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### Metal nanostructures formed by electrodeposition in microchannels: study of the growth mechanism and application to SERS

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The electrodeposition of a metal is known to be able to lead to the formation of metal *ramified structures* (RS) which are commonly called *dendrites*. Under particular conditions (Hele-Shaw/thin gap cell and no supporting electrolyte), RS exhibit a small structure which consists of metal nanocrystals [1]. The two interesting aspects of this electrochemical formation of nanostructures are 1) the in situ formation and 2) the immobilization inside the cell. The use of microfluidic connections then allows both the required purification of the nanostructure by flushing and the controlled injection of reagents/solutes [2]. This can be advantageously implemented, by the use of the deposited nanostructure as Surface Enhanced Raman Spectroscopy (SERS) substrate, for flow chemistry applications (chemical imaging).

Since the SERS signal strongly depends on nanostructure properties, how the size and shape of nanocrystals depend on the electrodeposition conditions (current density  $j$  and metal salt concentration) is studied. For Cu and Ag, SEM imaging shows a morphological transition of the nanocrystals: below a critical current density, the nanocrystals are non-dendritic (equilibrium shape) while above they are dendritic. The RS formation is ensured by a nucleation/growth (re-nucleation) regime at low  $j$  [1] and only by growth (without re-nucleation, dendrite=single crystal) at high  $j$ . It is shown that the theoretical description of this transition (by a Mullins & Sekerka shape stability analysis) requires taking into account of the deviation from electroneutrality through a space charge layer. In situ formed RS, made of Ag nanodendrites, showed an enhancement of the Raman signal.

References:

[1] V. Fleury, Nature 390, 145 (1997)

[2] A. Iranzo and F. Chauvet, Microfluidics and Nanofluidics 23, 45 (2019)