Modifier-Free Microfluidic Electrochemical Sensor for Heavy Metal Detection

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Heavy metals are hazard pollutants to the environment and impose severe risks to human health. Therefore, heavy metal detection is playing important role in environmental and clinical analysis. In this work, a simple, cost-effective and portable miniaturized electrochemical carbon-based sensor (µCS) is designed and proved to be highly sensitive towards Cd$^{2+}$ and Pb$^{2+}$ detection in aqueous solution. The µCS possess a novel 3D structure with working and reference electrodes directly facing each other but separated by the microfluidic paper channel. The electrodes in µCS are inexpensive graphite foil without any additional surface modifier such as mercury or bismuth. It is found that impressive low detection limits of 1.2 µL/L for Cd$^{2+}$ and 1.8 µL/L for Pb$^{2+}$ can be achieved on the µCS. The µCS also exhibits stable sensing performance up to 10 repetitive measurements, demonstrating the robustness of a sensing device for heavy metal detections. We believe that a proper design in the device configuration can completely eliminate the necessity to modify the working electrode by using additional surface modifier, which could provide new ideas for portable electroanalytical/sensing systems.

**Device fabrication:**

- **WE, CE & RE:** graphite foil
- **Paper channel:** filter paper, pore size 15 µm

**Electrochemical measurements**

1. Metal deposition; 2. Square wave voltammetry

**Individual detection of Cd$^{2+}$ and Pb$^{2+}$**

- **Cd$^{2+}$**
  - LOD = 1.2 µL/L
  - Deposition condition:
  - Cd$^{2+}$: -1.2 V, 60 s
  - Pb$^{2+}$: -1.1 V, 180 s

- **Pb$^{2+}$**
  - LOD = 1.8 µL/L
  - The limit of detection (LOD) are below the allowable limits in drinking water proposed by US Environmental Protection Agency (Cd: 5 µgL, Pb: 15 µgL) and World Health Organization (Cd: 3 µgL, Pb: 10 µgL).

**Simultaneous detection of Cd$^{2+}$ and Pb$^{2+}$**

- The deposition condition for simultaneous detection is (-1.2 V, 180 s).
- The detection limit is 6 µgL for both Cd$^{2+}$ and Pb$^{2+}$.

**Stability and reproducibility of the µCS**

- Very good electrocatalytic stability was observed on µCS.

**Structure analysis of the graphite foil**

- The electrodeposited Cd species are selectively located at the edge positions of graphite flakes.

**Conclusions:**

- A modifier-free, low cost, reusable, electrochemical microfluidic carbon-based sensor was developed for heavy metal detection.
- High sensitivity and low detection limit at short detection time are obtained on the sensor during individual detection for Cd$^{2+}$ and Pb$^{2+}$.
- The high sensitivity may originate from the combined microfluidic configuration and novel 3D electrode layout, which may provide some new ideas for other portable electroanalytical/sensing systems.

**References:**

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