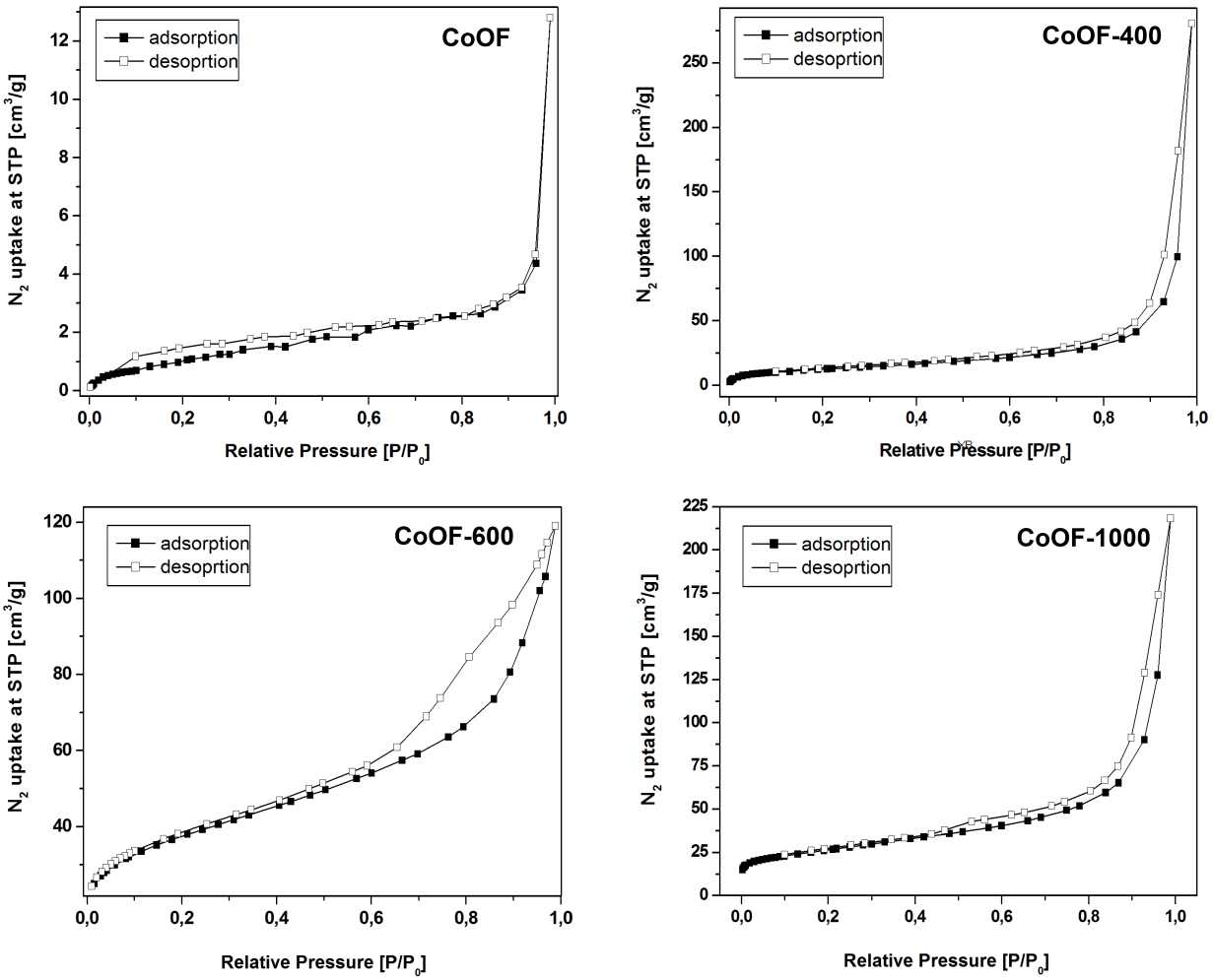

Figure 6s. Isotherms of the pristine (CoOF) and carbonized CoOF structures in the temperature of: 400 ºC (CoOF-400); 600 ºC (CoOF-600) and 1000 ºC (CoOF-1000).

References

1. B. Liu, R.Q. Zou, R.Q.; Zhong, S. Han, H. Shioyama, T. Yamada, G. Maruta, S. Takeda, Q. Xu, *Microporous Mesoporous Mater.*, 2008, **111**, 470–477.