

A simple method for modifying glassy carbon electrode to simultaneously determine dopamine and ascorbic acid

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Experimental

All chemicals were used as received without further purification: Na₂SO₄ (high purity grade), NaOH (analytical grade), glacial CH₃COOH, Na₂HPO₄ (98 %), NaH₂PO₄ (98 %), dopamine hydrochloride (98 %), and ascorbic acid (high purity grade). Aqueous solutions were prepared using doubly distilled water. Prior to each electrochemical measurement, the working solution was deaerated by purging with high-purity argon for 20 minutes.

Electrochemical experiments were conducted in a standard three-electrode glass cell. The glassy carbon plate (2.5 cm² geometric area) or disk sealed in epoxy (4 mm diameter) served as the working electrode, a GC plate as the counter electrode, and an Ag/AgCl (saturated KCl) electrode as the reference. All potentials (*E*) are presented versus this reference. During measurements, the solution was stirred continuously by a gentle argon purge (approximately one bubble every 3 seconds). Cyclic voltammetry (CV) was performed using an Elins P-8nano potentiostat. The scan rate (*v*) was varied between 0.0025 and 0.02 V/s. Prior to use, the glassy carbon electrode surface was polished with 0.3 μm alumina slurry. The GC electrode was then modified in a thermostatted two-electrode cell containing 1 M Na₂SO₄ solution, using a graphite rod (ca. 10 cm²) as the counter electrode. A series of 5–10 alternating cathodic (–10 V) and anodic (+30 V) voltage pulses (34 Hz) were applied to the working electrode. Each pulse had a duration of 5 ms and a rise time of 0.5 μs.^{S1} Slight gas bubble formation on the electrodes was observed under these conditions.^{S2}

XPS analysis was conducted using a Specs PHOIBOS 150 MCD9 spectrometer with Mg Kα X-ray source (1253.6 eV). The base pressure in the analysis chamber was maintained below 3·10^{–10} Torr. The spectra were collected in the constant energy transmission mode (40 eV for the survey spectrum and 10 eV for individual lines). The survey spectra and individual peak spectra

were recorded with a step of 1 eV and 0.1 eV, respectively. Background subtraction was carried out according to the Shirley method and spectra deconvolution was performed using the CasaXPS processing software (version 2.3.19). Quantification of atomic content was carried out using the sensitivity factors from the elemental library of CasaXPS. The studied area was 300–700 mm² while the information depth, 1–2 nm. The spectra were acquired sequentially in parallel mode. The sample current was monitored during the measurements to ensure that charging effects are minimized, which is of great importance for consistency of further analysis.^{S3} The transfer procedure includes sample keeping in the spectrometer chamber at 10^{−6} Pa for 24 hours before investigation starts.

Analysis of the anodic peak currents as a function of concentration (see Figure S1 Online Supplementary Materials) reveals a linear relationship for both compounds.

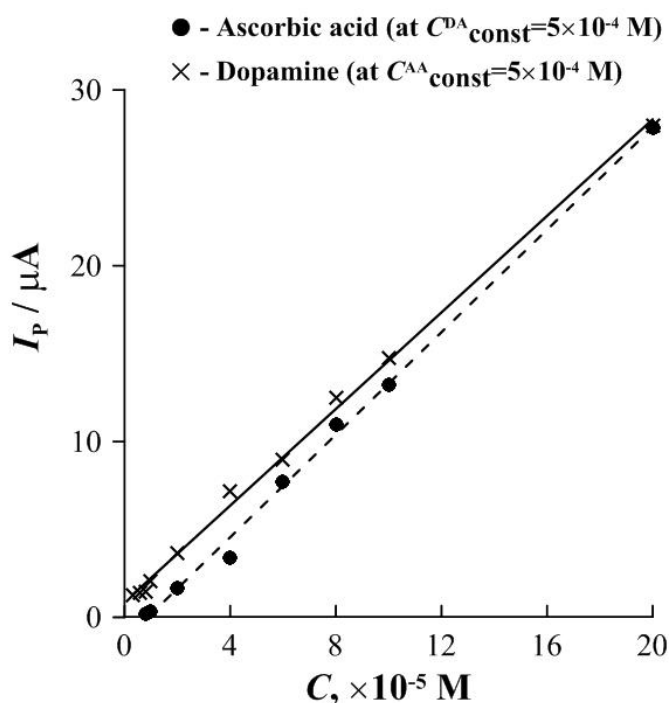


Figure S1. Dependence of the anodic peak current on the concentration of ascorbic acid in the presence of 0.5 mM DA, and dopamine in the presence of 0.5 mM AA. Measurements were performed in 0.1 M acetate buffer (pH=4) at a scan rate of 5 mV/s. Peak currents were determined from CVs recorded after the stepwise addition of one analyte to a solution containing a fixed concentration of the other.

High-resolution C 1s XPS spectrum of a glassy carbon plate modified by voltage pulses (Figure S2) shows the emergence of distinct oxygen-containing functional groups and a π - π^* shake-up satellite.

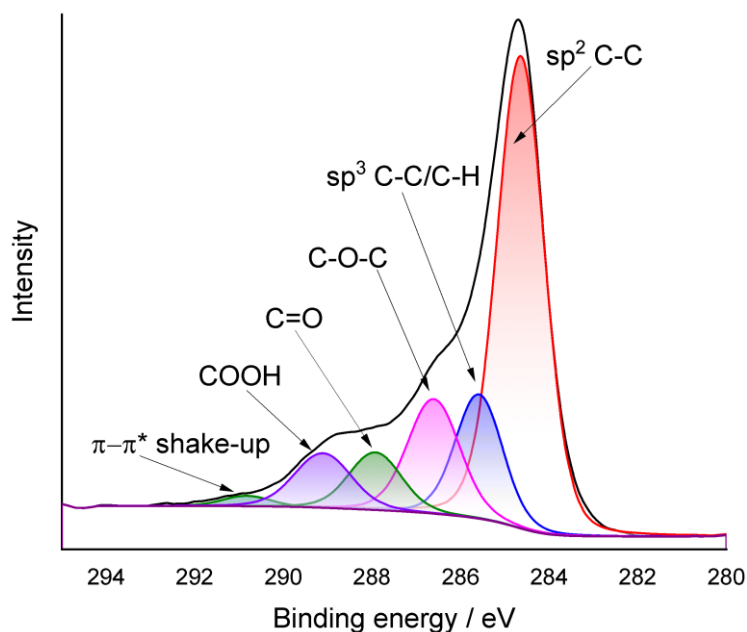


Figure S2. High-resolution C 1s spectra of the modified GC surface. The fitted components correspond to distinct carbon functional groups and the π - π^* shake-up satellite.

References

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