Dramatic photoluminescence quenching in carbon dots induced by cyclic voltammetry

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Electronic Supplementary Information (ESI)

Experimental

Materials: Citric acid (CA), citrazinic acid, nitric acid, potassium chloride were purchased by Sigma-Aldrich and ethanolamine (EA) was purchased by Alfa Aesar.

Synthesis of C-dots: The synthesis of C-dots was based on the protocol described elsewhere (1). In brief, C-dots were synthesized by controlled pyrolysis of CA and EA (molar ratio 3 : 1) at 180 ℃for 30 mins under reflux, followed by a 30 min further heating at 230 ℃in the absence of the reflux condenser. The product received at 230 ºC was heated in the oven at 300 ºC for one more hour, in order to synthesize C-dots with a higher degree of carbonization. In both cases, the C-dots were dialyzed against deionized water via SnakeSkin Pleated Dialysis Tubing

membrane (with a molecular weight cutoff of 3500 Da) and were freeze-dried. Elemental analysis indicated that C-dots prepared at 230 ^{o}C contain 44.85% C, 5.75% H, 10.85% N, compared to 50.5% C, 3.7% H, 13.1% N for those prepared at 300 ^{o}C (1).

Cyclic Voltammetry (CV): CV scans of 0.1 mg/mL of aqueous dispersions of C-dots in the presence of 0.1 M KCl were obtained using a Gamry Interface 1000 potentiostat. The electrochemical cell was equipped with graphite rod as working electrode, platinum wire as counter electrode, and Ag / AgCl as reference electrode. Typically, the voltage scan range was from -2 V to 0.5 V (unless otherwise stated) and the scan rate=50 mV/s.

Fluorescence analysis: Fluorescence analysis was conducted on a Horiba Fluoromax spectrofluorometer and the samples were excited at wavelengths between 320-500 nm, with 30 nm increment.

Fourier Transform Infra-Red (FTIR) spectroscopy: FTIR spectra were recorded using a Nicolet IR2000 spectrophotometer at room temperature. Typically, 32 scans were averaged, each one of them within a range of 3000-700 cm^{-1} at a resolution of 8 cm^{-1}.

X-ray photoelectron spectroscopy (XPS): The XPS spectra of C-dots were recorded using ESCALAB 250Xi spectrometer (Thermo Fisher) equipped with a monochromatic Al Kα X-ray radiation source. The data were fitted using the Thermo Avantage software.

Transmission Electron Microscopy (TEM): TEM images were obtained using a Tecnai F20 TEM/STEM from Fisher operated at 200 kV. Digital imaging was accomplished via an eagle camera and TIA software. Sample preparation consisted of dispersing the sample in ethanol before depositing one drop to a carbon coated copper grid. The sample recovered after CV was dialysised against water to remove the salt impurities.

