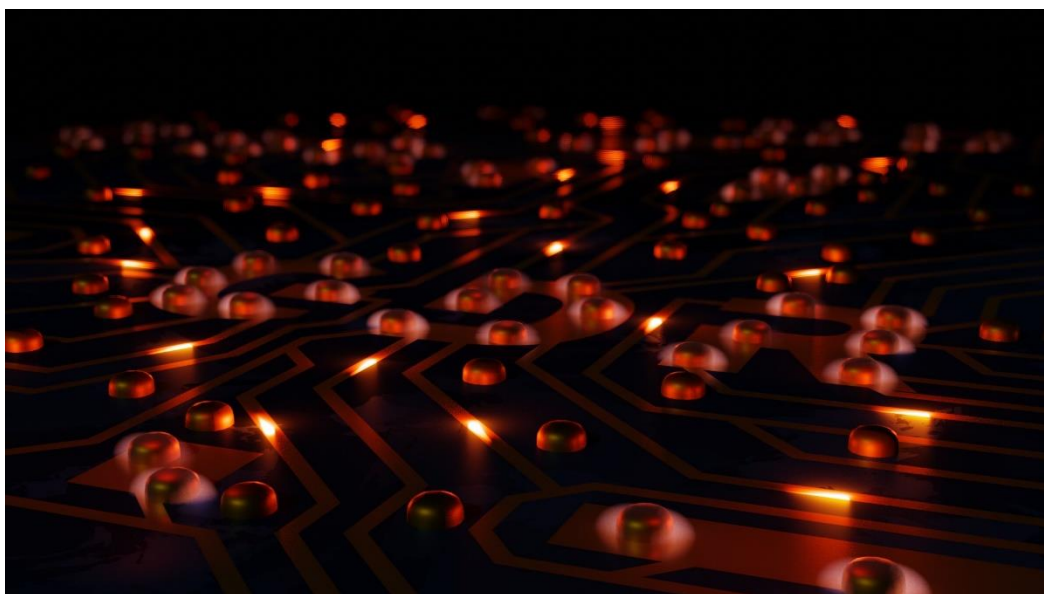


Journée thématique 2021
Processus photo-induits et plasmon de surface

10 Novembre 2021

Université de Nantes, Laboratoire CEISAM

Livret des résumés



Chères et chers collègues,

Nous sommes ravi(e)s de vous accueillir à la journée thématique du GDR *Plasmonique Active* (CNRS, GDR 2090) qui se tiendra au laboratoire CEISAM, à l'Université de Nantes, le Mercredi 10 Novembre 2021. Cette journée est organisée par Clémence Queffélec. Au nom du bureau du GDR, je tiens à remercier chaleureusement Clémence, qui a pris le soin d'organiser de façon remarquable cette journée. Je tiens également à remercier l'Université de Nantes pour son accueil et son soutien logistique, ainsi que le CNRS sans qui nos manifestations ne pourraient se tenir.

Cette journée sera consacrée aux processus photo-induits, en relation avec l'excitation des plasmon de surface. Elle combine l'axe 2 (plasmonique et réactions chimiques) et l'axe 3 (plasmonique et transformations physiques) des thématiques développées au sein de notre GDR. L'ensemble des séminaires proposés montre la richesse et la diversité des projets menées à l'échelle nationale autour des processus photo-induits. Alors, si Nantes est fameuse pour ses monstres mécaniques, et notamment ses éléphants géants, ne soyez pas effrayé(e)s pour nous rejoindre. Nous aurons en effet le plaisir de vous accueillir pour discuter de processus photo induits, autour de spécialités Nantaises.

Lu et approuvé,

Bien cordialement,

Au nom du bureau du GDR *Plasmonique Active*
M. Nordin FELIDJ, directeur du GDR

Informations pratiques

Le laboratoire CEISAM se situe sur le campus de la Faculté des Sciences et Techniques de l'Université de Nantes.

CEISAM UMR-CNRS 6230, Faculté des Sciences et Techniques, 2 Rue de la Houssinière, BP 92208, 44322 NANTES CEDEX 3

Transports en commun : Arrêt Michelet Sciences (tram Ligne 2, Bus n°10 et n°23).

En voiture : Il est préférable d'arriver par le 28 Rue de la Haute Forêt 44300 Nantes (Entrée Sud du Campus)

Le laboratoire CEISAM est le bâtiment 22.

