Electrochemical methods

basic aspects in theory, instrumental scheme, and utilization + new trends

Analytical Chemistry: Instrumental Analysis

Peter Mikus, Faculty of Pharmacy Comenius University in Bratislava

Definition of group of electrochemical methods

- techniques in analytical chemistry which study an analyte (quality and quantity) by measuring an electrochemical parameter such as:
  - the potential (volts)

  and/or

  - current (amperes)

  in an electrochemical cell containing the analyte

Main categories of electrochemical methods

- Electrochemical methods can be broken down into several categories depending on which aspects of the cell are controlled and which are measured:
- potentiometry (the difference in electrode potentials is measured)
- coulometry (the cell's current is measured over time)
- voltammetry (the cell's current is measured while actively altering the cell's potential)

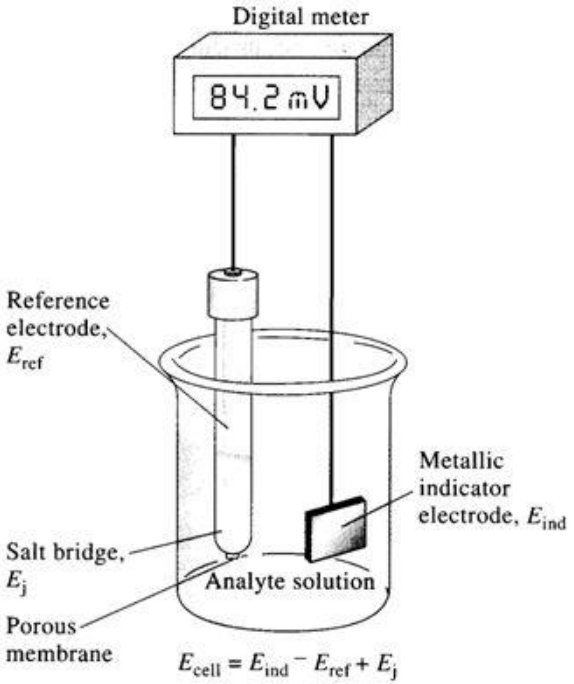
Potentiometry

- Method measuring the potential of a solution between two electrodes
- One electrode is called the reference electrode and has a constant potential, while the other one is an indicator (or working) electrode whose potential changes with the composition of the sample.
- The difference of potential between these two electrodes gives an assessment of the composition of the sample (throught the potential of the solution).
- Potentiometry usually uses indicator electrodes made selective (and also sensitive) to the ion of interest, such as fluoride in fluoride selective electrodes, so that the potential solely depends on the activity of this ion of interest. The most common potentiometric electrode is by far the glass-membrane electrode used in a pH meter.
- The time that takes the electrode to establish equilibrium with the solution will affect the sensitivity or accuracy of the measurement.
- In aquatic environments, platinum is often used due to its high electron transfer kinetics (i.e. quick establishing of equilibrium), although an electrode made from several metals can be used in order to enhance to electron transfer kinetics.
- In potentiometric titration, potentiometric indication of the point of equivalence is used instead of a chemical indicator