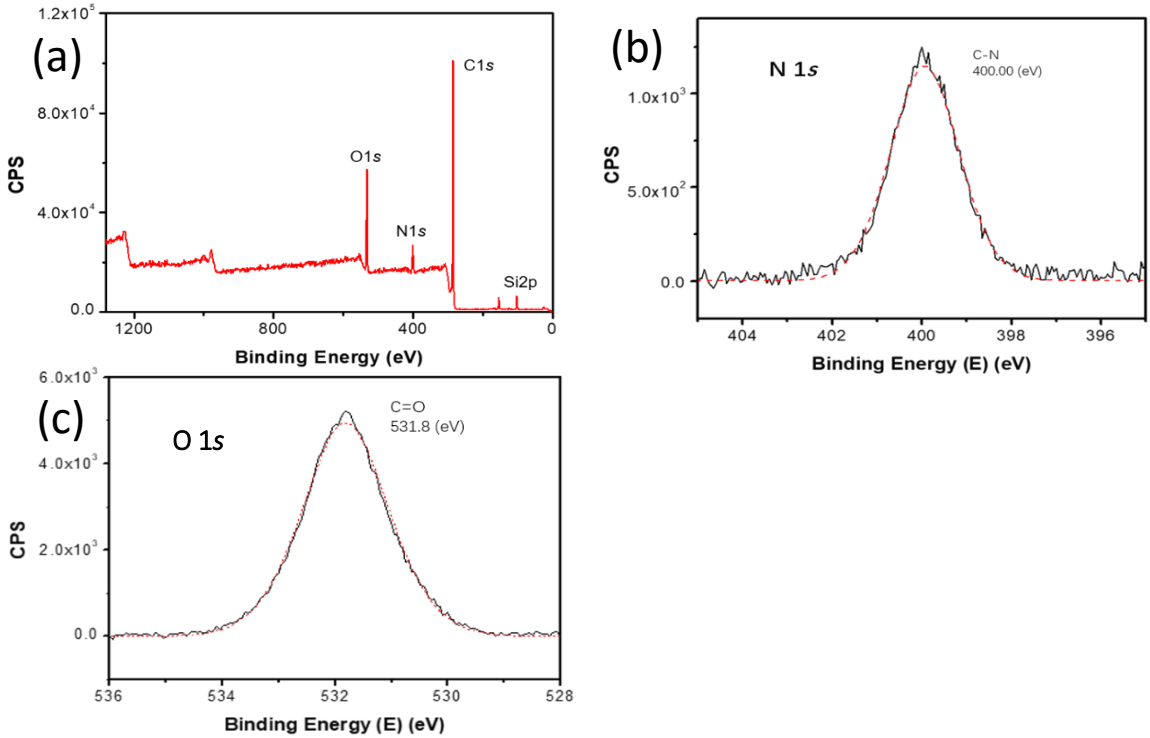
FTIR spectra

E.S.I. Table 1. Analysis of the FTIR spectra of C-dots prior and after the application of 42 CV scans.

Bond	Position prior CV (cm^{-1})	Position after CV (cm^{-1})
C=O$^{\alpha}$	1776	1772
C=O$^{\alpha}$, C=N$^{\alpha}$	1691	1691
C=O$^{\alpha}$	1652	1654
N-H$^{\beta}$	1567	1550
C-O$^{\alpha}$	1261	1261
C-N$^{\alpha}$	1185	1185
C=C-H$^{\beta}$ (sp^2)	935	absent
C=C-H$^{\beta}$ (sp^2)	850	absent

