ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Binderless thin films of zeolite-templated carbon electrodes useful for electrochemical microcapacitors with ultrahigh rate performance

*Ángel Berenguer-Murcia[a], Ramiro R. Ruiz-Rosas[a], Jaime García-Aguilar[a], Khanin Nueangnoraj[b], Hirotomo Nishihara[b], Emilia Morallón[c], Takashi Kyotani[b], and Diego Cazorla Amorós[a,]**

[a] Departamento de Química Inorgánica and Instituto Universitario de Materiales, Universidad de Alicante, Campus de San Vicente del Raspeig, Ap. 99, 03080 Alicante (Spain). E-mail: cazorla@ua.es

[b] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Sendai, 980-8577 (Japan)

[c] Departamento de Química Física and Instituto Universitario de Materiales, Universidad de Alicante, Campus de San Vicente del Raspeig, Ap. 99, 03080 Alicante (Spain)

Zeolite colloidal suspension synthesis

A suspension of zeolite FAU nanocrystals was prepared following the methodology described by Schoeman et al.[1] by hydrothermal synthesis of a clear solution at 373 K for 96 hours with the following composition: 2.46 $(TMA)_2O$:0.04 Na_2O:Al_2O_3:3.4 SiO_2:370 H_2O. The synthesis mixture was prepared mixing the appropriate amount of ulltrapure water, aluminium isopropoxide, tetraethyl orthosilicate, tetramethylammonium hydroxide pentahydrate, and sodium hydroxide. The resulting zeolite nanocrystals were recovered by centrifugation at 22000 rpm, washed and dried. SEM, TEM, and XRD (See Figure S1) analyses clearly showed that the prepared FAU zeolite crystals were of sizes ranging between 25 and 60 nm in size. In order to perform EPD experiments, 300 mg of the obtained zeolite nanocrystals were resuspended in 50 mL of water containing a small amount of concentrated ammonia (pH 9-10).

Electrophoretic deposition of zeolites on current collectors

The nanozeolites were suspended in basic medium and transferred to an electrochemical cell where a platinum wire was used as the cathode. The anode, which in our case was the material intended as current collector, was a macroporous carbon disc (Poco Graphite DFP-1, semiconductor grade) with a mean pore size of 1 µm and a diameter of 13 mm. The area of the carbon disc exposed to the zeolite colloidal suspension was kept constant at 0.57 cm^2 by means of a Teflon device (See Refs. [11,12] in the manuscript). EPD of the nanozeolite crystals was performed by passing a constant current density of 9 mA/cm^2 for 15 minutes, which resulted in the exposed area of the current collector to become fully covered by a thin layer of FAU nanocrystals.

Synthesis of ZTC

Thin layers of zeolite templated carbon were prepared using the as-synthesized nanozeolite-coated current collectors by CVD in a vertical furnace (See Ref. [8] in the manuscript). In a typical experiment, one of the macroporous carbon discs coated with a thin layer of zeolite nanocrystals was placed vertically inside a quartz furnace and heated at 873 K with a heating rate of 5 K/min under a N_2 atmosphere with a flow rate of 150 sccm. Once the target temperature was reached, the gas stream was switched to a mixture of acetylene (15% vol.) and N_2 (85%) and CVD was performed two hours. The gas stream was switched to N_2 again (150 sccm) and the sample was heated to 1123 K at 5 K/min with a dwelling time of three hours. After recovery from the quartz furnace, the zeolitic template was removed by immersing the sample in 20% HF for 12 hours at room temperature and washing the resulting material with abundant distilled water.

In the case of the application of CVD to the as-synthesized powdered nanozeolite, 300 mg of the colloidal crystals were introduced in the quartz furnace and CVD was applied as described above. Removal of the zeolitic template was carried out by washing with concentrated HF (48 wt.%) for 6 hours.

In our approach the as-synthesized FAU nanozeolite crystals were used for all samples (powders and composites), and thus the templating agent (tetramethylammonium ions) acts as a complementary carbon source, as other authors have already reported[2]. It must be noted, however, that when the nanozeolite samples deposited by EPD on the current collectors were calcined prior to CVD, no ZTC formation was observed on the carbonaceous current collector for the conditions described in this study.

