Nano-Strategies in Analytical Chemistry

Henrique E. Toma

Full professor

Institute of Chemistry, University of São Paulo (USP), SP, Brazil

henetoma@iq.usp.br

Nanotechnology is impacting all the areas of Science, providing high performance materials and techniques, and introducing new concepts from the nanoscale. In particular, the great development of the **electronic and scanning probe microscopies** brought about chemical analysis into a new dimension, allowing to probe directly the composition and properties of the samples at the atomic/molecular level.

Even classic optical microscopy has been renewed by incorporating dark field and confocal design, laser sources for excitation, and CCD detectors for recording the electronic and vibrational spectra of micro/nanosize samples. Such advances allowed to access the molecular map from the **hyperspectral** images of the samples, by storing a complete spectrum into every single pixel. A typical example is the classical Feigl's spot test analysis of nickel(II) and palladium(II) with dimethylglyoxime (Hdmg). $[\text{Ni}(\text{Hdmg})_2]$ is a red planar complex, susceptible to attack of acids, while $[\text{Pd}(\text{Hdmg})_2]$ has a yellow color, and is acid resistant. While the red color of the $[\text{Ni}(\text{Hdmg})_2]$ disappears when exposed to acids, palladium ions, even in trace amounts, are able to protect the complex, preserving its original color. This fact has been explored by Feigl to develop a specific analytical test for palladium. Confocal Raman microscopy studies revealed that $[\text{Ni}(\text{Hdmg})_2]$ consists of wires of stacked molecules, with an external hydrophobic coating of methyl groups, leaving only the extremities exposed to the attack of acids. According to the hyperspectral images, this is the site occupied by the palladium complex, thus explaining the protection mechanism involved in Feigl's test [1].

Surface plasmon resonance (**SPR**) is being currently explored in analytical chemistry as a very sensitive technique for investigating adsorption and molecular interactions, specially at the electrodes. It is based on the interaction of the surface plasmons of metals such as gold, with the light evanescent waves projected at specific angles, and can be easily adapted to monitor the electrochemical processes at the surface. A similar plasmon resonance effect is observed in the interaction of gold plasmonic nanoparticles with light, leading to an enhancement of the local electric fields and light scattering, responsible for the rise of strong colors which can be monitored spectrophotometrically. The coupling of plasmonic nanoparticles can be chemically induced, giving rise to new extinction bands in the visible. This effect has been successfully explored in chemical and biochemical analysis, extending in many orders of magnitude the sensibility of the analytical tests.

Plasmonic nanoparticles also exhibit strong surface enhanced Raman effect or **SERS** [2,3]. Such effect involves three mechanisms: a) electromagnetic, typical of physical adsorption of the analytes, and b) chemical, involving the interaction of the analytes with the surface by means of charge-transfer or resonance absorption interactions. The electromagnetic effect is less specific, leading to a general enhancement of the adsorbed molecule vibrational peaks, while the charge-transfer and resonance Raman effects respond to specific chromophores in the molecules. Both mechanisms provide interesting analytical applications in chemistry and biology. In many favorable cases, the combined mechanisms lead to a huge enhancement of the Raman signals, up to 14 orders of magnitude, reaching the single molecule detection limit.

Nowadays, the use of nanoparticles in Electroanalytical Chemistry is already a very common practice. As a matter of fact, nanoparticles provide very large surface areas and can be suitably functionalized for coating electrodes and improving their chemical and electrochemical performance. Typical nanoparticle cores are made up of inorganic materials such as gold, silver, TiO_2 , Fe_3O_4 (magnetite) and $\gamma\text{-Fe}_2\text{O}_3$ (maghemite). Carbon nanomaterials also employed in electroanalytical chemistry comprise activated carbon, carbon nanotubes, fullerenes, graphene, graphene oxide, reduced graphene oxide, nanodiamonds and carbon quantum dots [4].

A special case is provided by the functionalized Fe_3O_4 **superparamagnetic nanoparticles**. After interacting directly with the analytes in solution, they can be magnetically confined at the electrode surface, with the aid of an external miniature strong magnet (e.g. $\text{Nd}_2\text{Fe}_{14}\text{B}$). The magnetic confinement approach [5] increases the electrochemical response, similarly to the classical stripping methods in analytical chemistry; however, it has a much broader and general use, allowing to explore the preconcentration effect for any species and electrode materials (gold, platinum, carbon, etc.). Such process has also proved very efficient as a greener alternative for hydrometallurgy [6]. Similarly, superparamagnetic nanoparticles have also been successfully employed as versatile support for catalysts, particularly the enzymes, for analytical purposes and industrial processing [7].

REFERENCES

1. Huila, M. F. G.; Lukin, N.; Parussulo, A. L. A.; Oliveira, P. V.; Kyohara, P. K.; Araki, K.; Toma, H. E. *Anal. Chem.*, **2012**, *84*, pp 3067-3069.
2. Grasseschi, D.; Toma, H. E. *Coord. Chem. Rev.*, **2017**, *333*, pp 108-131.
3. Aroca, R. F. *Surface-Enhanced Vibrational Spectroscopy*, John Wiley & Sons, Ltd., Chichester, **2006**.
4. Canevari, T. C.; Cincotto, F. H.; Gomes, D.; Landers, R.; Toma, H. E. *Electroanalysis*, **2017**, *29*, pp 1968-1975.
5. Condomitti, U.; Zuin, A.; Novaki, M. A.; Araki, K.; Toma, H. E. *Electrochem. Commun.*, **2011**, *13*, pp 72-74.
6. Toma, H. E. *Green Chem.*, **2015**, *17*, pp 2027-2041.
7. Netto, C. G. C. M.; Toma, H. E.; Andrade, L. H. *J. Mol. Catal. B: Enzym.*, **2013**, *85-86*, pp 71-92.