**Arrêt de tram ligne
2, Michelet Sciences**



La journée se tiendra dans la salle Marie-Curie du laboratoire CEISAM (bâtiment 22). La bâtiment sera libre d'accès.

Les pauses-café auront lieu dans le laboratoire CEISAM et le repas du midi sera pris au Restaurant Universitaire (RU).

Journée thématique 2021

Processus photo-induits et plasmon de surface

10 Novembre 2021
Université de Nantes, Laboratoire CEISAM

Programme

Lieu : Amphi Marie Curie – Laboratoire CEISAM

9.30 – 10.00	Accueil café - croissants
10.00 – 10.15	Accueil et introduction
10.15 – 11.00	Hynd REMITA – Surface modification of TiO₂ with plasmonic nanoparticles for photocatalysis under visible light
11.00 – 11.20	Miguel Comesaña-Hermo – Multimodal plasmonic hybrids: efficient and selective photocatalysts
11.20 – 11.40	Leila Hammoud – Designing titania-interfaced gold nanostructures for plasmonic CO ₂ reduction with water
11.40 – 12.00	Nathalie Destouches – Laser-induced physical chemistry in Ag:TiO ₂ nanocomposites and application to security color printing
12.00 – 12.20	François Lagugné-Labarhet – Three-color plasmon-mediated reduction of diazonium salts over metasurfaces
12.20 – 14.00	Déjeuner (Restaurant Universitaire)
14.00 – 14.45	Céline FIORINI – De l'émission de lumière à la fonctionnalisation contrôlée de nanoparticules d'or : rôle de la relaxation du plasmon
14.45 – 15.05	Fabien Miomandre – Smart surfaces made of gold nanoparticles functionalized by luminescent and redox-active molecules
15.05 – 15.25	Renaud Bachelot – Advanced hybrid plasmonic nano-emitters using smart photopolymer
15.25– 15.55	Pause-café
15.55 – 16.15	Nordin Felidj – The grey side of plasmonics: from pure to hybridized surface lattice plasmon modes
16.15 – 16.35	Marc Lamy de la Chapelle – Polymérisation radicalaire induite par excitation optique de nanoparticules d'or
16.35 – 16.50	Conclusions et clôture de la journée thématique 2021

Surface modification of TiO₂ with plasmonic nanoparticles for photocatalysis under visible light

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Development of efficient photocatalysts under solar light for depollution and solar fuel production is a main challenge to solve energy and environment issues. TiO₂ is a very efficient photocatalyst due to its photocatalytic activity, high photochemical stability and low cost. The limitation in TiO₂ application results from low quantum yield due to fast charge carriers (electron/hole e⁻/h⁺) recombination and its activation only under UV irradiation because of the value of its band gap. Its surface modification with metal nanoparticles (NPs) can lead to enhancement of the photo-conversion quantum yield and may allow the extension of the light absorption of wide band-gap semiconductors to the visible light.¹⁻⁴ In particular, plasmonic photocatalysts have appeared as a very promising way to induce a photocatalytic activity of TiO₂ in the visible range.¹⁻³

Modification of TiO₂ with Au-NPs leads to an increase of its photocatalytic activity under UV and visible light for H₂ generation and water treatment. Time resolved microwave conductivity (TRMC) signals show injection of electrons from Au-NPs to the conduction band of TiO₂ under visible-light excitation, due to the activation of localized surface plasmon resonance (LSPR) of the Au-NPs. Action spectra (AS) correlate with the absorption spectra proving that decomposition of model pollutants is carried out by a photocatalytic mechanism.¹⁻²

Modification of titania with CuO@Ag and bimetallic Ag-Au nanoparticles (induced by radiolysis) leads to higher photocatalytic activity compared to titania modified with the monometallic nanoparticles (for water treatment and hydrogen generation): a synergetic effect is obtained.³

Finally, an example of plasmonic catalysis with Pd nanosheets for Suzuki–Miyaura reactions (C-C coupling) under visible light irradiation will be presented.⁴

