Abstract: we herein show for the first time a reproducible method for renewing solid electrodes whenever their surfaces are non-specifically changed without any surface treatment. These renewable electrodes are the closest analogue to the mercury drop electrodes. Our approach was applied in microfluidics, where the downsides related to contaminations of the electrode are more critical. The renewal consisted in manually sliding metal-coated microwires across a channel with the sample. For this purpose, the chip was composed of a single piece of polydimethylsiloxane (PDMS) with three parallel microchannels interconnected to one perpendicular and top channel to pump sample. The microwires were inserted in each one of the parallel microchannels acting as working, counter, and quasi-reference electrodes for voltammetry. This assembly allowed the renewal of all the three electrodes by simply pulling the microwires. The absence of any interfaces in the chips and the elastomeric nature of the PDMS allowed us to pull the microwires without the occurrence of leakages for the electrode channels even at harsh flow rates of up to 40.0 mL min$^{-1}$. We expect this paper can assist the researchers to develop new microfluidic platforms that eliminate any steps of electrode cleaning, thus representing a powerful alternative for precise and robust analyses to real samples.

Keywords: Microdevice; PDMS; Cleaning; Electroanalytical chemistry; Voltammetry.
L⁻¹ Fe(CN)₆³⁻/⁴⁻ in 100.0 mmol L⁻¹ KCl were used again to study the renewal reproducibility. The experimental conditions were the same in relation to those described above to the Au working electrodes.

Results and discussion: the walls of the electrode (671 ± 3 µm) and sample (795 ± 6 µm) channels showed well-defined edges and low roughness (Fig. 1(e)). The microwire/channel ratio of 1.1 was great by ensuring an easy manual sliding of the electrodes and avoiding leakages even at harsh flow rates of up to 40.0 mL min⁻¹. The reproducibility of the electrochemical recovery when using Fe(CN)₆³⁻/⁴⁻ as redox couple was satisfactory in all the cases (Fig. 1(d,e)). The best data were obtained when Ag/AgCl was used as reference electrode. In this case, the global averages of the peak currents to Fe(CN)₆³⁻/⁴⁻ oxidation and reduction were 11.1 ± 0.2 µA and 10.9 ± 0.2 µA (n = 18), respectively. The RSDs were only 2.1% for oxidation and 1.8% for reduction. The confidence intervals ranged from 0.1 to 0.3 µA. With regard to the test involving analytical curves for MEG (Fig. 1(f,g)), the renewal processes showed a satisfactory reproducibility again. Considering the four curves, the analytical sensibilities exhibited a global average of 3.8 ± 0.1 µA mmol⁻¹ L (n = 4) with a RSD of 3.5%. The analyte contents obtained by the four renewals pulling only the working electrode would be reproducible according to Student’s t tests at 95% confidence level. For a response of 24 µA, e.g., the MEG amounts determined by the curves would show an average of 6.3 ± 0.2 mmol L⁻¹ (n = 4). In terms of the RSD, its value would be only 3.1%. For the evaluation of the renewal after passivating the electrodes (Fig. 1(h)), the peak currents to Fe(CN)₆³⁻/⁴⁻ after the thiol passivation were reduced in roughly 80% compared with the initial currents. This data was because the increase in the resistance to electron transfers. Otherwise, the electrochemical activity was effectively and reproducibly recovered by pulling all of the three electrode according to Student’s t tests at a confidence level of 95%. The global averages of the peak currents were 17.2 ± 0.5 µA (oxidation) and 17.9 ± 0.4 µA (reduction) (n = 12). The RSDs were 2.8% for oxidation and 2.1% for reduction. In relation to the intra-assay precision, the confidence intervals for the same surface changed of 0.2 up to 0.6 µA only.

Conclusion: renewable solid electrodes are, to the best of our knowledge, described for the first time assuming the absence of any surface treatment. This process offers reproducibly recovering the electrochemical activity of the working, reference, and counter electrodes. The renewal relied on simply pulling metal film-coated microwires across a top channel containing the sample. The electrochemical activity regeneration herein shown eliminates the necessity for constructing new analytical curves in order to achieve reproducible results of analyte concentration. Furthermore, the absence of any interfaces in the chips and the elastomeric nature of the PDMS allowed us to easily pull the wires without leakage in the electrode channels even at a flow rate of 40 mL min⁻¹. A paper about the results herein discussed was recently published in ‘Analytical Chemistry’.

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