Electrochemical measurements

The selected samples were tested for their electrochemical performance by cyclic voltammetry in a three-electrode cell in 1 M H_2SO_4 using a Pt wire as the counter electrode and a Ag/AgCl/Cl^-(sat.) reference electrode using an Autolab PGSTAT30 potentiostat with SCANGEN module, In the case of the binderless samples the exposed electrode surface was 0.57 cm^2 in all experiments. The employed active mass of a electrode in the case of the powdered sample was 9.05 mg, with a loading density of 6.82 $mg \cdot cm^{-2}$. Different scan rates going from 1 to 10000 mV/s have been performed. Galvanostatic charge-discharge experiments were performed using current intensities which ranged from 1 to 40 mA. In the case of the ZTC sample directly synthesized on the current collector, the sample was directly used as working electrode. In the case of the powdered sample, the ZTC electrode was prepared as reported elsewhere (See Ref. [15] in the manuscript). All experiments were carried out at room temperature unless stated otherwise

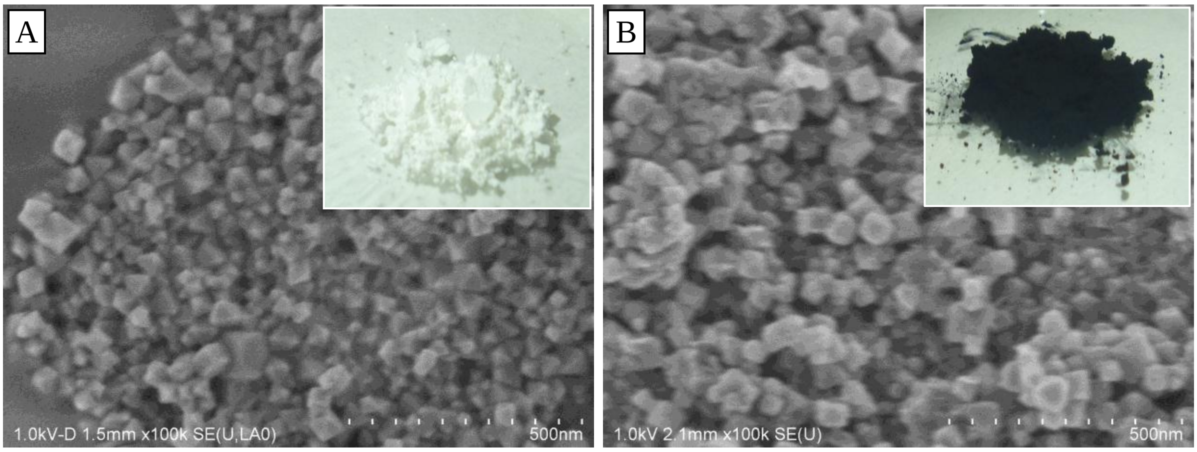


Figure S1. FE-SEM images of the (A) as-synthesized nanozeolite powder and (B) ZTC powder obtained from the nanozeolite after HF washing. Insets are photographs of these samples.

