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SUPPORTING INFORMATION

Metal-Free Carbon Dot-Microporous Graphitic Carbon Heterojunctions as Photocatalysts for CO₂ Reduction.

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EXPERIMENTAL SECTION

Carbon dots synthesis. For the preparation of the carbon dots, 3 g of citric acid (Aldrich) were dissolved in 8 mL of pure water (Milli-Q quality) with 1 g of urea (Aldrich). After that, the mixture was irradiated for 10 min in a 700 W microwave. The black solid was dried at 100 °C overnight to remove the volatile byproducts. The following day, the carbon dots were suspended in water to remove b the bigger particles y centrifugation at 600 rpm for 1 h. The supernatant was extracted using the solvent mixture 20 mL H₂O+ 20 mL MeOH + 40 mL dichloromethane and then, 20 mL H₂O+ 20 mL MeOH + 20 mL dichloromethane.

Synthesis of the photocatalysts. 400 mg of α -cyclodextrin were dissolved in 20 mg of pure water and stirred until their complete solution. Then, different amounts of CDs were added to this solution to get CD-x/mpC (x being the percentage of CD vs. cyclodextrin. After 24 h of stirring, the mixture was dried at 60 °C. Finally, the brown solid was pyrolyzed using a heating slope of 10 °C×min⁻¹ up to 900 °C and maintained in inert atmosphere at this temperature for 2 h.

*Photocatalytic CO*₂ *reduction.* First, the CD-x/mpC was ultrasonicated in 40 mL of acetonitrile ((>99.9%, Sigma-Aldrich), 1,3 mg×mL⁻¹, with a FisherbrandTM Model 705 Sonic tip, 40% of amplitude. power 700 W. The 1-h sonication consisted in pulses of 1 s ultrasound on, 1 s ultrasound off.

For the reaction, the needed amount of the previous suspension to have a concentration of 0.5 mg×mL⁻¹ was dispersed in to have a total volume of 20 mL. 4 mL of triethanolamine (Sigma-Aldrich) was added as electron donor and 4 mL of MilliQ water as proton donor. Acetonitrile was added to reach 20 mL of the total volume for the reaction.

The suspension was introduced in a 51 mL quartz reactor provided with a manometer, an inlet and outlet valves. It was purged with pure CO_2 for 10 min to get the complete saturation of the acetonitrile and finally, pressurized until 1.4 bar (absolute pressure).

The irradiation was carried out using a 300 W Xe lamp (Hamamatsu, 1.6 sun power) with UV-Vis light range. The gas phase was periodically sampled with an air-tight syringe for their analysis using a gas chromatograph (Agilent 490 MicroGC) equipped with a molecular sieve 5 Å column with TC detector and Ar as carrier gas. For the CO production, a 7890A chromatograph with a Carboxen[®]-1010 PLOT L × I. D. 30 m × 0.53 mm column, average thickness 30 μ m with a TC detector and He as the carrier gas.

For the stability test, after 22 h of irradiation, the material was washed three times using pure water and centrifugation for 20 min at 6000 rpm.

Sample characterization. Isothermal gas adsorption measurements were carried out in a Micromeritics ASAP2000 apparatus. The samples were activated under vacuum

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until constant weight, before N2 or CO2 adsorption at 77 or 296 K, respectively. Raman spectra were recorded with 514 nm laser excitation on a Renishaw Raman spectrometer ("Reflex") equipped with a Leica optical microscope and a charged coupled device camera. The laser power in the sample was 25 mW. Each spectrum was the average of 20 acquisitions at a resolution of 4 cm⁻¹.

The XRD pattern was recorded using a Cubix-pro PANalytical diffractometer in the range from 5 to 90° at the scan rate of $1^{\circ} \times s^{-1}$.

The combustion elemental analyses were measured with a Euro EA 3000 analyzer.

TEM images were recorded on a JEOL JEM 2100F electron microscope with a voltage of 200 kV coupled with an X-Max energy-dispersive X-ray detector (EDS). FESEM images were taken on a ZEISS ULTRA 55. Samples were prepared by casting one drop of the suspended material in acetonitrile onto a carbon-coated copper TEM grid and allowing it to dry at room temperature.

Valence band maximum energy values for mpC and CD were by XPS. The Fermi energy value (E_F) were first obtained from the interception with the baseline of the tangent corresponding to the onset of emitted electrons. E_f corrected by the work function of the instrument (Φ_{sp}) gives the E_{vb} value: E_{vb} = E_F + Φ_{sp} . Conduction band energy minimum was obtained from this data by adding the optical band gap energy.

Electrochemical characterization. First, the FTO was cleaned by sonicating the pieces in pure water for 15 min and then, in ethanol for 15 min to remove the impurities from the surface. After that, they were dried using compressed air.

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10 mg of the CD/mpC were suspended in 800 μ L of isopropanol by sonication for 30 min. Then, 200 μ L of a Nafion suspension (20 %) was added as binder. This ink was added to a surface of 1 × 1 cm of the FTO in aliquot of 30 μ L 6 times. It was dried overnight at room temperature.

These electrodes were immersed in the electrolyte overnight to ensure complete equilibration of the material with the electrolyte.

The electrolyte was a 0.1 M aqueous solution of KHCO₃, and a bar of graphite and Ag/AgCl as counter and reference electrodes, respectively. The working electrodes were the film material on FTO previously described.

The cyclic voltammetry studies were carried out from 1 to -1 V vs Ag/AgCl under inert atmosphere using N₂ to purge, at a scan speed of 10 mV × s⁻¹, and, for 5 to 10 cycles to check the stability.

Transient photocurrent measurements were carried out with selected potentials between -1 to 1 V vs Ag/AgCl. The working electrode was stabilized at the selected potential for 300 s and then, cycles of on/off were carried out using the same irradiation source as in the photocatalytic tests.

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RESULTS



Figure S1. a) XRD pattern and b) Raman spectra of the samples 1) CD-08/mpC and 2) CD-12/mpC.



Figure S2. High-resolution deconvoluted XP spectra of the samples a) CD-08/mpC, b) CD-12/mpC, c) CD, and d) reused CD-1/mpC for the different components: C1s (left), N1s (center), and O1s (right).



b)





Figure S3. a) GC-MS of ${}^{12}CO_2$; b) GC-MS of ${}^{13}CO_2$ accompanied by N₂ c) GC-MS of ${}^{13}CH_4$ and H₂O.



Figure S4. Blank reactions with no CDs (black), no light (red), no CO_2 (green) and no mpC (blue).



Figure S5. Cyclic voltammetry of CD-1/mpC measured in a single cell using FTO coated with CD-1/mpC, Pt and Hg/HgO as working, counter and reference electrodes, respectively, in 0.5 M Na_2SO_4 as electrolyte.