Potentiometry – instrumental scheme

reference electrode | salt bridge | analyte solution | indicator electrode

E_{ref} E_j E_{ind}

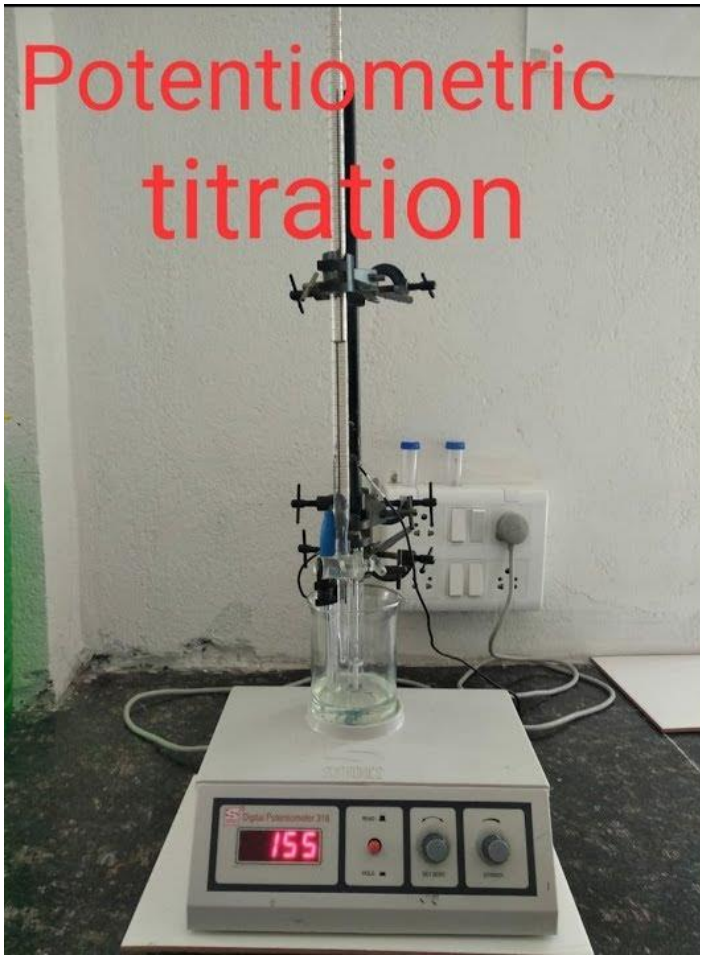


A cell for potentiometric determinations

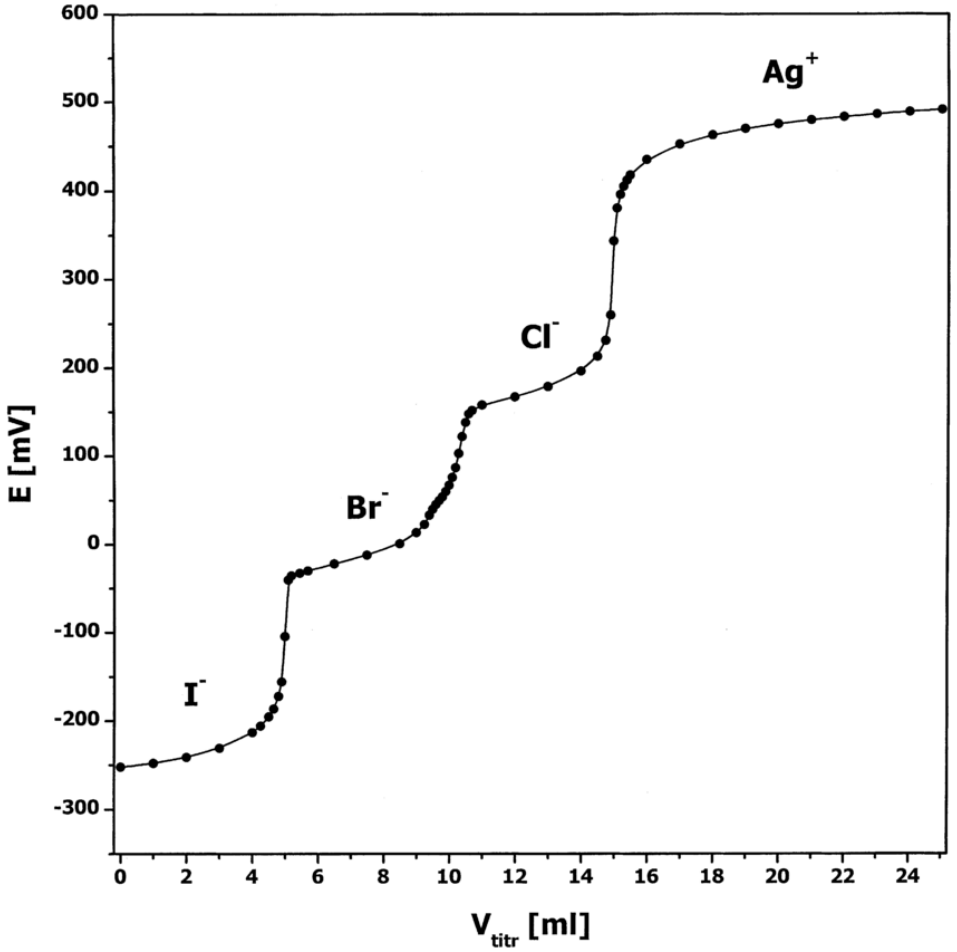
Reference electrode : E_{ref}
Indicator electrode : E_{ind}
The potential of cell

$$E_{cell} = E_{ind} - E_{ref}$$

Potentiometry – titration experiment

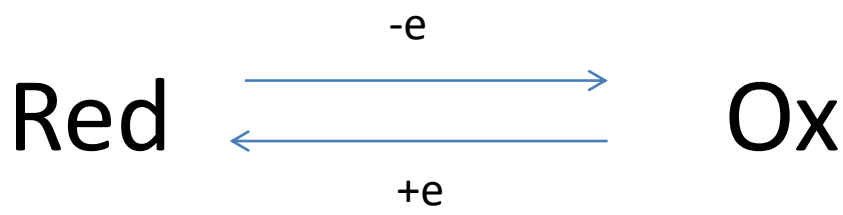


Potentiometry – titration curve



Illustrative example:
Argentometric titration of the solution containing mixture of KI, KBr and KCl

Coulometry



- Coulometry uses applied current or potential to completely convert an analyte from one oxidation state to another.
- The total current passed is measured directly or indirectly to determine the number of electrons passed.
- Knowing the number of electrons passed can indicate the concentration of the analyte or, when the concentration is known, the number of electrons transferred in the redox reaction.

Voltammetry

- Voltammetry applies a constant and/or varying potential at an electrode's surface and measures the resulting current with a three electrode system (reference, working, auxiliary electrodes).
- This method can reveal the reduction potential of an analyte and its electrochemical reactivity.
- Chemically modified electrodes are employed for analysis of organic and inorganic samples with enhanced selectivity (and in most cases also sensitivity).