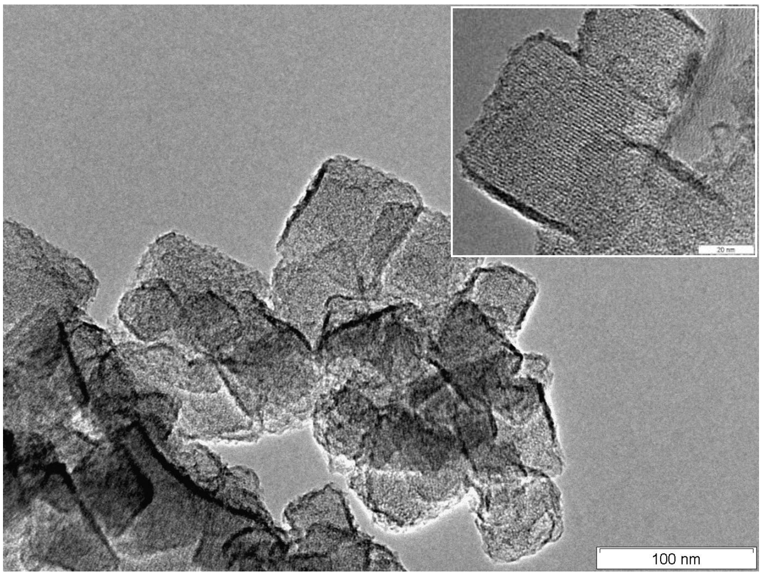
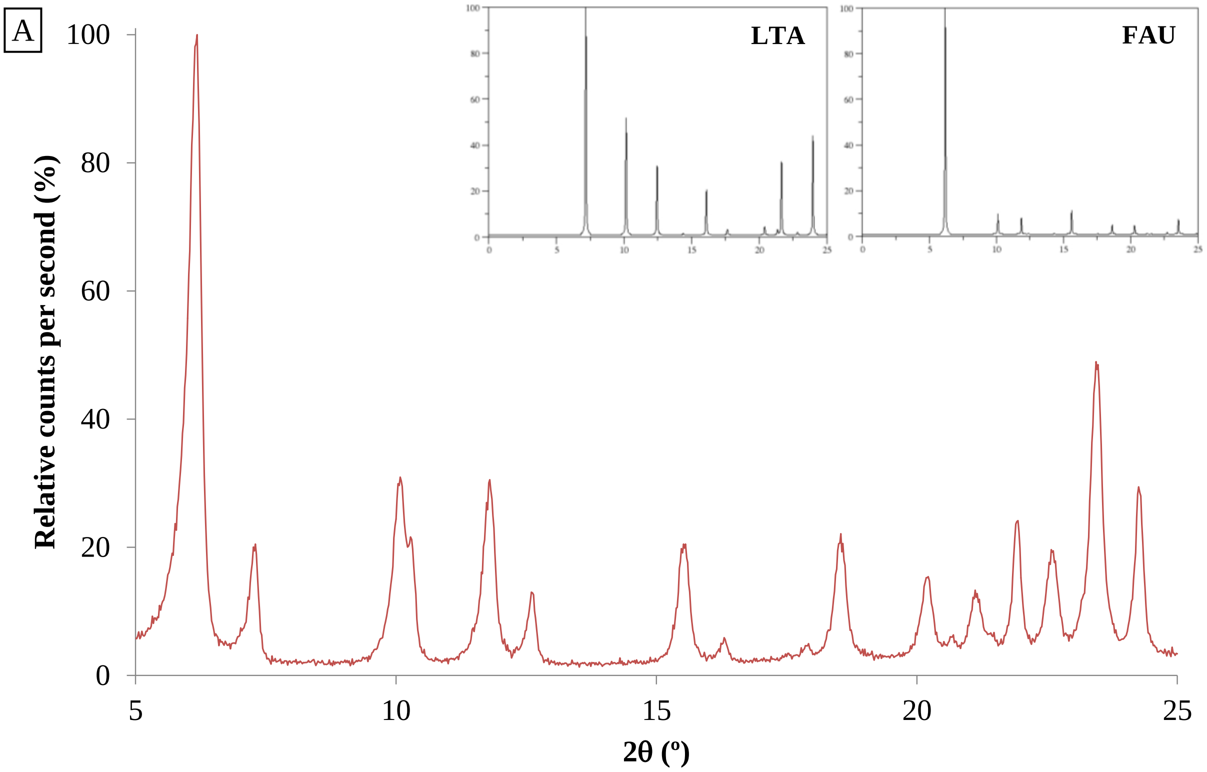


Figure S2. TEM images of ZTC obtained from the powdered nanozeolite after HF washing, and Scale bars: 100 nm; Inset scale bars: 20 nm.

The amount of ZTC layer deposited on the current collector by the aforementioned method (EPD followed by CVD) was very small due to the thin film of nanozeolite deposited in the first place, and thus analysis of the resulting material by either XRD or Thermogravimetry was complicated. For this reason the ZTC in powder form obtained using the same starting nanozeolite and following the same CVD protocol was analyzed in order to determine the amount of deposited carbon inside the nanozeolite crystals and to determine its purity (Figures S3 and S4). Thermogravimetric analysis of the powder ZTC sample before HF washing revealed that the carbon content of the sample was 43.7%, which is very high for this kind of materials.[3] This high carbon loading may be due to a very significant amount of carbonaceous materials with poor crystallinity, as reported previously.[4] XRD (Figure S3) and TG analysis of the powder ZTC sample after HF washing were performed in order to confirm this hypothesis. Pyrolytic carbon materials show a broad band at 2θ angles of 23-

26º,[5] but in our case a very weak band could be observed, which was only visible upon zooming in the aforementioned region. This clearly indicates that the carbon loading of the zeolitic template takes place in the inner porosity of the nanozeolite crystals, with a very small fraction of the carbon being deposited in their outer surface as pyrolytic carbon, giving rise to a ZTC with a more dense structure. Furthermore, TG analysis (Figure S4) revealed that the amount of pyrolytic carbon present in our ZTC sample was lower than 5 wt %. Thus, the size of the zeolitic template crystals plays a key role in the efficiency with which the carbon precursor fills their porosity. The N_2 adsorption isotherm obtained at 77 K for the powder ZTC (Figure S5) showed a typical type I shape and BET analysis indicated that its apparent surface area was 1250 m^2/g.



