

Synthesis of MOF-derived bimetallic nanocarbons CuNi@C with potential applications as counter electrodes in solar cells

Lizbeth Marroquín Tijerina, Cesar M. Oliva González, Boris I. Kharisov, Thelma E. Serrano Quezada, Yolanda Peña Méndez, Oxana V. Kharissova and Idalia Gómez de la Fuente

For the **counter electrode preparation**, 80 mg of copper-nickel carbon-based material was mixed with 20 mg of Nujol, then the samples were put in a mortar grinding for a while, using a Teflon tube 0.5 mm diameter and copper wire. This way, a carbon paste electrode was created.

Table S1. Atomic percentages of carbons derived from MOFs by EDS.

Temperature	300 °C				500 °C			
	Cu%	Ni%	C%	O%	Cu%	Ni%	C%	O%
Cu@C	22.29	–	47.59	30.12	18.84	–	74.75	6.71
Ni@C	–	7.91	89.45	2.64	–	16.41	81.79	1.81
CuNi _{0.25} @C	9.96	5.44	73.22	11.38	19.67	6.26	70.31	3.76
CuNi _{0.5} @C	8.66	8.7	74.5	8.14	16.1	8.66	71.92	3.29

Table S1 shows the atomic percentages of different carbon samples derived from MOFs. As it is seen, when the pyrolysis temperature increases from 300 to 500°C, the atomic percentage of oxygen decreases. This is since at 300°C the carbonization of the MOFs is still incomplete, allowing them to still retain carboxylic groups from the binder. As the temperature of the pyrolysis increases, they are released in the form of water or carbon oxides. However, after pyrolysis at 500°C, a small proportion of oxide of the cations in the sample is still retained, mainly copper, since it is easier to be oxidized than nickel. This is independent of the inert atmosphere of nitrogen that is used, since it comes from the oxygen deposited in the form of water from the same sample. Therefore, it was decided only to perform the pyrolysis at 500°C.

Figure S1 shows mixed peaks for the copper and nickel MOF; peaks are shown shifted a bit due the presence of both metals in the structure. Major peaks are observed at $2\theta = 6.69^\circ$, 11.5° , 13.46° , 17.52° , 18.75° , 21.30° and 26.04° which corresponds to (200), (400), (151), (052), (333) and (111) planes, respectively. The strong peaks indicate a combination of structures of monometallic MOF, giving birth a new and similar structure for bimetallic MOF. The diffractograms were obtained on a Bruker D2 Phaser X-ray diffractometer at room temperature with a monochromatic radiation of Cu 1.5418 Å; the intensity was measured in the range of 2° to 70° with a step of 0.05 every 0.5 s.

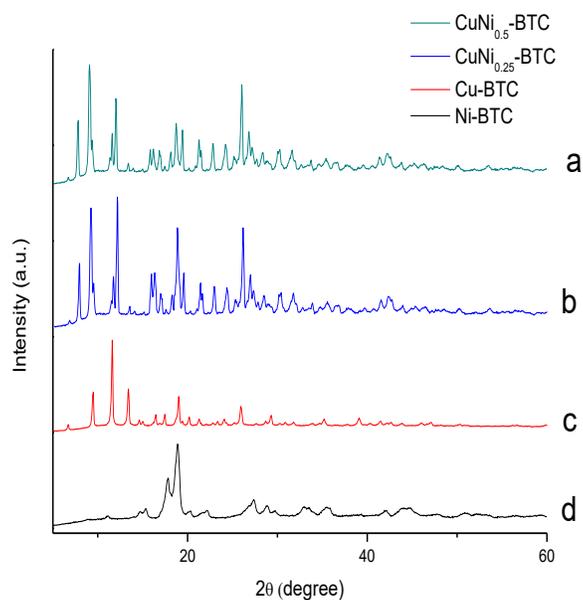


Figure S1 XRD of mono and bimetallic MOFs.

In **Figure S2**, it is seen that the Ni@C carbon material contains different needles, converged in a core. The individual needles have an average width starting from 135 nm, while the particles on their surface have an average size of 34 nm. The micrographs were obtained using a scanning electron microscope JEOL JSM6701F.