Voltammetry subclasses

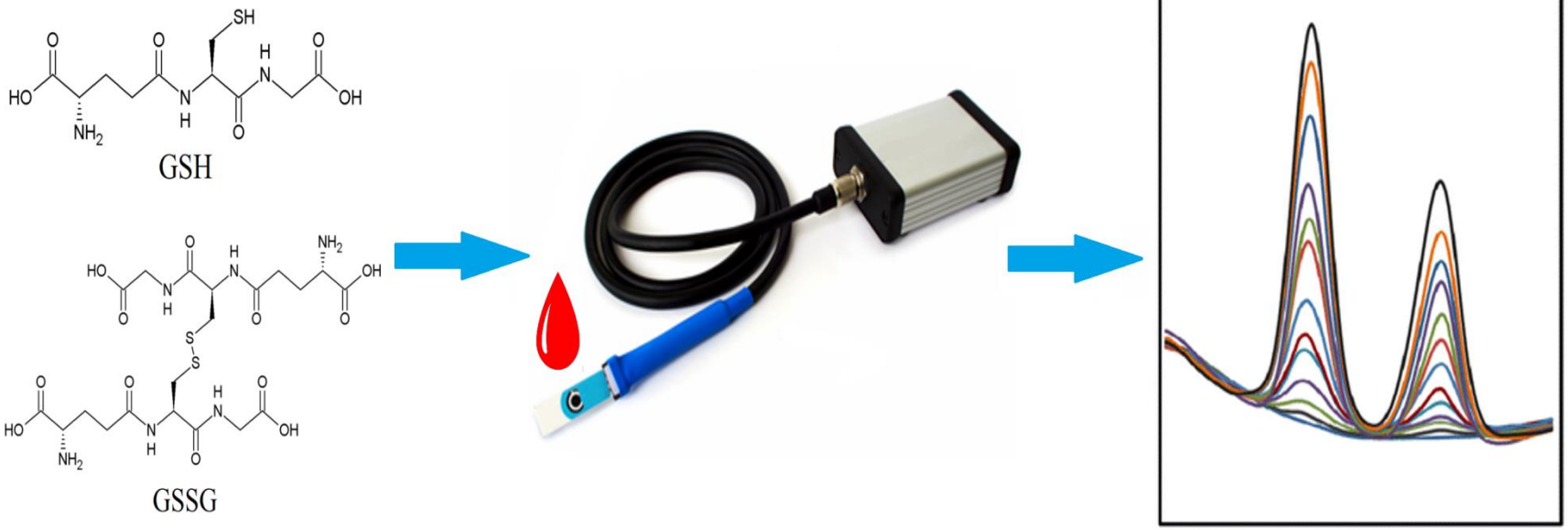
- Polarography is a subclass of voltammetry that uses a dropping mercury electrode as the working electrode.
- Amperometry represents a group of electrochemical techniques in which a current is measured as a function of an independent variable that is, typically, time or electrode potential.
  - Chronoamperometry is the technique in which the current is measured, at a fixed potential, at different times since the start of polarisation.
  - Voltamperometry is a subclass of amperometry, in which the current is measured by varying the potential applied to the electrode.

Utilization of electrochemical methods

- Determination of electrochemically active compounds, evaluation of electrochemical properties of analyzed compounds
- Benefits: simple experimental arrangement, fast analysis, low-cost instrumentation as well as experiment, high sensitivity
- Limitations: lower selectivity (not suitable for the analysis of samples with complex matrices, for such cases a proper modification of the electrochemical sensor is necessary)