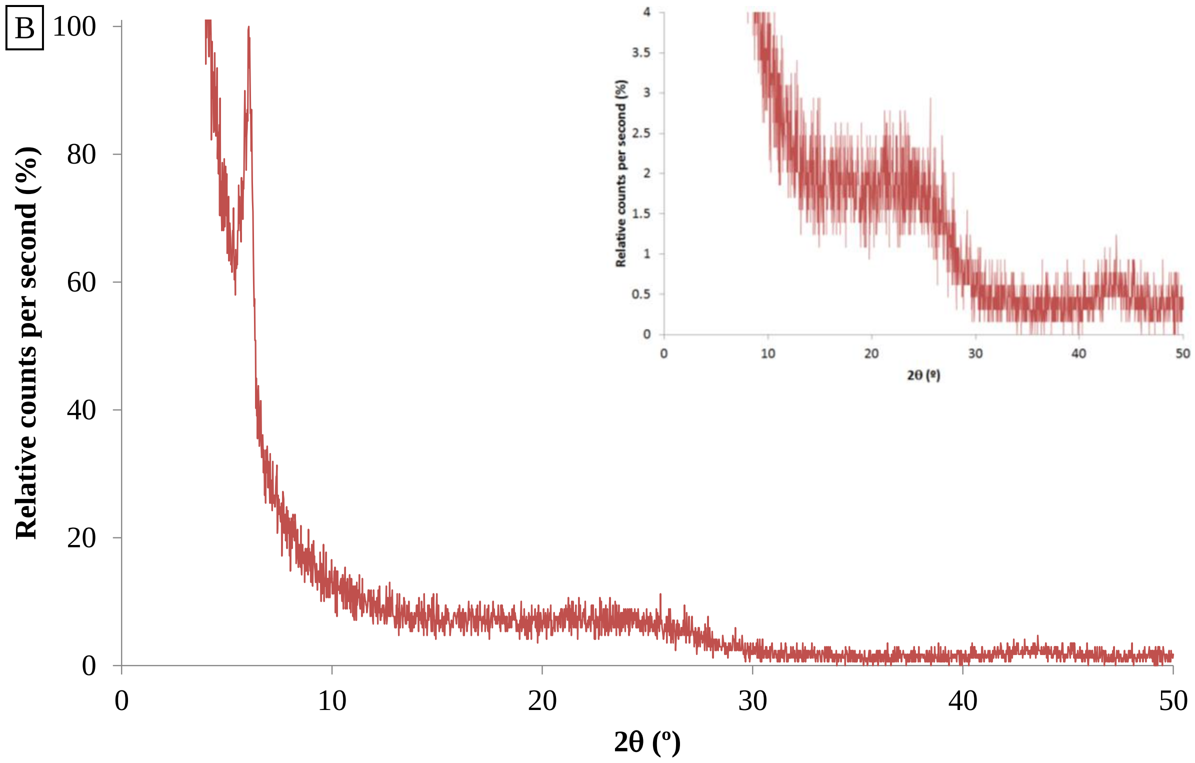


Figure S3. XRD patterns of (a) the as-synthesized FAU nanozeolite powder (the inset shows the simulated XRD patterns for both pure FAU and LTA zeolites), (b) ZTC sample obtained from the FAU nanozeolite after 4 hours of CVD and HF washing. The inset in Figure S1B shows an enlarged view of the spectrum in which the band corresponding to pyrolytic carbon appears.

Fig. S3 clearly shows that the CVD method employed successfully replicates the FAU zeolite structure with an almost negligible presence of pyrolytic carbon, as evidenced by the very weak band at 2θ angles between 23-26º. In this respect, it is remarkable that the contamination of the FAU nanozeolite samples due to the presence of small LTA crystals does not seem to influence the outcome of the CVD process.