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Notes

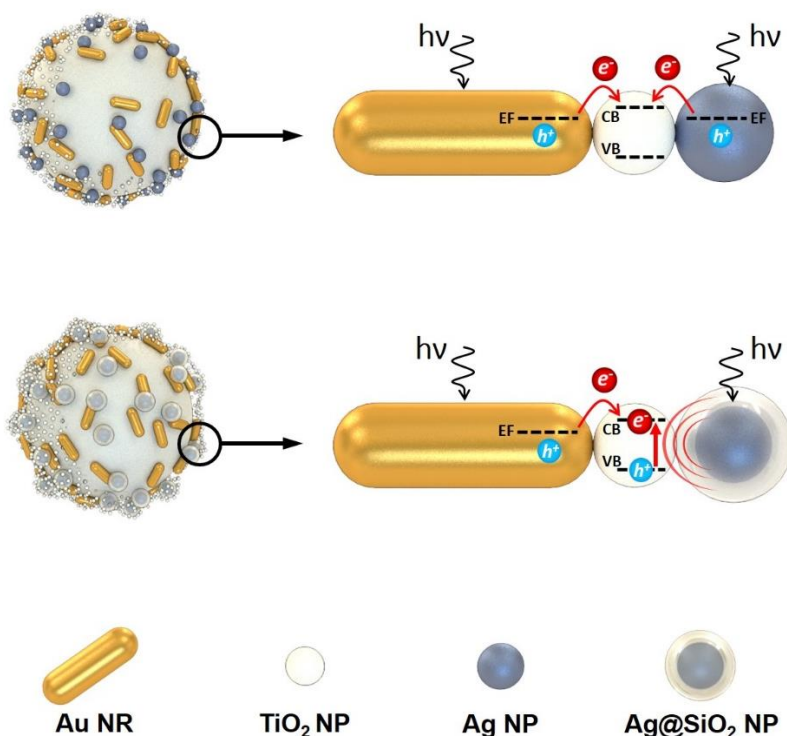
Multimodal Plasmonic Hybrids: Efficient and Selective Photocatalysts

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In this presentation we will discuss a synthetic strategy that brings together two of the main physical mechanisms driving plasmonic photocatalysis into an engineered system by rationally combining the photochemical features of energetic charge carriers and the electromagnetic field enhancement inherent to the plasmonic excitation. We do so by creating hybrid photocatalysts that integrate multiple plasmonic resonators in a single entity, controlling their joint contribution through spectral separation and differential surface functionalization. This strategy allows us to study the combination of different photosensitization mechanisms when activated simultaneously. Our results show that hot electron injection can be combined with an energy transfer process mediated by near-field interaction, leading to a significant increase of the final photocatalytic response of the material. Furthermore, our multimodal hybrids offer a test system to probe the properties of the two targeted mechanisms and open the door to wavelength-selective photocatalysis and novel tandem reactions.



Notes

Designing titania-interfaced gold nanostructures for plasmonic CO₂ reduction with water

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The photoreduction of CO₂ with water in the gas phase may generate valuable chemicals and fuels, including methane (synthetic natural gas). In this artificial photosynthesis process, selectivity for the 8 electron/8 proton reduction of CO₂ into methane is limited by the competing 2 electron/2 proton reduction of water into H₂¹ and by poor adsorption of the CO₂ molecule on most semi-conductor (SC) surfaces.² Only one titania-based photocatalyst, loaded with specific Pd₇Cu₁ co-catalytic nanoparticles (NPs), has been found 100% selective so far, when irradiated with UV light.³ We have recently achieved 100% selectivity under visible irradiation by plasmonic excitation of titania-interfaced gold NPs.⁴

In this presentation, we will present our efforts towards the optimization of such plasmonic photocatalysts for the gas-phase reduction of CO₂ with water into synthetic natural gas. We will show how the size, arrangement and composition of gold-based NPs over titania, as well as the interaction between these plasmonic NPs and titania, impact the photocatalytic behavior of the composite under visible irradiation. We will further show how irradiation with the full solar spectrum modifies this behavior and how the SC-based and plasmon-driven mechanisms can be synergistically combined to achieve full selectivity at high methane production rates.

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Notes

Laser-induced physical chemistry in Ag:TiO₂ nanocomposites and application to security color printing

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Plasmonic color generation has attracted intensive attention because of the high color contrast and long lifetime of metal nanostructures protected by dielectric cover. Strong technological impact has been predicted, however industrial applications are still limited. Recently, lasers have emerged as powerful tools to control the plasmonic properties of metal nanoparticles, with some assets such as their high flexibility and rapidity to process large areas with a control of the plasmonic properties at the micrometer scale. The laser creates a micro-reactor in the material in which thermal and optical gradients can be controlled precisely in space and rapidly in time. This leads to specific physical chemical mechanisms during the laser process and to innovative properties of the resulting nanostructured material. Our material of interest is a plasmonic metasurface made of silver nanoparticles covered with TiO₂.