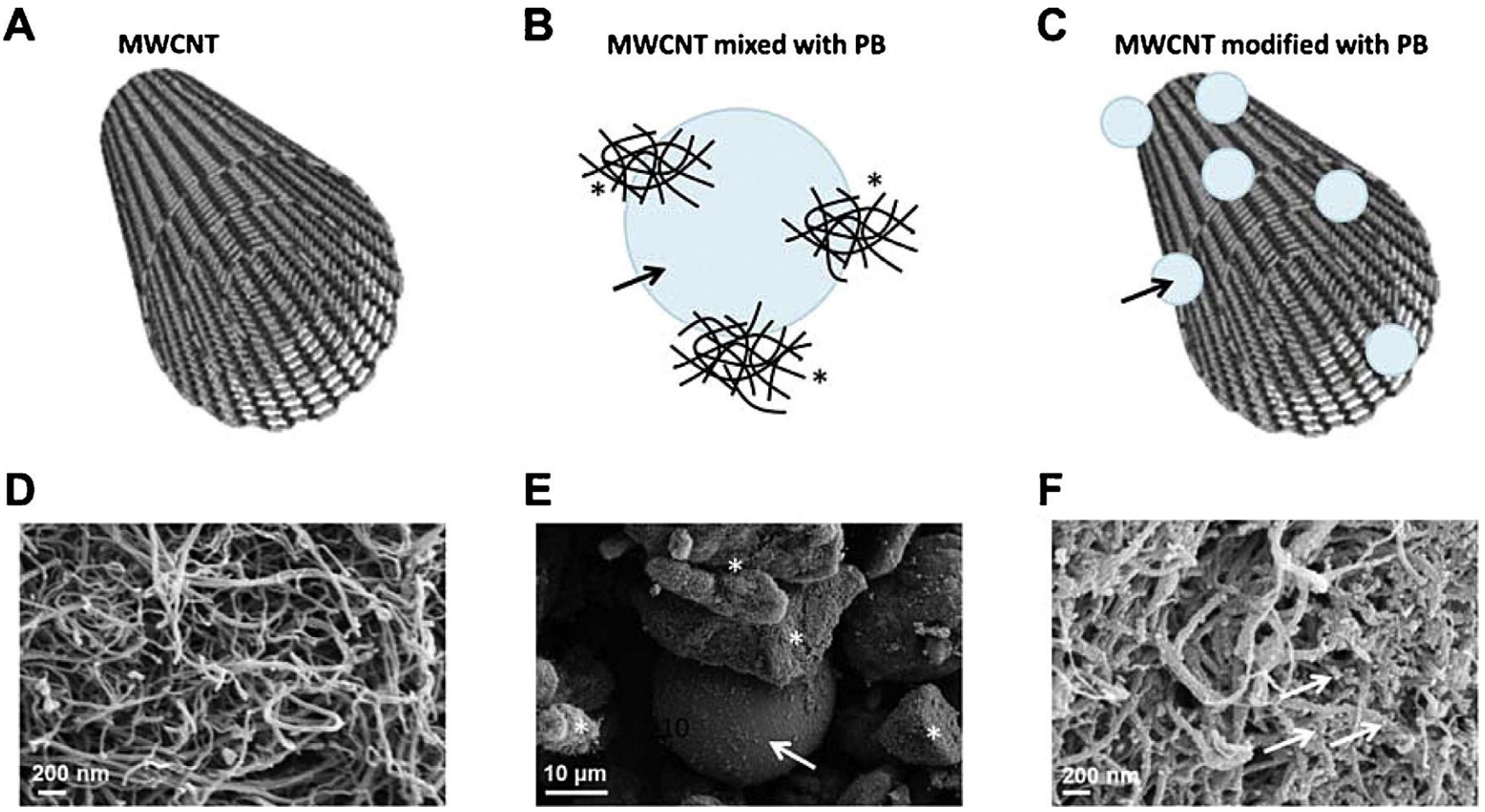
New trends in electrochemical methods

M. Hanko et al. / Analytica Chimica Acta 1062 (2019) 1-27 and references cited therein



New trends in electrochemical methods

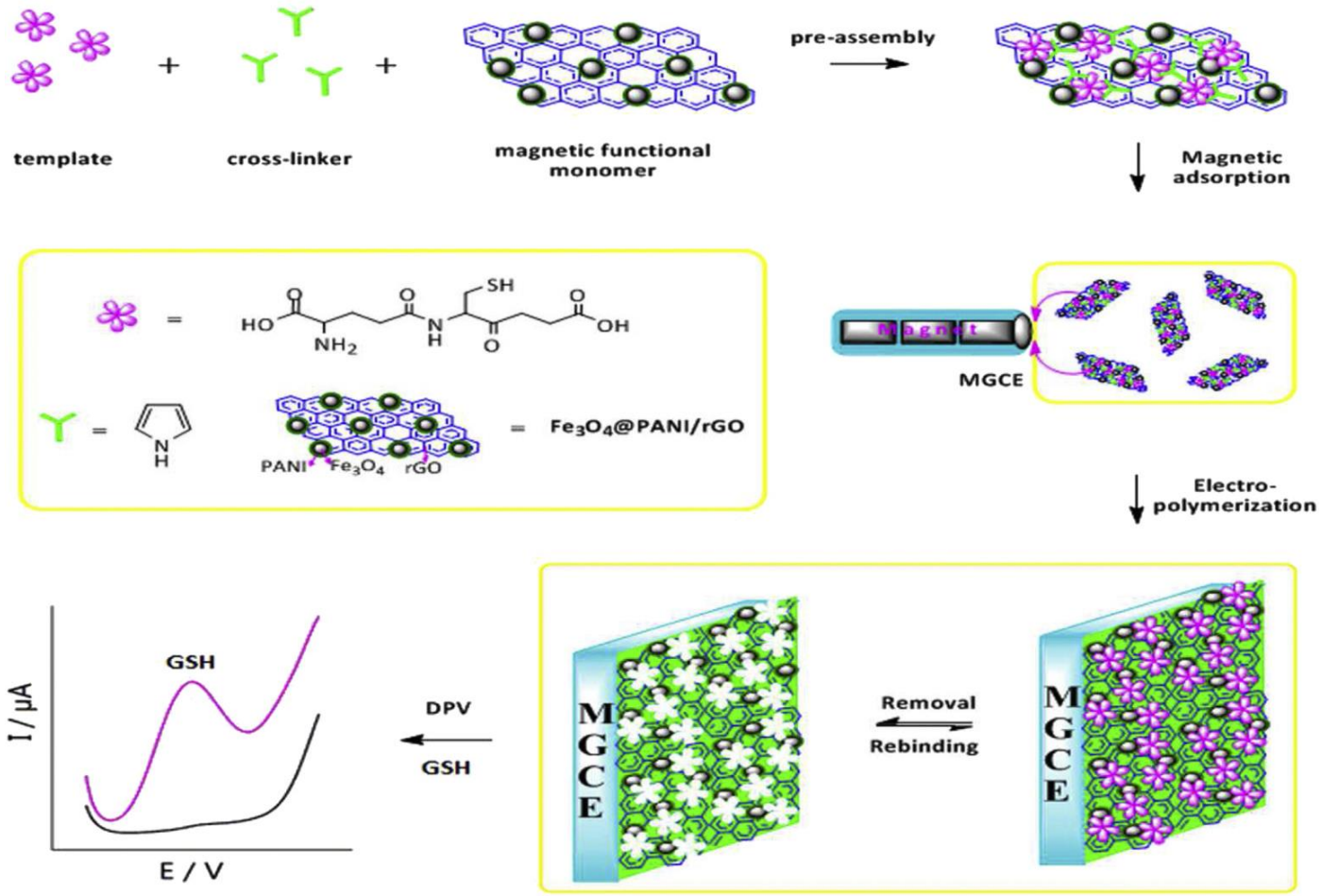
advanced electrode materials



Characterization of multiwalled carbon nanotube MWCNT materials. Schematic diagrams of MWCNT and its modifications, based on the obtained scanning electron microscopy (SEM) images D–F, are shown in A–C. Data is shown for the MWCNT material alone (A&D), a mixture of MWCNT with Prussian blue (PB) (B&E), and MWCNT modified with PB (C&F). The arrows indicate the presence of the PB particles/spheres on/within the two materials. The star symbol indicates the large agglomerate bundles of MWCNTs. Reprinted from Ref. [112].