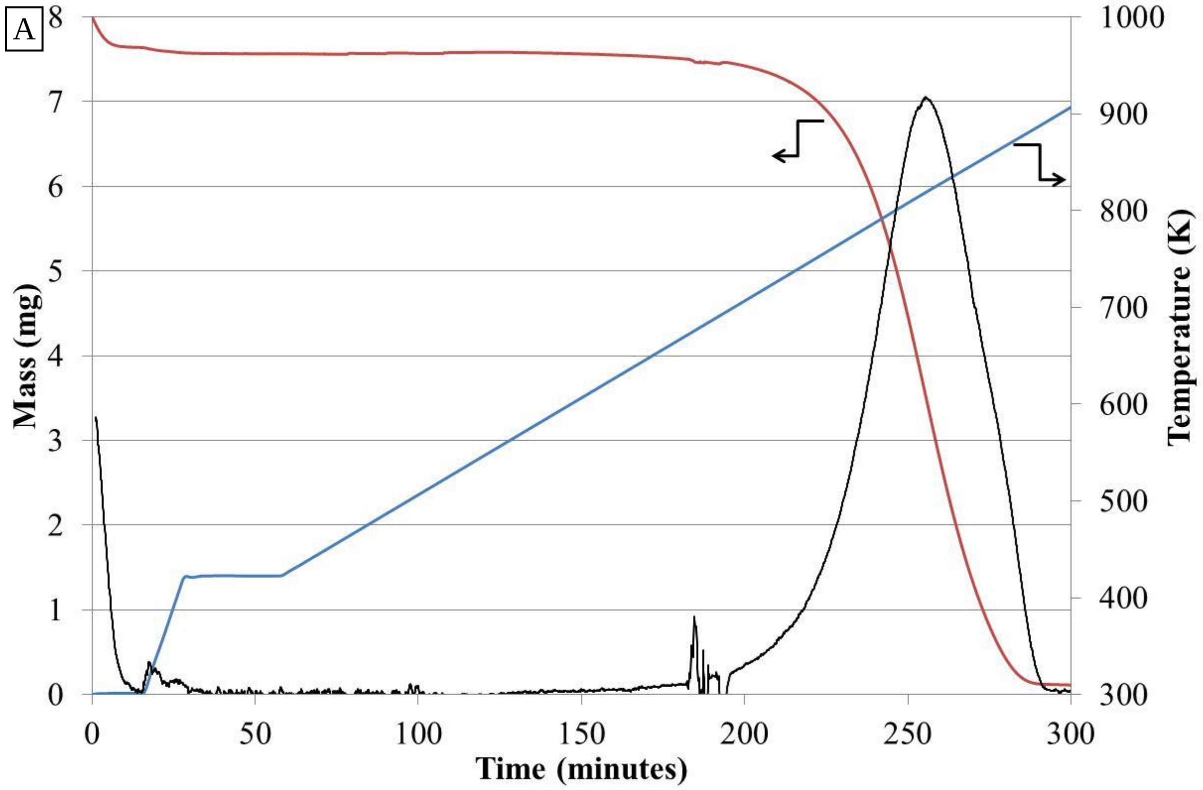


Figure S4. Thermogravimetry profile of the ZTC sample obtained from the FAU nanozeolite after 4 hours of CVD and HF washing. Experimental conditions: Atmosphere: Synthetic air; Flow rate: 80 sccm; Heating rate: 2K/min. The differential TG curve is shown (black line) for a better differentiation of the burn-off process of the ZTC and the pyrolytic carbon present in the sample.

Figure S4 corroborates the observations made from the XRD experiments. The ZTC material prepared in this study present a very low amount of non-ZTC carbon material, as evidenced by the TG profile. This is further supported by the differential curve shown. The amount of pyrolytic carbon was obtained by deconvolution of the differential curve was estimated at 4 wt %, which clearly reflects the high purity of the ZTCs obtained using FAU nanozeolite crystals. It is remarkable that the burn-off of the ZTC takes place at higher temperatures than those reported previously in the literature. This observation has not been hitherto reported and may only be attributed to the outstanding influence of the use of nanocrystals as templates for the preparation of ZTCs. In this respect, considering the very short diffusional pathway that the carbon precursor must go through inside the nanozeolite inner surface the filling of the zeolite channels takes place to a larger extent, up to reaching a point in which a more stable carbon structure is formed.

