Quantum dots avec ligands actifs : vers des photocatalyseurs redox actifs en lumière visible

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Stage pouvant se poursuivre en thèse : Oui

Résumé :

Stage proposé en co-direction avec le Dr Fabien Dubois de l'institut Néel (fabien.dubois@neel.cnrs.fr).

Dans ce projet nous proposons d'étudier une nouvelle classe de photocatalyseurs basés sur des quantum dots colloïdaux i) peu chers, ii) absorbant la lumière visible et iii) capables de photocatalyse des réactions redox dans des conditions douces [1], ainsi que nous l'avons montré dans une étude récente [2]. L'originalité des systèmes développés dans ce projet sera de connecter des quantum dots à des nanoparticules d'argent de façon contrôlée par chimie "click" (cycloaddition de Huisgen entre ligands azotures et alcynes) [3]. Ces assemblages quantum dots/nanoparticules d'argent visent à favoriser la séparation des paires électron/trou photoinduites dans les quantum dots et à augmenter ainsi l'efficacité des systèmes photocatalytiques étudiés par notre équipe.[1]

Sujet détaillé :

Several studies in the literature demonstrated that when CdSe or CdS quantum dots are used as redox photocatalysts, the transfer of photoinduced charge carriers from the core of the quantum dots to electron acceptors or electron donors in the surrounding solution is limited by unwanted electron/hole charge recombination.

A promising strategy to promote the charges separation and avoid charges recombination is to connect the quantum dot with a molecule or another nanoparticle that is a very good hole or electron acceptor. So the separated charges live longer and react more efficiently with the substrates in the surrounding solution.

In this internship we propose to connect CdSe quantum dots with silver nanoparticles, which are known to be efficient electron acceptors. The controlled size connection will make profit of the ligands shells of both types of nanoparticles and of the very versatile technique of "Huisgen azides-alkynes cycloaddition called Click chemistry". Ligands bearing appropriate moieties (azide or alkyne) will by grafted on the surface of quantum dots and silver nanoparticles [3], and then "cliked" together in order to connect the two types of nanoparticles together.

The efficiency of these new photocatalytic systems will be tested quantitatively for the photooxidation of 8oxo-deoxyguanosine (a very common DNA lesion) in the presence of nitroaromatic electron acceptors, which was already described as occurring but rather slowly, when quantum dots are used as photocatalysts in the absence of silver nanoparticles [1].

This internship will provide the trainee with some skills in nanoparticles functionalization, click chemistry, photochemistry and photophysics of nanoparticles and in various techniques for monitoring reactions such as HPLC, mass spectroscopy and magnetic resonance.

[1] Wilker, M.B.; Schnitzenbaumer, K.J.; Dukovic, G., Recent Progress in Photocatalysis Mediated by Colloidal II-VI Nanocrystals, Isr J Chem, 2012, 52, 11-12, p1002-1015.

[2] Chauvire, T.; Mouesca, J.-M.; Gasparutto, D.; Ravanat, J.-L.; Lebrun, C.; Gromova, M.; Jouneau, P.-H.; Chauvin, J.; Gambarelli, S.; Maurel, V.; Redox Photocatalysis with Water-soluble Core-shell CdSe-ZnS Quantum Dots, J. Phys. Chem. C, 2015, 119, (31), pp 17857-17866.

[3] (a) Yao, Y.; Demei, T.; Haibing, L., Cooperative binding of bifunctionalysed and click-synthesized silver nanoparticles for colorimetric Co2+ sensing. (b) Barbara, A.; Dubois, F.; Ibanez, A.; Eng, L.; Quemerais, P. SERS

Compétences requises :

Des connaissances dans le domaine des nanoparticules ou en photochimie seraient un plus, mais ne sont pas indispensables