New trends in electrochemical methods

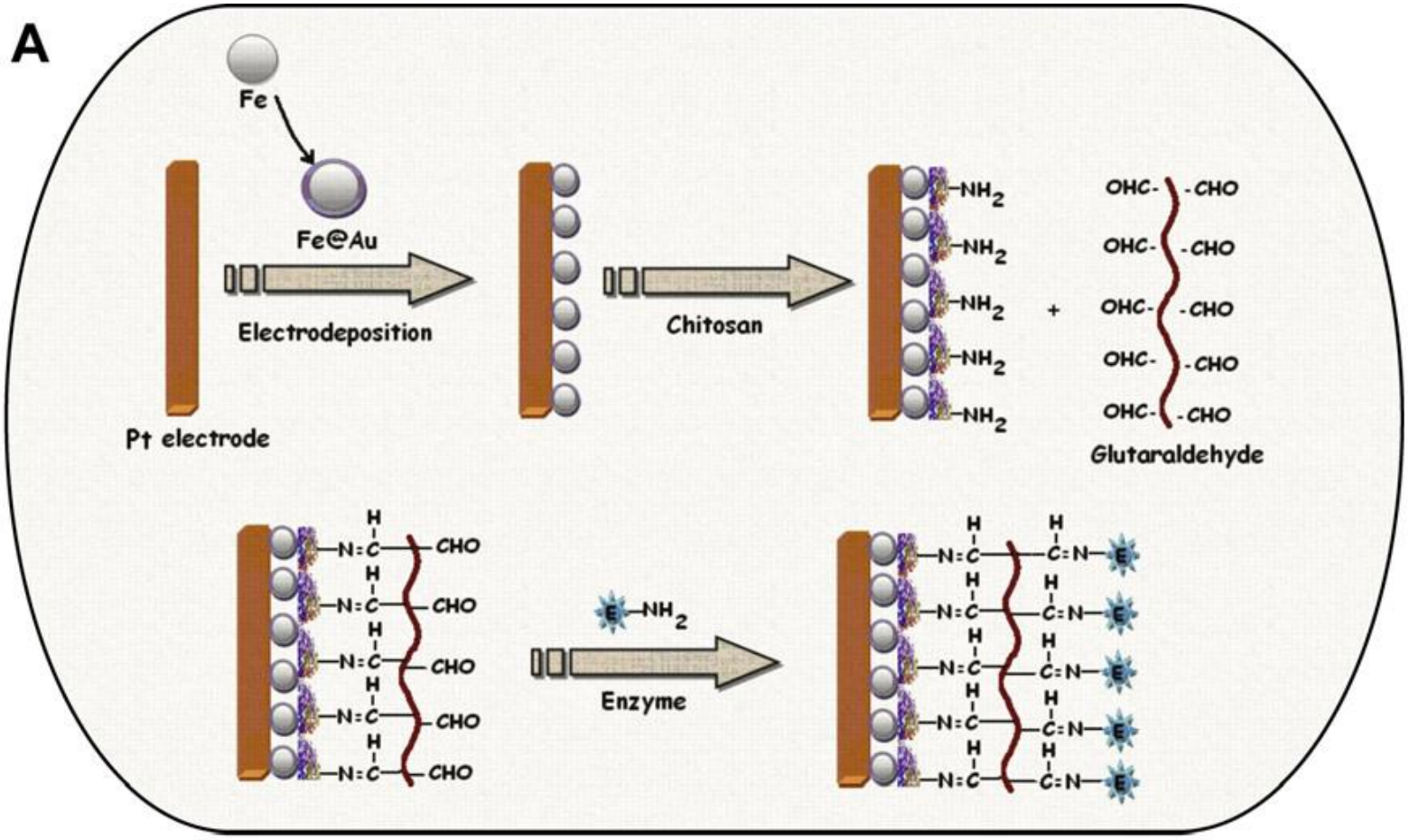
advanced electrode modifications



Scheme of preparation procedure for magnetic molecularly impinted polymer (MMIP). Reprinted from Ref. [83].