$^{\alpha}$ stretching vibration, $^{\beta}$ bending vibration

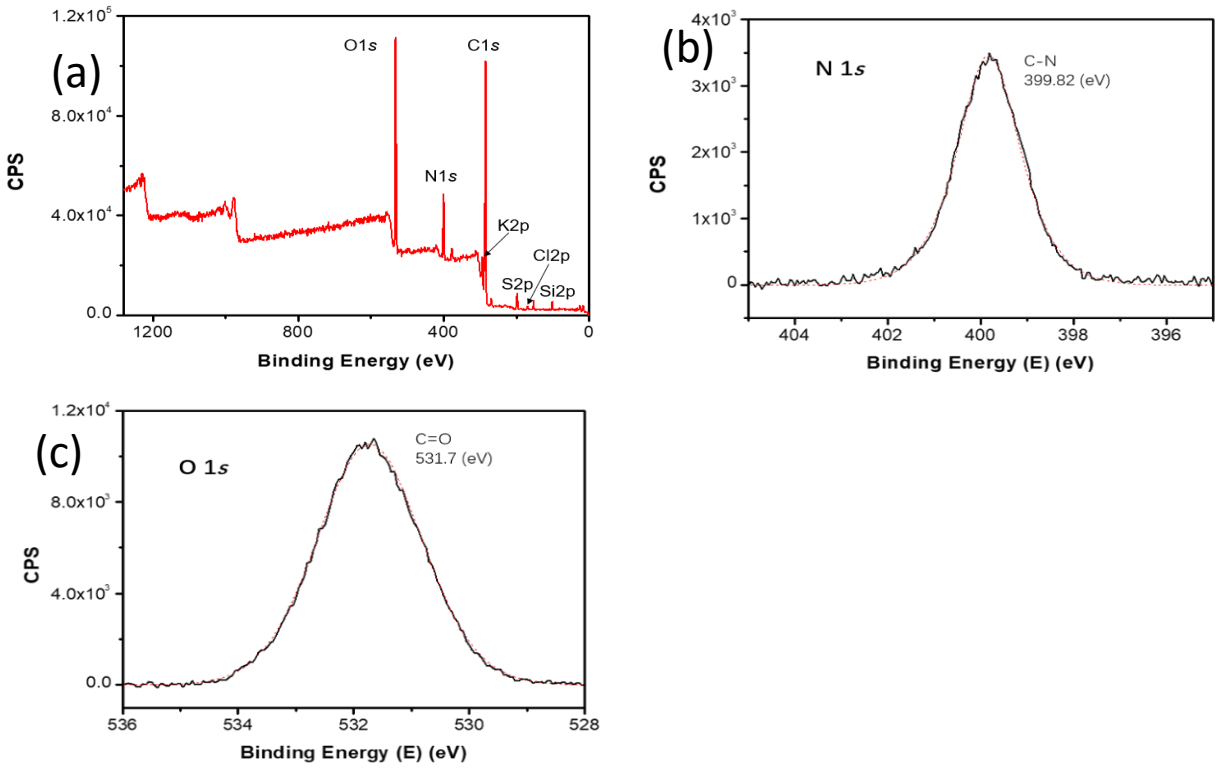
XPS spectra



E.S.I. Figure 1. XPS spectra of C-dots prior the application of the electrochemical filed; (a) survey spectrum, (b) N 1s, (c) O 1s. Solid and dashed lines represent the data recorded and the fitted curves, respectively.

E.S.I. Table 2. Analysis of the C1s XPS spectrum of C-dots prior the application of 42 CV scans

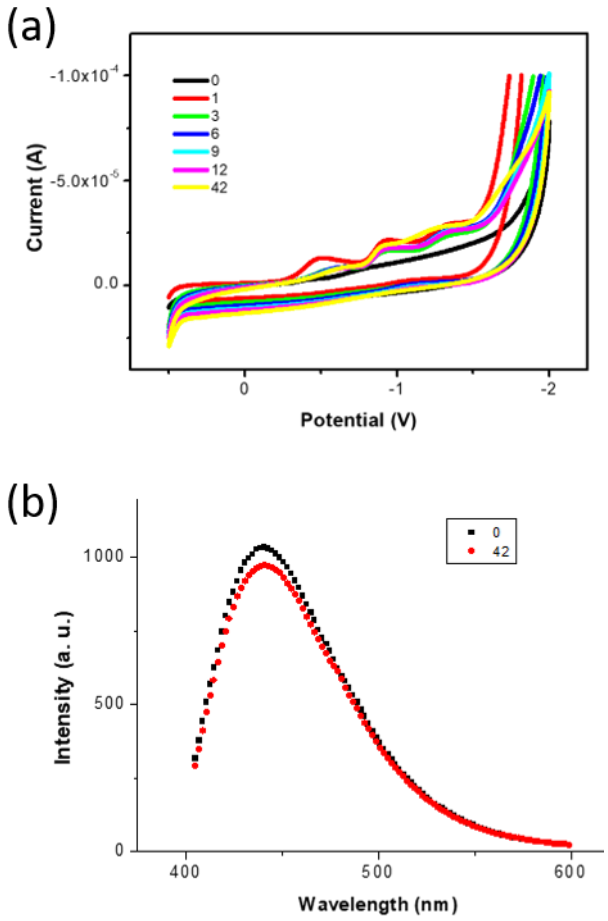
Bond	Peak BE (eV)	FWHM (eV)	%C	Reference
sp^2	284.19	0.84	52.00	1, 2
sp^3	284.8	1.22	34.39	2
C-O	286.05	1.22	9.07	3
C=O	287.96	0.82	2.45	3
π-π* satellite	291.05	1.09	2.09	4



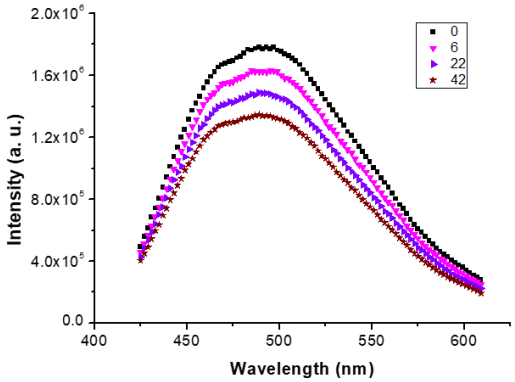
E.S.I. Figure 2. XPS spectra of C-dots after the application of the 42 CV scans; (a) survey spectrum (note the presence of K and Cl traces from the electrolyte solution), (b) N 1s, (c) O 1s. Solid and dashed lines represent the data recorded and the fitted curves, respectively.

