Supporting information

Formation Mechanism and Chirality Evolution of Chiral Carbon Dots via Radical Assisted Synthesis at

Room Temperature

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³Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin Brook-Taylor-Str. 2, 12489 Berlin, Germany Fig. S1. TEM images of L-CDs

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Fig. S18. FTIR analysis of L-Cysteine and L-CDs isolated at different reaction times (2, 48 and 84 h).



Figure S1: TEM images of L-CDs. a)-c): scale bar 50 nm; d)-f): scale bar 20 nm.



Figure S2: X-Ray Powder Diffraction pattern for L-CDs and reference pattern for graphite (ICSD: 76767).

 Table S1. Quantum yield measurement using quinine sulfate as a standard.

Sample	Abs at 350 nm	Integrated emission intensity (arb. un.)	Quantum yield (%)
Quinine sulfate	0.082	1.91*107	0.54 [1]
CDs 2h in water	0.092	$1.70^{*}10^{5}$	0.8±0.2
CDs 2h in H_2SO_4 0.1M	0.094	3.28*106	1.5±0.2
CDs 84h in H_2SO_4 0.1M	0.094	3.22*106	1.5±0.2

By-Product: isolation and characterization

This fraction, that is about 10 % of the mass of the product, is composed by micrometrical carbon structures with broad distribution of sizes and shapes (see SEM micrographs of Fig S2). As described in the main text, this fraction can be isolated by precipitation at acidic pH and it is easily removed by centrifugation and collected as a powder after vacuum distillation at room temperature. Sample suitable for the UV/Vis, PL and CD characterization can be prepared by dispersion of the powder in deionized water after the addition of NaOH 0.2 M solution to neutralize the pH (see experimental section). The PL behavior of the by-product resembles the L-CDs one, the most intense emission is observed in the 375 - 500 nm range and the emission wavelength is strongly affected by the excitation wavelength. As shown in Fig. 3f, this fraction does not present any significative ECD signal, feature that can be related to a high degree of decomposition (see main text).

Considering all these findings, we can conclude that the by-product fraction is produced by an extended carbonization of the organic substrate that strongly reduce its optical chirality. The EDS analysis (Fig. S3) of the by-product reveals the average composition ($\%_{at}$): C 24.48, N 7.94, O 5.33, Na 0.59, S 25.80, Cl 2.44, Cu 33.42. In contrast with the L-CDs, this fraction is rich of copper and sulfur and poor in carbon and oxygen. Considering the copper concentration added in the reaction mixture, and the amount of the by-product collected, the copper mass present in the by-product could be estimated close to the total amount of copper added during the synthesis. Evidence that confirms the absence of copper in the carbon dots as observed by energy dispersive X-ray spectrometry EDS (Fig S3) and XPS. The FTIR analysis Fig S4 allows to investigate the functional group that are present in this fraction: the wide band in the range 3500 -2500 cm⁻¹ is ascribed to v_{O-H} of carboxylic acids, the strong band between 1700 and 1550 cm⁻¹ is related to v_{CO} of carboxylic acid and amides that overlaps the amide II band at 1590 cm⁻¹. The band at 1470 cm⁻¹ is related to v_{C-C} in the graphitic structures and the sharp peak at 1375 cm⁻¹ is related to v_{CN} . Finally, intense bands at 1180 and 1030 cm⁻¹ are ascribed to v_{-SO3} . suggesting the presence of sulfonic acids.



Figure S3. SEM images showing the by-product morphology. The scale bars in the figure corresponds to: (i), (ii): 10 μ m; (iii)-(vi): 2 μ m.



Figure S4. PL spectra of the by-product excited with radiations at different excitation wavelengths (in nm)



Figure S5. EDS analysis of the by-product (left) and L-CDs (right).



Figure S6. FTIR analysis of the by-product, in the 4000 - 500 cm⁻¹ range (left) and detail of the 1800 - 500 cm⁻¹ range (right).

Table S2. Main reaction conditions (see main tex
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Entry n°	Organic substrate	mol (mmol)	рН
1	Glycine (Gly)	1.24	10.5
2	Thioglycolic Acid (TGA)	1.24	10.5
3	Gly + TGA	1.24, 1.24	10.5
4	Met	1.24	10.5
5	Penicillamine	1.24	10.5
6	Cysteamine	1.24	10.5
7	Cysteine	1.24	7.0
8	Cysteine	1.24	10.5
9	Cysteine	1.24	12.0



Figure S7. ¹H-NMR analysis of L-Cysteine in D_2O pH = 10.5. The signals from cystine protons are evidenced in the inset.



Figure S8. UV/Vis spectroscopy investigation on the reaction between Cu(II) and different organic substrates: Glycine, Thioglycolic acid, mixture of Glycine and Thioglycolic acid and Methionine.



Figure S9. ¹H-NMR analysis of the reaction of Cu(II) with penicillamine.



Figure S10. UV/Vis spectroscopy analysis of the reaction between Cu(II) and cysteamine. A detail of the spectrum collected at the moment of the metal addition is shown in the inset.



Figure S11: ¹H-NMR analysis of the reaction of Cu(II) with Cysteamine.



Figure S12. PL analyses of the sample collected at 30 min, 1 h and 1.5 h. The different pH valued and excitation wavelength λ_{exc} during the measurement are reported in the graphs



Figure S13. PL analyses of the sample collected at 2h, 8 h and 16 h. The different pH valued and excitation wavelength λ_{exc} during the measurement are reported in the graphs



Figure S14. PL analyses of the sample collected at 24 h, 48 h and 84 h. The different pH valued and excitation wavelength λ_{exc} during the measurement are reported in the graphs



Figure S15. TEM images of the L-CDs sample isolated after a reaction time of 2 h. The scale bars in the figures correspond to: (i) 100 nm; (ii)-(iv) 20 nm.



Figure S16. TEM images of the L-CDs sample isolated after a reaction time of 48 h. The scale bars in the figures correspond to (i),(ii) 20 nm, (iii) and (iv) 5 nm.



Figure S17. TEM images of the L-CDs sample isolated after a reaction time of 84 h. The scale bars in the figures correspond to: (i) 500 nm, (i, inset) 5 nm⁻¹; (ii)-(iv) 20 nm, (ii, inset)-(iv, inset) 5 nm.



Figure S18. FTIR analysis of L-Cysteine and L-CDs isolated at different reaction times (2, 48 and 84 h).

Reference:

1. L. Hu, Y. Sun, S. Li, X. Wang, K. Hu, L. Wang, X. Liang and Y. Wu, Carbon, 2014, 67, 508–513.