In this presentation, we will present a counterintuitive thermal behavior where the temperature increases when the deposited energy decreases^{1,2}, and different configurations where light plays with growing nanoparticles to spontaneously drive self-organization processes^{3,4,5}. Then, we will show few surprising optical properties of these laser-induced metallic metasurfaces that allow to develop a new approach for security color printing^{6,7}.

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Notes

Three-color plasmon-mediated reduction of diazonium salts over metasurfaces

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Surface plasmon-mediated chemical reactions are of great interest for a variety of applications ranging from micro- and nanoscale device fabrication to chemical reactions of societal interest for hydrogen production or carbon reduction. Fractal-type structures are of interest since the number and position of plasmon resonances can be tailored and are dependent on the fractal generation. In this work, a crosshair-like nanostructure (Fig. 1) is investigated due to its ability to induce local enhancement of the local electromagnetic field at three distinct wavelengths corresponding to three plasmon resonances. The structures are irradiated in the presence of a solution containing diazonium salts at wavelengths that match the resonance positions at 532 nm, 632.8 nm, and 800 nm. The resulting grafting shows polarization and wavelength-dependent growth patterns at the nanoscale. The plasmon-mediated reactions over arrays of the crosshair structures are further investigated using scanning electron microscopy and supported by finite domain time domain modelling revealing wavelength and polarization specific reactions. Such an approach enables nanoscale molecular printing using light source opening multiplexing applications where different analytes can be grafted under distinct opto-geometric conditions.

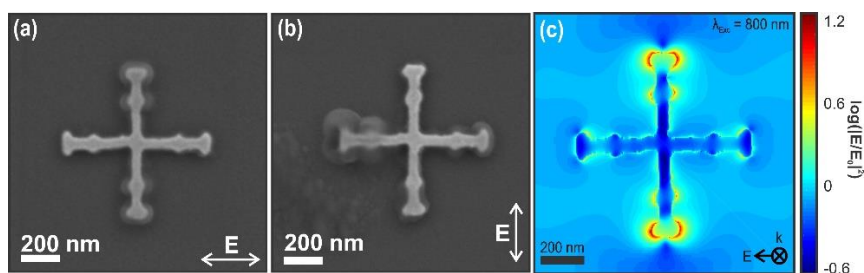


Fig. 1. Polarization dependent Plasmon-mediated grafting of diazonium salts under 800 nm irradiation over cross-hair structures

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Notes

De l'émission de lumière à la fonctionnalisation contrôlée de nanoparticules d'or : rôle de la relaxation du plasmon

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La photochimie médiée par les plasmons est devenue un domaine de recherche actif dans le domaine des nanosciences, car elle ouvre de nombreuses perspectives d'application de la conversion d'énergieⁱ à la photocatalyseⁱⁱ, en passant par la photothérapie et la nanofabrication.ⁱⁱⁱ En particulier, la fonctionnalisation déclenchée par plasmons peut être mise à profit pour la réalisation de nanostructures hybrides avancées pour la photonique^{iv}.

Malgré de nombreuses démonstrations, les mécanismes et principaux paramètres qui régissent le contrôle des réactions photochimiques médiées par plasmons restent cependant flous et controversés.^{v,vi} La difficulté provient de l'existence de différents effets issus de différentes voies de relaxation des plasmons: (1) effets photoniques liés aux exaltations locales de champ favorisant les interactions lumière-matière dans des endroits spécifiques autour des NPs, (2) effets électroniques liés au transfert de porteurs de charge chauds de la NP excitée vers des espèces chimiques à proximité, (3) effets thermiques, provenant de l'échauffement local résultant de la thermalisation du réseau suite aux interactions électrons-phonons.