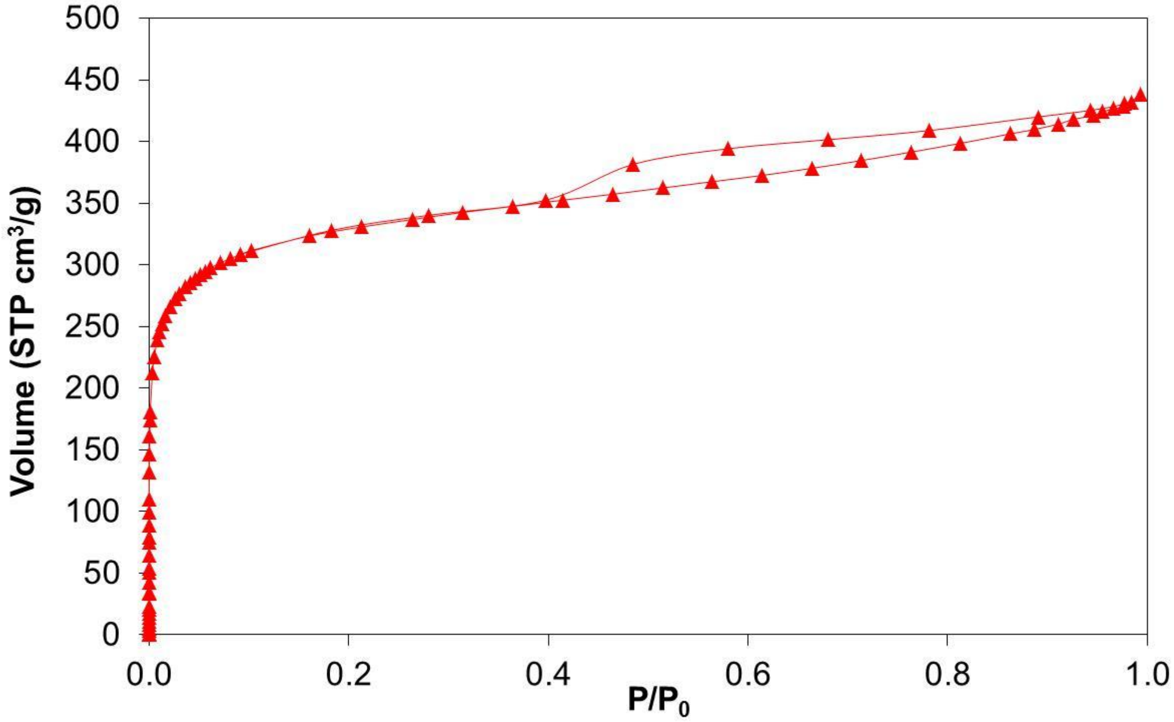
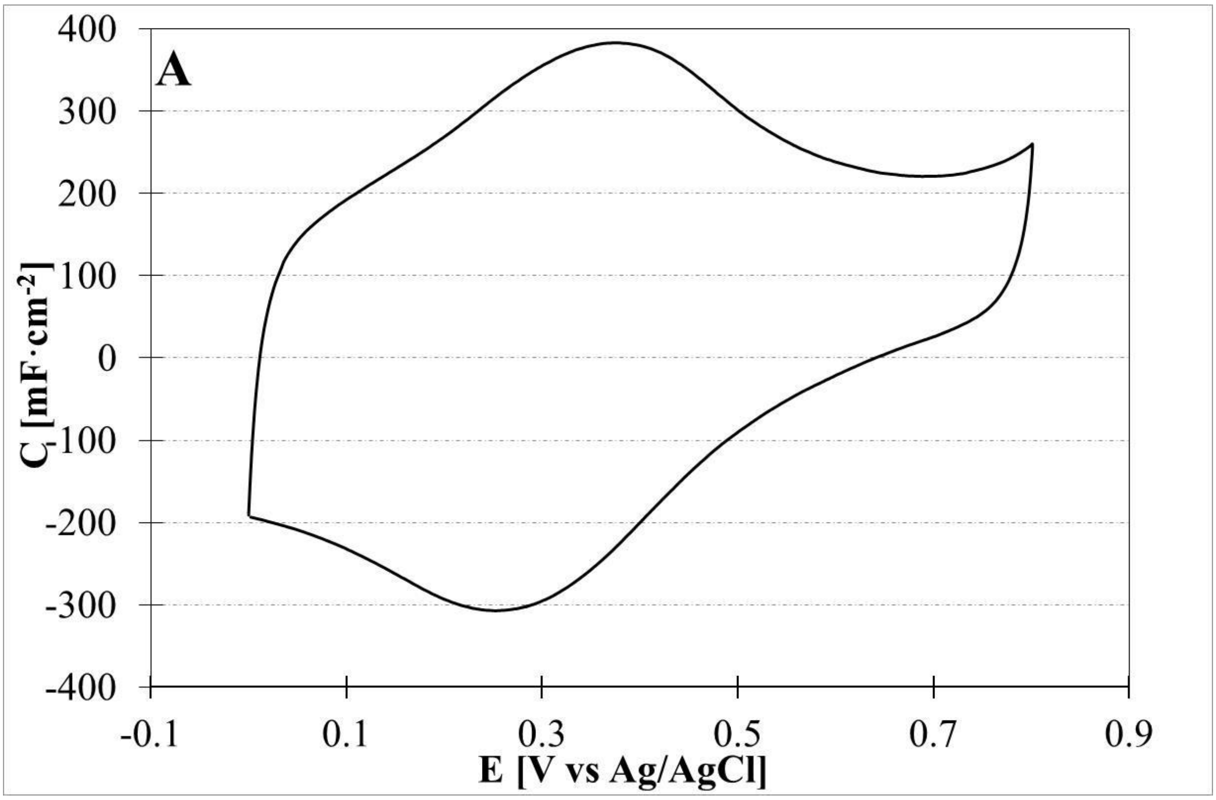