New trends in electrochemical methods

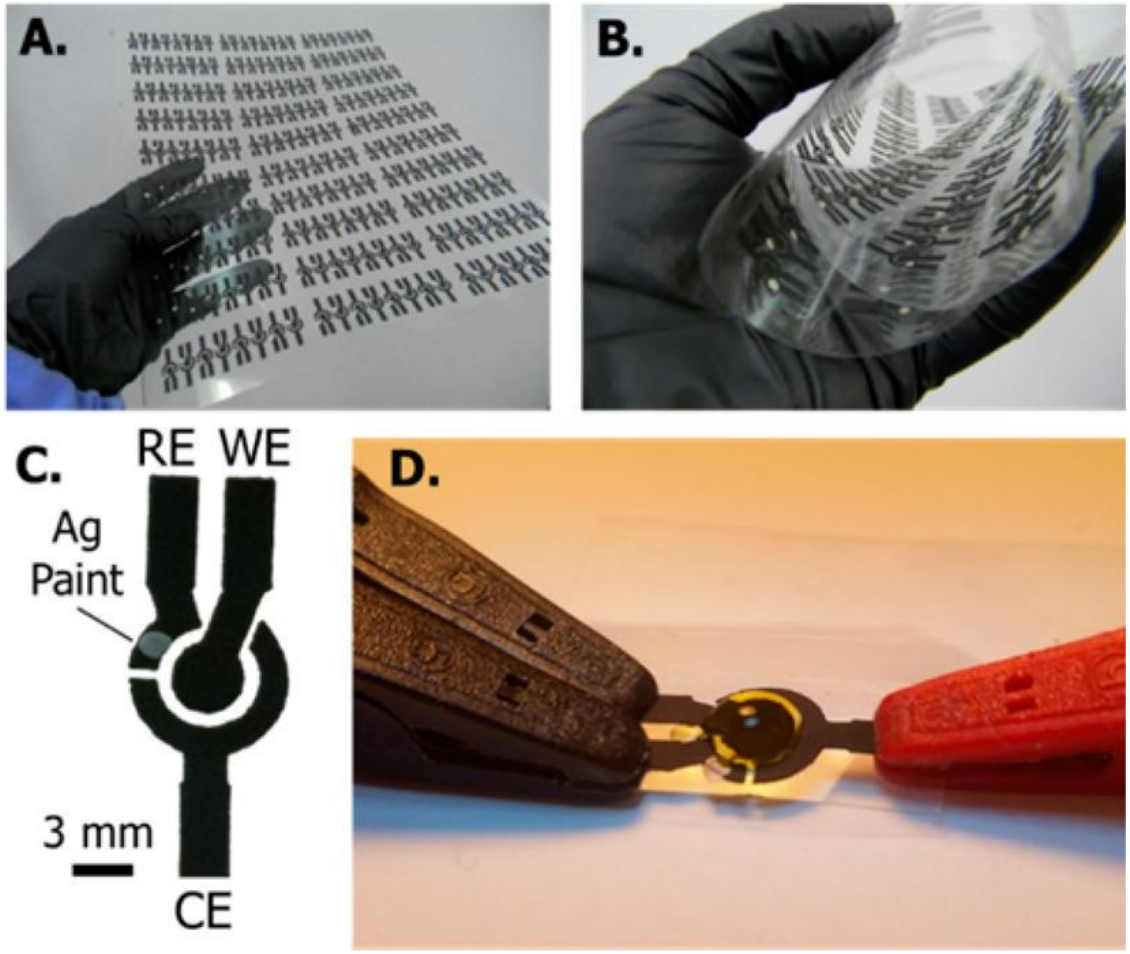
advanced electrode modifications



Scheme of preparation procedure for enzymatic biosensor. Modification of Pt electrode with nanoparticles (NPs) incorporated in chitosan with immobilized enzyme (GSHOx/CHIT/Fe@Au NPs/Pt). Reprinted and modified from Ref. [55].

New trends in electrochemical methods

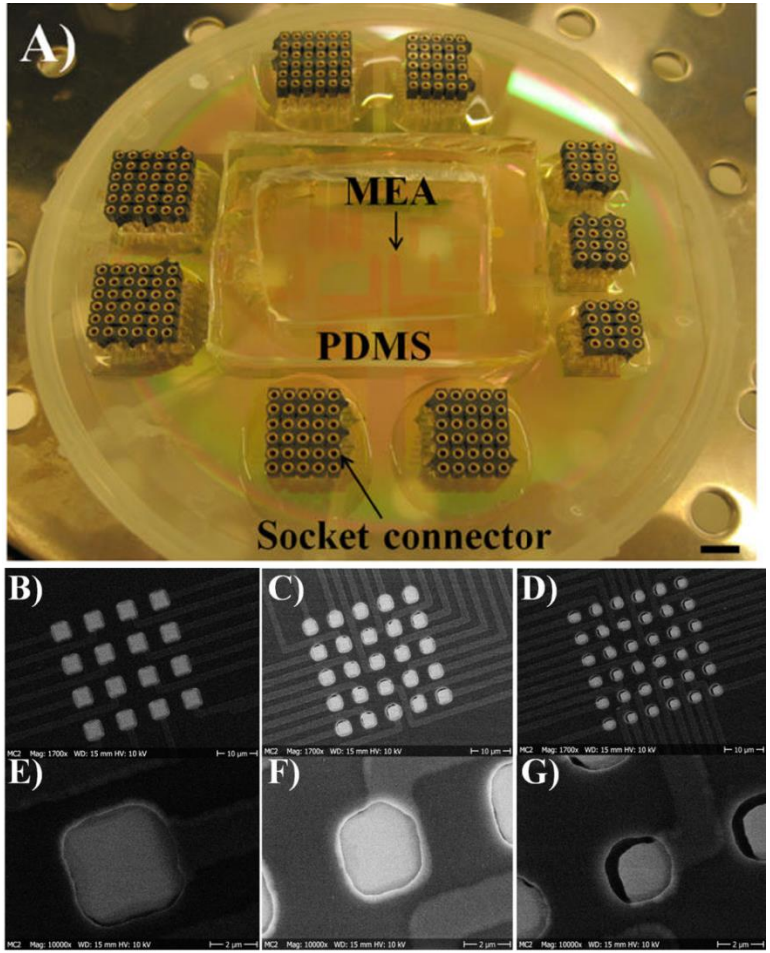
advanced electrode formates



Screen-printed carbon electrode (SPCE). SPCEs on transparent film shown as a (A) printed sheet that is (B) flexible. (C) A single printed electrode image (with background removed for visualization) showing working (WE), silver paint reference (RE), and counter (CE) electrode geometries and connections. (D) Final device image with 30 µL of solution contained within the central well and connected to potentiostat leads. Reprinted from Ref. [171].

