Nano-plasmonics tuned "click chemistry" monitored in situ by Surface Enhanced Raman Spectroscopy

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Surface functionalization and surface chemistry modifications play an important role in many fields. Among all surface modification strategies, "click chemistry" gained meaningful attention for its numerous benefits: high efficiency, simple realization, rapidity, chemoselectivity, feasibility in water media and enhanced yields. UV light-mediated thiol-ene or thiol-yne reactions involve the addition of the thiol to an alkene or alkyne respectively, induced by radicalar mechanism. These reactions have already been reported to allow great diversity of functionalization on several surfaces [1]. Moreover, these reactions also permit multiple functionalization by conjugating other "click chemistry" methodologies.

Herein, in order to perform local molecular immobilization at the microscale, thiol-ene click reaction was implemented *in situ* on plasmonic nanostructures using a visible irradiation at 660 nm laser excitation wavelength. The kinetics of reaction was then monitored by Surface Enhanced Raman Spectroscopy (SERS) in real time using the same laser wavelength. We demonstrate the effectiveness of the reaction even if the excitation wavelength is out of the UV range. By investigating reaction rates, on different diameters of nanocylinders made by electron-beam lithography (EBL), we claim that this reaction is induced by plasmonic effects and by the enhanced electromagnetic field around the nanostructure. In order to prove these assessments various negative controls were performed.

The authors want to acknowledge the ANR REMANTAS project (ANR-11-ECOT-0010) for the financial support.

[1] P. Demay-Drouhard, E. Nehlig, J. Hardouin, L. Motte, E. Guenin, Chemistry-a European Journal, 2013, 19, 8388-8392.

[2] T. Vong, J. ter Maat, T.A. van Beek, B. van Lagen, M. Giesbers, J.C.M. van Hest, H. Zuilhof, Langmuir, 2009, 25, 13952-13958.

[3] D.I. Rozkiewicz, W. Brugman, R.M. Kerkhoven, B.J. Ravoo, D.N. Reinhoudt, Journal of the American Chemical Society, 2007, 129, 11593-11599.

[4] G.-J. Zhang, T. Tanii, T. Zako, T. Funatsu, I. Ohdomari, Sensors and Actuators B: Chemical, 2004, 97, 243-248.

[5] C.C. Wu, D.N. Reinhoudt, C. Otto, V. Subramaniam, A.H. Velders, Small, 2011, 7, 989-1002.

[6] C. Wendeln, S. Rinnen, C. Schulz, T. Kaufmann, H.F. Arlinghaus, B.J. Ravoo, Chemistry-a European Journal, 2012, 18, 5880-5888.