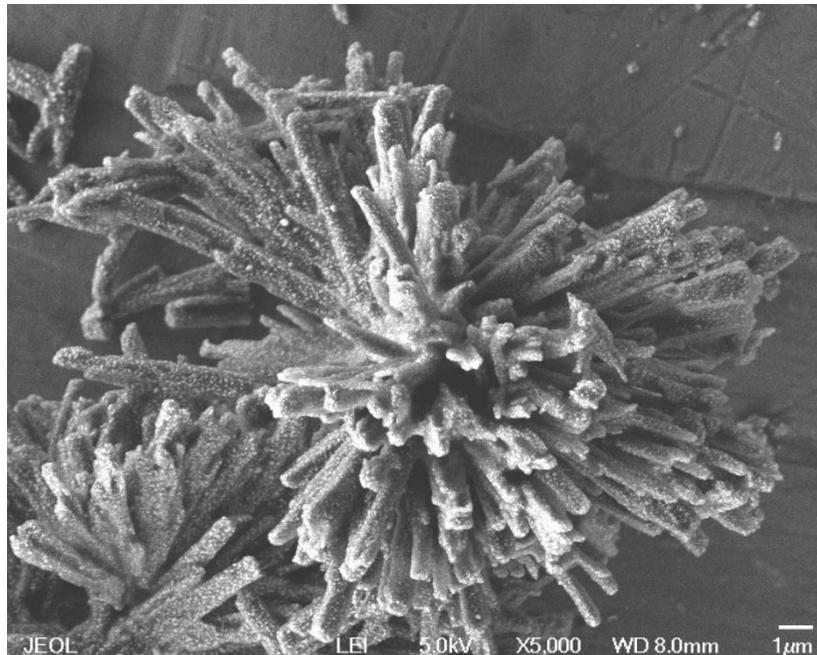


Figure S2 SEM image of Ni@C.

Figure S3 shows that Cu@C sample contains particles in the form of a sphere on its surface, with an approximate size of 48 nm. These particles are the metallic copper, propagating uniformly on the surface of the material, as inside the cavities with medium size of 269 nm.

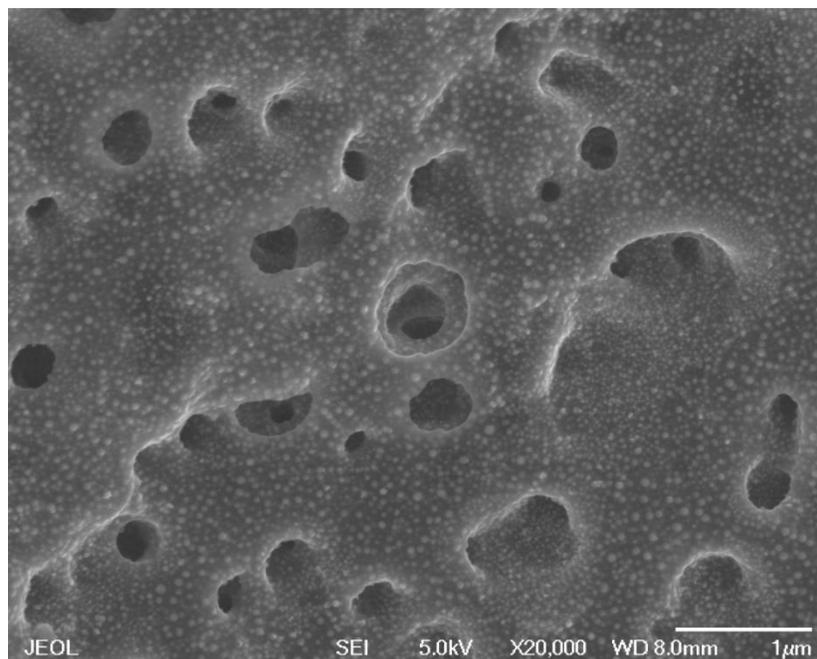


Figure S3 SEM images of Cu@C.

In the case of **Figure S4**, it is observed that CuNi_{0.25}@C contains spherical agglomerates having sizes starting from 125 nm; it should also be noted that the spheres are highly rough and are formed by needles.