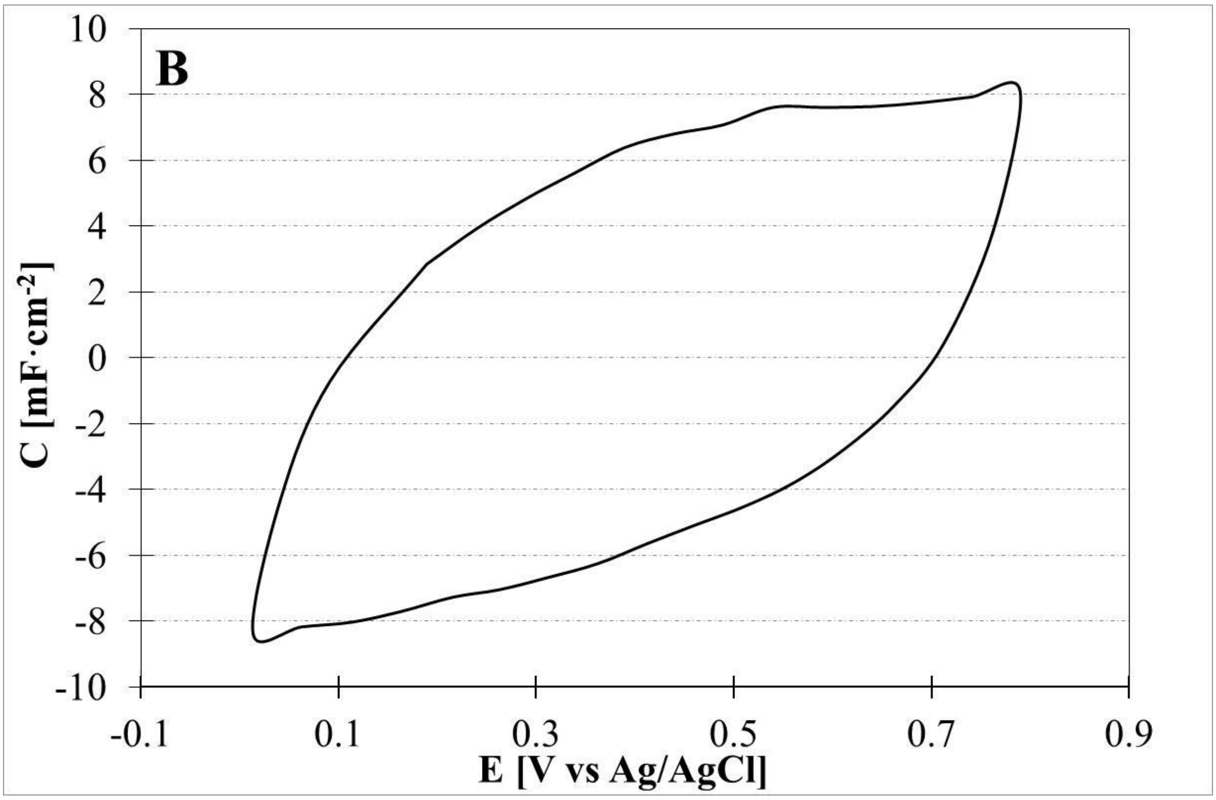