L'objectif de mon exposé sera de discuter ces différents processus à la lumière d'une étude récente concernant la nanophotopolymérisation radicalaire autour de NPs d'or^{vii}. Je montrerai également que la luminescence à deux photons de NPs d'or se révèle être une technique particulièrement sensible^{viii}, permettant une évaluation quantitative de l'ampleur des points chauds plasmoniques.^{ix}

Remerciements : Les auteurs remercient l'Agence Française pour la Recherche (ANR) pour son soutien financier (projet sous subventions HAPPLE : ANR-12-BS10-016 et SAMIRE : ANR-13-NANO-0002).

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Notes

Smart surfaces made of gold nanoparticles functionalized by luminescent and redox-active molecules.

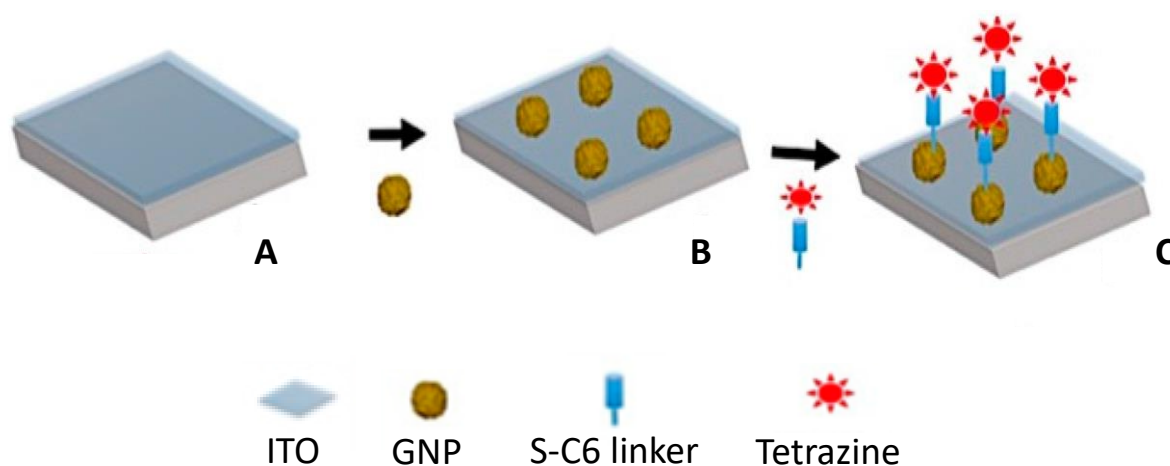
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Plasmonic surfaces made of gold nanoparticles coated on ITO have been functionalized by luminescent and redox active molecules. The aim of this study is to design smart surfaces that can be activated by a light stimulus and lead to an output signal, namely the emission of the molecule, that is strongly dependent on multiple factors among which the redox state of the molecule. Information coding systems can be envisioned according to this principle.

The grafted molecules are made of a fluorophore unit connected to an alkyl chain terminated by a thiol precursor. The functional surfaces are characterized by microscopy, XPS, cyclic voltammetry and time-resolved photoluminescence. The dependence of the luminescence properties on the gold nanoparticle size, surface density and grafting method has been analyzed and the results shown in this communication.



Notes

Advanced hybrid plasmonic nano-emitters using smart photopolymer

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The integration of nano-emitters into plasmonic devices with spatial control and nanometer precision has become a great challenge. In this paper, we report on the use of a smart polymer for selectively immobilizing nano-emitters on specific preselected sites of gold nanocubes (GNC). The cunning use of the polymer is twofold. First, it records both the selected site and the future emitters-GNC distance through plasmon-assisted photopolymerization. Second, because the polymer is chemically functionalized, it makes it possible to attach the nano-emitters right at the preselected polymerized sites which subsequently “recognize” the nano-emitters to get attached. Since the resulting active medium is a spatial memory of specific plasmonic modes, it is anisotropic, making the hybrid nanosources sensitive to light polarization. The ability to adjust their statistical average lifetime by controlling the thickness of the nanopolymer is demonstrated on two kinds of nano-emitters coupled to GNC: doped polystyrene nanospheres and semiconductor colloidal quantum dots.