New trends in electrochemical methods

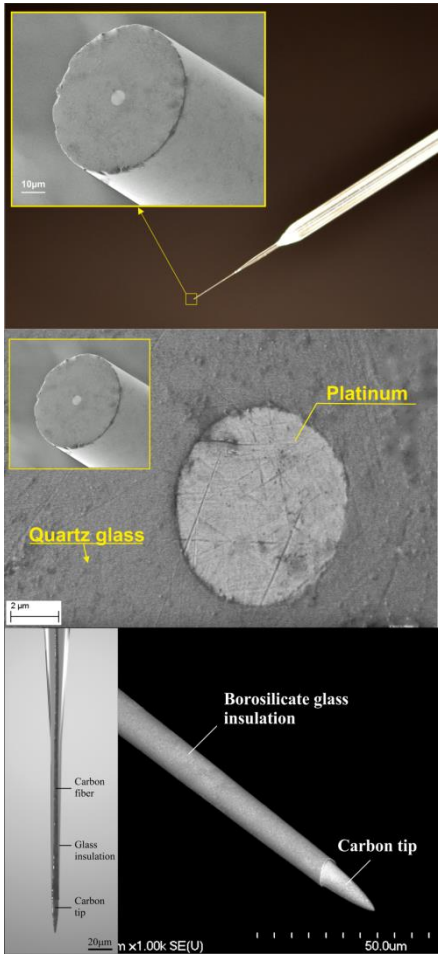
advanced electrode formates



Measurements even within single biological cells that are not possible using conventional-sized electrodes.
Microelectrode array (MEA). Optical photo of the whole MEA device and SEM pictures of the MEAs with 16, 25, and 36 ultramicroelectrodes. (A) Typical device containing a PDMS (poly(dimethylsiloxane)) chamber, pin connectors, and the MEAs (scale bar, 10 mm); one arrow points to one of the nine MEAs, and the other arrow points to one of the nine socket connectors. (B-D) SEM pictures of MEAs containing 16, 25, and 36 microelectrodes, respectively (scale bar is 10µm); (E-G) SEM pictures of single microelectrodes in the corresponding MEAs of 16, 25, and 36 microelectrodes, respectively (scale bar is 2µm). Reprinted from Ref. [172].

New trends in electrochemical methods

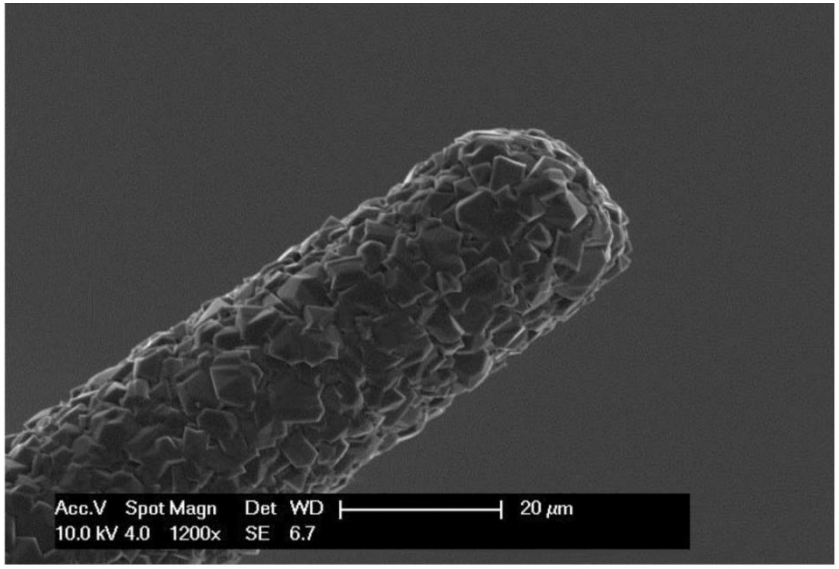
advanced electrode formates

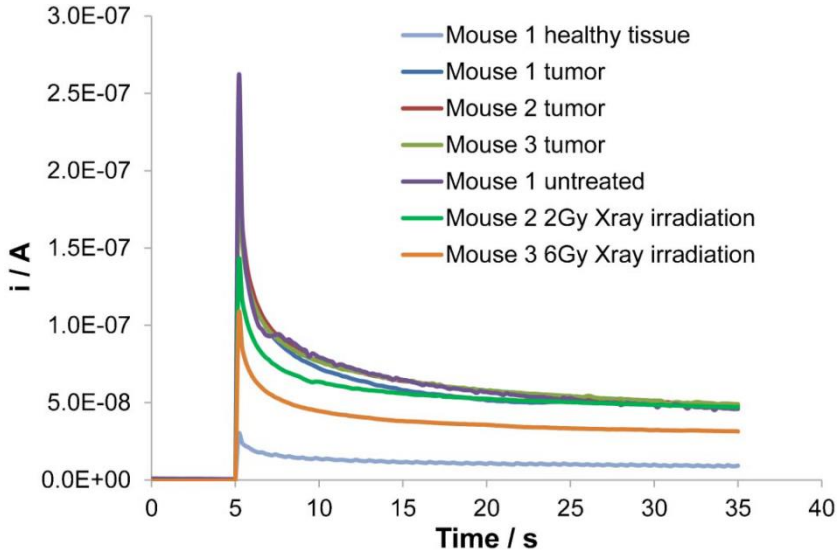


Measurements even within single biological cells that are not possible using conventional-sized electrodes.
Microdisk and microfiber electrodes. Upper and middle panel: The microdisk electrode is based on unique single metal core fiber of platinum insulated with quartz glass and typical flat shape ending. Adapted from [173]. Lower panel: Single barrel carbon microfiber electrode for extracellular recording and/or *in vivo* electrochemistry. A 7 µm in diameter carbon fiber is galvanically attached to the industry standard pin atop and built in a 1.5 mm diameter borosilicate glass capillary tubing. On the other end, the standard carbon tip is conically shaped and protrudes from the glass insulation by 20 µm +/- 5 µm. This tip is optimized for extracellular recordings. Adapted from [174].