Figure S5. N_2 adsorption isotherm obtained at 77K for the ZTC sample obtained after 4 hours of CVD.

From Fig. S5, it is clear that the sample shows a type I isotherm, characteristic of microporous solids arising from the porous structure of the ZTC. A small degree of mesoporosity is also observed, most likely due to adsorption of N_2 in the intercrystalline spaces of the ZTC crystals of nanometric size. By using a simple approximation considering spherical ZTC particles, for the size interval analyzed in this study, the interparticle space should range from 4 to 6 nm. Comparing the relative pressures at which desorption takes place for the two samples with a thorough analysis on the pore size of mesoporous materials reported previously,[6] the estimated mesopore size would be between 4-5 nm for the sample prepared after 4 hours of CVD, which fits our estimation quite well. One very important aspect to take into account is that despite the fact that the ZTC sample possesses high purity (as shown in Figs. S3 and S4), the N_2 adsorption isotherm differs markedly in terms of the initial N_2 uptake and subsequent apparent surface area. This observation could be a direct consequence of a more compact (and thermally stable) carbon structure due to the high loading of carbon inside the zeolitic porous structure as a result of the CVD process.


A
400
300
200
100
0
-100
-200
-300
-400
C [mF·cm⁻²]
-0.1
0.1
0.3
0.5
0.7
0.9
E [V vs Ag/AgCl]


B
10
8
6
4
2
0
-2
-4
-6
-8
-10
C [mF·cm⁻²]
-0.1
0.1
0.3
0.5
0.7
0.9
E [V vs Ag/AgCl]

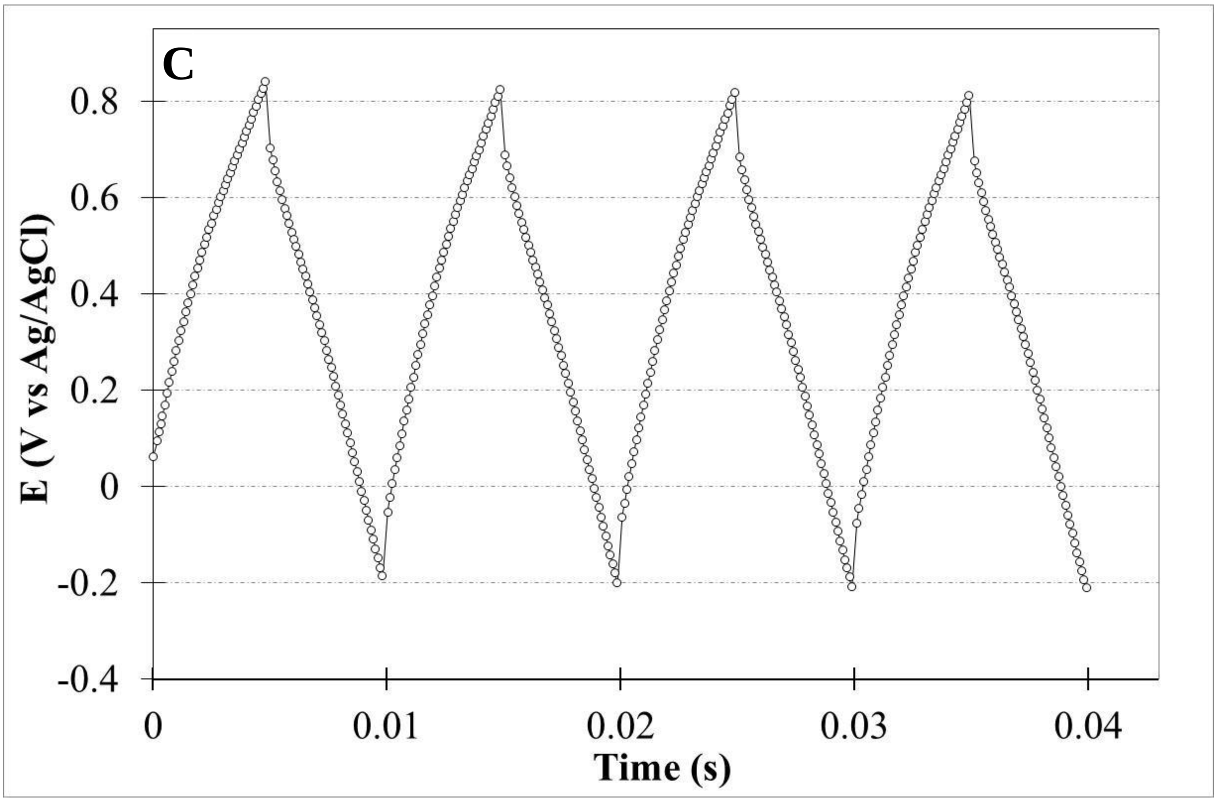


Figure S6. (A) Cyclic voltammogram obtained for the ZTC powder a scan rate of 2 mV·s^{-1} (B) Cyclic voltammogram obtained for the binderless ZTC layer at a scan rate of 10000 mV·s^{-1} (C) Galvanostatic charge-discharge experiment for the macroporous carbon support using a specific current of 70 mA/cm^2.

As it can be clearly observed, the observed ohmic drop in Figure 3C for the binderless ZTC sample described in this study may be attributed to the macroporous carbon disc used as current collector and to the mass transfer resistance of the electrolyte , which further highlights the outstanding electrochemical performance of the thin ZTC films analyzed in this study.

References

1 B.J. Schoeman, J. Sterte, J.-E. Otterstedt, Zeolites, 1994, **14**, 110
2 A. Pacula, R. Mokaya, J. Phys. Chem. C, 2008, **112**, 2764
References
3 Z. Ma, T. Kyotani, A. Tomita, Chem. Comm. 2000, 2365
4 J. Rodríguez-Mirasol, T. Cordero, L.R. Radovic, J.J. Rodríguez, Chem. Mater.1998, **10**, 550

5 Z. Ma, T. Kyotani, A. Tomita, Carbon 2002, **40**, 2367

6 A. Galarneau, D. Desplantier, R. Dutartre, F. Di Renzo, Micropor. Mesopor. Mater. 1999, **27**, 297