E.S.I. Table 3. Analysis of the C1s XPS spectrum of C-dots after the application of 42 CV scans

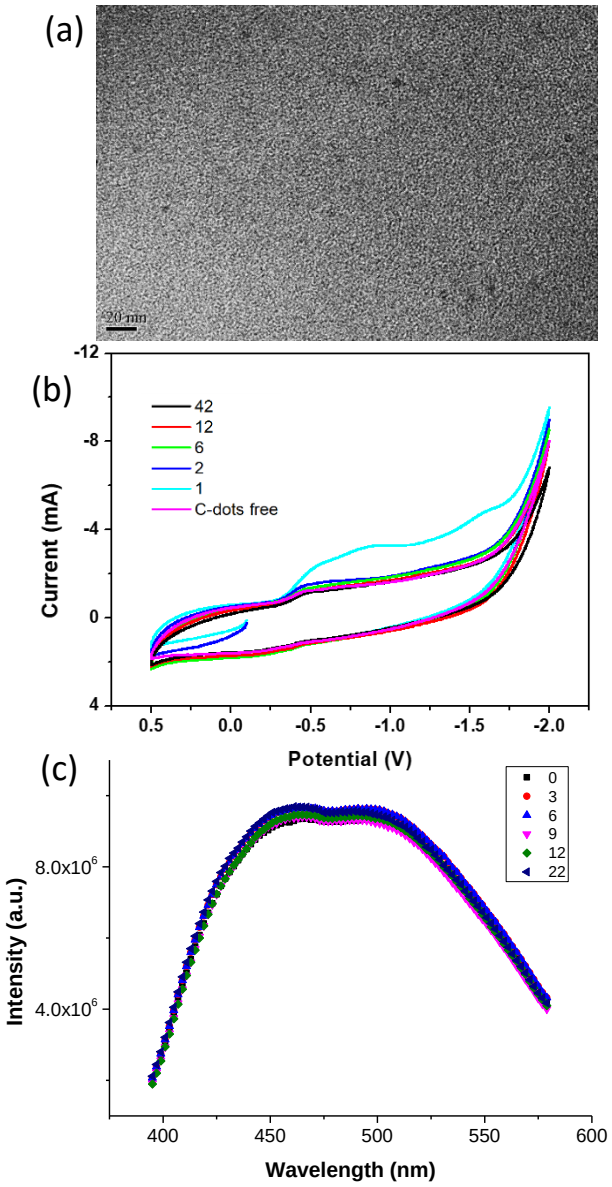
Bond	Peak BE (eV)	FWHM (eV)	%C	Reference
sp^2	284.2	1.41	11.40	1, 2
sp^3	284.81	1.28	38.89	2
C-O	285.94	1.41	35.47	3
C=O	287.96	1.36	14.24	3



E.S.I. Figure 3. (a) Multiple-cycle voltammograms of aqueous dispersions containing 0.1 mg/ml citrazinic acid (for clarity only cycles 0, 1, 3, 6, 9, 12, 42 are shown). b) The corresponding fluorescence emission spectra at excitation wavelength 380 nm (only cycles 0 and 42 are shown).



E.S.I. Figure 4. The fluorescence emission spectra (excitation wavelength 400 nm) of C-dots that have been subjected 42 CV scan within the range -1.3 V to 0.0 V. For clarity only cycles 0 , 6, 22 and 42 are shown.



E. S. I. Figure 5. C-dots prepared at 300 ºC: a) TEM image. b) Multiple-cycle voltammograms of aqueous dispersions containing 0.1 mg/ml C-dots (for clarity only cycles 1,2,6,12,42 are shown). c) The corresponding fluorescence emission spectra at excitation wavelength 380 nm (only cycles 0,3,6,9,12,22 are shown).

References

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