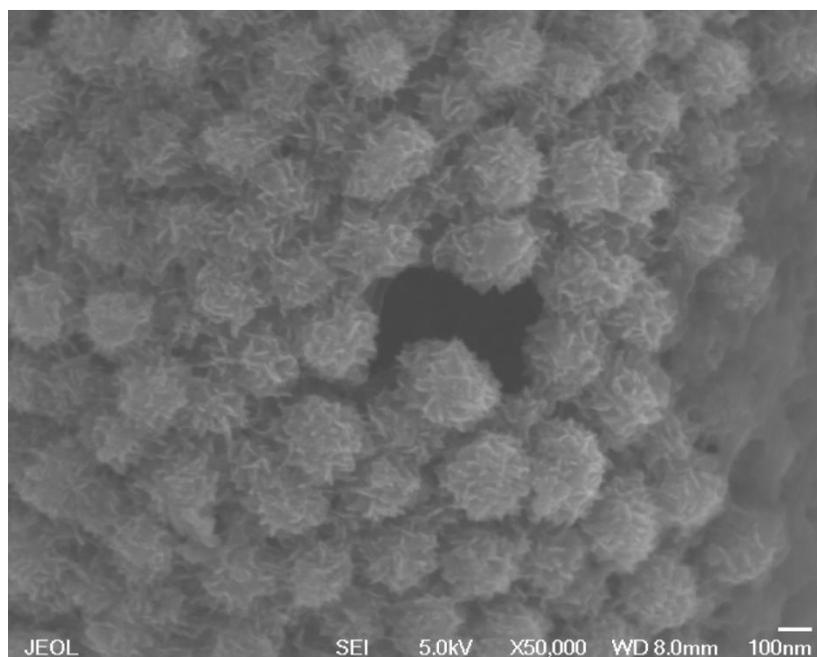


Figure S4 SEM images of $\text{CuNi}_{0.25}\text{@C}$.

The morphology of $\text{CuNi}_{0.5}\text{@C}$ is shown in **Fig. S5**, representing fibers, ending with spherical shapes, whose thickness vary a lot. However, small spheres of approximately 21 nm are observed on the surface of these fibers.

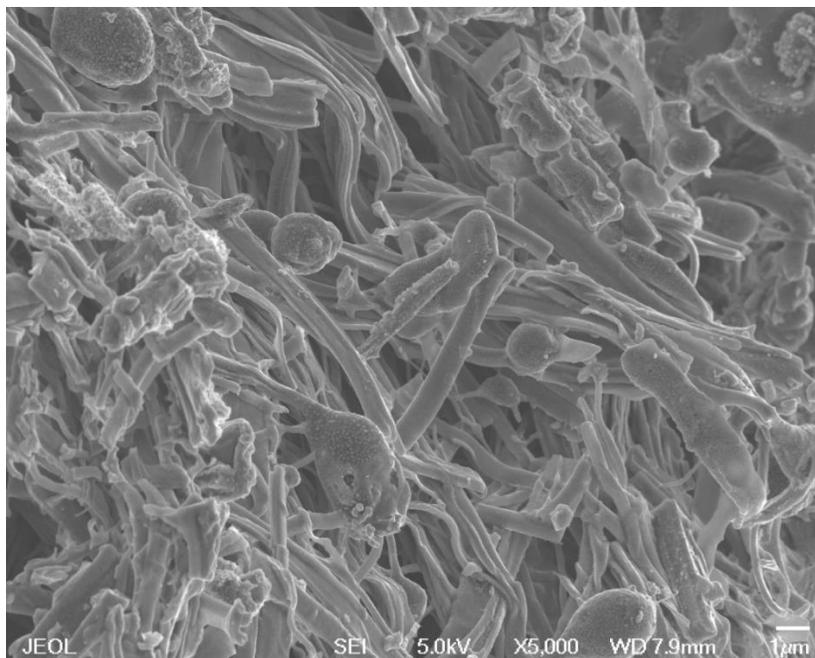


Figure S5 SEM images of $\text{CuNi}_{0.5}\text{@C}$.