New trends in electrochemical methods

advanced electrode formates



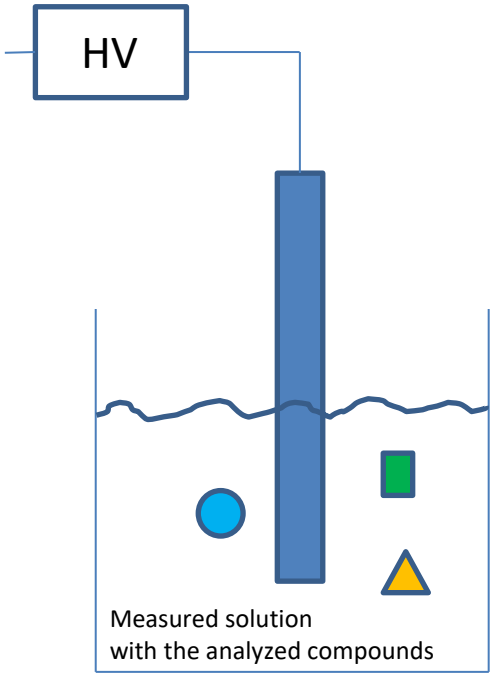


Measurements in-vivo.
Real-time *in vivo* monitoring of GSH marker with the boron-doped diamond (BDD) microelectrode inserted directly in tumor of mice. Upper panel: SEM image of the BDD microelectrode. The image shows the tip of the needle shaped BDD microelectrode that was inserted into the tumor. Lower panel: Determination of GSH in HSC-2-derived xenograft tumor before and after X-ray treatment using BDD microelectrode. Chronoamperometry measurements recorded on BDD microelectrode at 1.3 V vs. Ag/AgCl: in the HSC-2- derived xenograft tumor of mouse 1 (untreated), in the HSC-2-derived xenograft tumor of mouse 2 (three hours after the tumor had been X-ray irradiated for 2 minutes at 2 Gy) and in the HSC-2-derived xenograft tumor of mouse 3 (three hours after the tumor had been X-ray irradiated for 2 minutes at 6 Gy). T=37 °C. Reprinted from Ref. [122].

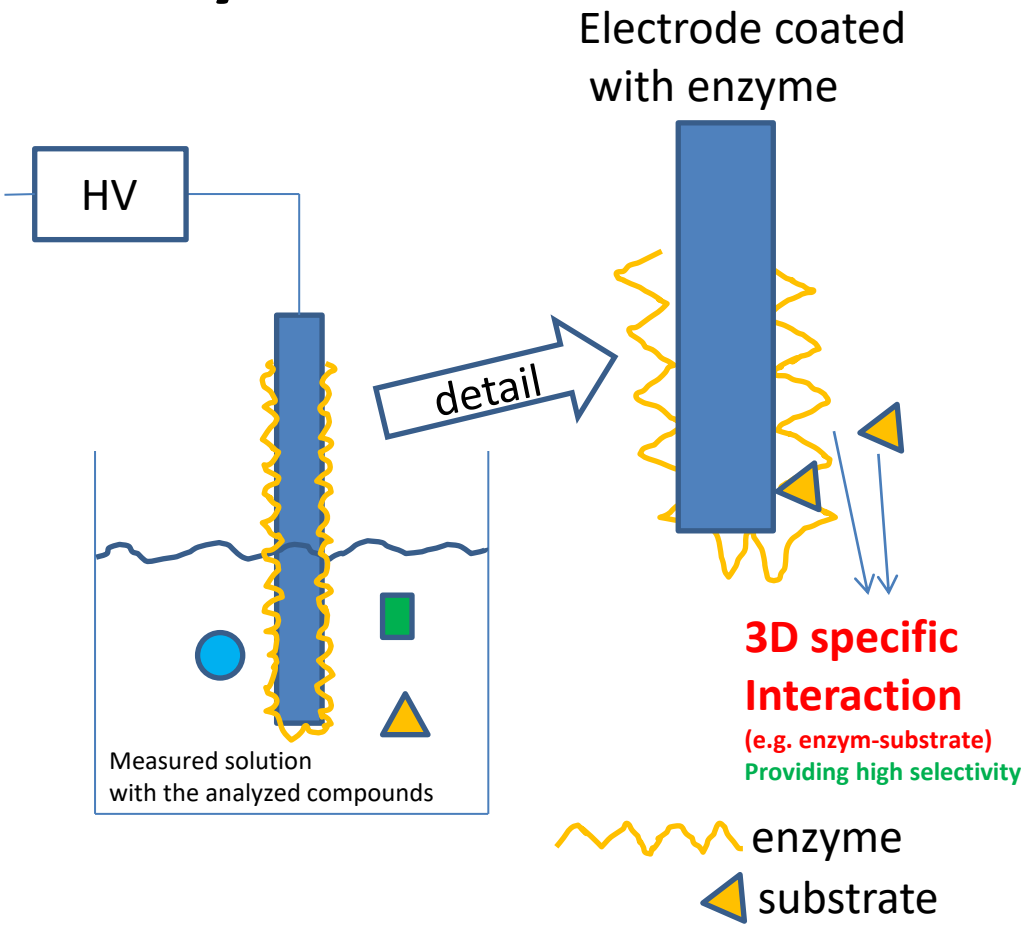
New trends in electrochemical methods - summary

- Determination of electrochemically active compounds, evaluation of electrochemical properties of analyzed compounds, possible to determine also electroneutral compounds
- Benefits: simple experimental arrangement, fast analysis, low-cost instrumentation as well as experiment, high sensitivity, low consumption of the samples (microelectrodes), in-vivo analysis, high selectivity (specificity – based on 3D interactions, e.g. enzyme-substrate, antigen-antibody, etc.) - suitable for the analysis of samples with complex matrices (with properly modified electrodes)
- Limitations: ~~lower selectivity (not suitable for the analysis of samples with complex matrices, for such cases a proper modification of the electrochemical sensor is necessary)~~ difficult preparation of modified electrodes, higher cost

New trends in electrochemical methods - summary



Convential electrochemical sensor



Advanced (modified) electrochemical sensor
- biosenzor