Notes

The grey side of plasmonics: from pure to hybridized surface lattice plasmon modes

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The tuning of hybridized localized surface plasmon (LSP) modes in coupled metallic nanostructures has appeared recently as an emerging strategy to control their optical properties. When assembling in periodic arrangements, the nanostructures support collective surface lattice (SL) plasmon resonances, which are radically different from LSP resonances observed for instance in a short-range coupling. In the same way as the hybridization of LSP resonances, we evidence experimentally a hybridization of SL plasmon resonances, without providing a short-range interaction [1]. The plasmonic platforms are made of binary arrays with unit cells made of two gold disks of distinct diameters, resulting in the emergence bonding and anti-bonding SL plasmon modes, analogous to the hybridized LSP modes observed in short-range interactions. Our study includes an experimental near-field optical plasmonic mapping through a plasmon-induced functionalization strategy using the diazonium strategy [2]. We also demonstrate the possibility to cancel or maximize the interaction between the hybridized SL resonances by simply controlling the relative position of the particles. All our experimental results are supported by FDTD calculations. The hybridization of SL modes results in a rich hybridization scenario, offering numerous opportunities to generate innovative optical devices.

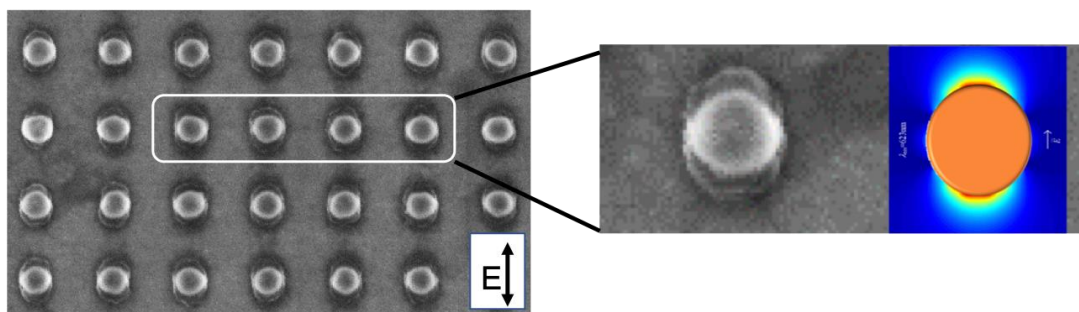


Fig. 1: (left) SEM image of a regular array of gold disks, after a laser irradiation (at 785 nm) in presence of diazonium salts; (right) zoom of a single disk displaying an aryl film layer, after a plasmon-induced grafting of the diazonium salt; its location follows the maximum of the intensity of the local electric (calculations obtained by the FDTD method).

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Notes

Polymérisation radicalaire induite par excitation optique de nanoparticules d'or

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Grace à leurs propriétés optiques et plasmoniques remarquables, les nanoparticules métalliques (NPs) peuvent provoquer différents phénomènes physiques comme une élévation de température, la création d'une nano-source exaltée de lumière ou le transfert d'électrons chauds vers des molécules.[1] De tels phénomènes peuvent être valorisés pour modifier des molécules, activer des réactions chimiques ou bien améliorer leurs cinétiques ou leurs rendements.[2]

Notre travail propose d'explorer un nouveau processus d'activation radicalaire (formation de radicaux primaires) de polymérisation via l'exploitation des propriétés plasmoniques des NPs d'or afin d'élaborer des polymères bien définis. Le plasmon est donc utilisé pour induire la formation de radicaux primaires nécessaires à la polymérisation de monomères vinyliques sous irradiation lumineuse ($\lambda = 458, 515, 611$ ou 630 nm). Une étude systématique des conditions expérimentales (concentration en NPs, taille des NPs, position de la résonance plasmon, concentration en monomère N,N-diméthylacrylamide) d'un tel système nous a permis de démontrer que le plasmon améliore les performances de synthèse (cinétique et rendement de polymérisation) à 458 nm et que ces performances sont optimales à 515 nm, longueur d'onde proche de la résonance plasmon des NPs d'or. Au contraire, aucun effet du plasmon sur la réaction de polymérisation n'a été détecté à 611 et 630 nm (longueurs d'ondes hors résonance). De plus, même si la concentration en NPs influence la cinétique de polymérisation, il est à noter qu'une très faible concentration en NPs de quelques pmol/L est suffisante pour identifier des performances cinétiques intéressantes.

Cette étude permet de mieux comprendre les phénomènes mis en jeu lors de l'activation radicalaire en polymérisation photo-induite et d'évaluer l'influence réelle du plasmon. Grace à cette étude, les paramètres plasmoniques tel que la position de la résonance sont identifiés comme ceux impliqués dans le processus de l'activation radicalaire en polymérisation.

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Notes