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SERS sensors made of polymers and Aluminum to check the health of artworks

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Introduction
Conservation and restoration of works of art face many problems caused by degradation of bulk materials, varnishes, binding media and dyes. Identification and characterization of these degradation products has always been of high importance because it is the first step to develop and apply the appropriate treatments to preserve our cultural heritage.
The concern is more acute for modern and contemporary art, because the materials used are so radically different from those used in classical art, that there is a significant lack of established conservation protocols that can deal with the often extremely fast degradation of materials used by contemporary artists.
In this work we show our approach to detect early degradation products of common polymers by means of surface enhanced Raman scattering (SERS) sensors developed in our lab, and based on the fabrication of regular micro and nanostructured polymers coated with a thin layer of aluminum as plasmonic metal.
Checking the health of artworks by SERS
Raman spectroscopy is a nondestructive method that provides the vibrational fingerprint spectrum of the molecular structure of materials, so it might be the perfect tool to analyze artworks where the sampling is highly restricted. But Raman signal is intrinsically weak due to the low number of scattered photons available for detection.
Surface Enhanced Raman Scattering (SERS) comes to help, because it is a method to amplify the Raman signals of molecules by an increment of their apparent Raman cross-section [1]. To do this trick, the excitation laser is shined over metallic nanoparticles or nano-structured metal surfaces, typically made of noble metals, with gold and silver as common choice. The laser resonantly drives the metal surface charges, creating highly localized plasmonic light fields, known as hot-spots. When a molecule is close to one of these hot-spots, a large amplification of its Raman signal can be observed, allowing the detection of very low concentrations of chemical species or even single molecule detection [2].
The main problem to use SERS as everyday lab technique is the lack of appropriate substrates. Few commercial substrates are available, they are expensive and quite unstable, requiring to keep them in controlled atmospheres and careful handling to maintain their enhancing activity. Another problem is repeatability due to variability in size and distribution of nanostructures.
To tackle the main drawbacks of SERS substrates we developed an easy and cheap fabrication process in just two steps: replica molding based on ultraviolet nanoimprint lithography (UV-NIL), followed by coating with a thin metal layer by metal evaporation. The molding step guarantees the same shape and structure in all the substrates and the UV-NIL provides freedom to design any 2.5D structure and, in combination with the photoresist used, reduces the fabrication time to just a few seconds. In our case we choose a crosslinkable di- or tetrafunctional perfluoropolyether derivate [3] and a commercial ormocer photoresist.
As plasmonic metal we relies on aluminium, initially because its low cost compared to gold or silver and also because the Al2O3 passivation layer, that far from being a problem is an advantage because after reaching a thickness of 1.5 to 3.0 nm it stops growing and protect the metal from further oxidation, while still allows the plasmonic excitation of molecules attached to the surface. Aluminium has properties that enable strong plasmon resonances spanning from the UV to the NIR region [4].

Fig.1. Polymer and Al SERS substrates and SEM image of the periodic nanostructure showing the inverted pyramids geometry and the nanocrystals of Al on the surface.

Initial tests where made with organic analytes like Rhodamine 6G, Coumarin 440, Rhodamine B or Crystal Violet, using 514 nm and 785 nm excitation lasers with powers ranging between 0.01-1.0 mW. The signal enhancement is comparable or higher than that obtained with commercial substrates made of gold or silver.

Fig.2. SERS spectra of photo-oxidation products of: a) linseed oil and b) polyisoprene rubber.

As an actual application we are testing the SERS substrates to detect and identify early degradation products formed by ageing or weathering of modern and contemporary artworks made of different polymers and blends. This diagnostic information is relevant for material science researchers and conservators which can develop and apply appropriate treatments to fight against degradation and preserve valuable cultural heritage goods. The sensibility of SERS substrates is a keystone in a field where sampling is strongly limited due to the value of the pieces. Tests on different polymers, binders, inks, pigments and other materials are yielding promising results those showed in Fig.1b.

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References

[1] E.C. Le Ru, E. Blackie, M. Meyer, and P.G. Etchegoin, J.Phys. Chem. 111 (2007) 13794.

[2] K. Kneipp, Y. Wang, H. Kneipp, L.T. Perelman, I. Izkan, R. R. Dasari and M. S. Feld, Phys. Rev. Lett. 78 (1997) 9, 1667.

[3] M. Gómez and M. Lazzari, Microelectronic Engineering, 97 (2012) 208.

[4] M. W. Knight, N. S. King, L. Liu, H. O. Everitt, P. Nordlander, and N. J. Halas, ACS Nano 8 (2014) 834.

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