Spécialité : CHIMIE / Chimie des matériaux

Laboratoire : /NIMBE/LEDNA

Électrodes poreuses à base de nanodiamant pour la production photoélectrocatalytique de combustibles solaires

Responsable de stage : GIRARD Hugues

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Stage pouvant se prolonger en thèse : Oui
Durée du stage : 6 mois

Résumé:

L'objectif de ce stage est d'étudier le nanodiamant pour la photo(electro)catalyse, en synthétisant des électrodes poreuses faites de nanoparticules de diamant fonctionnalisées.

Sujet :

Among nanoscale semiconductors, nanodiamonds (ND) were not really yet considered for photo(electro)catalytic reactions. This originates from the confusion with ideal monocrystalline diamond behaving a wide bandgap (5.5 eV) that requires a deep UV illumination to initiate photoreactivity. At nanoscale, ND enclose native defects (sp2 carbon, chemical impurities) that can create energetic states in the diamond band gap decreasing the light energy needed to initiate the charge separation. This is supported by a recent study that involved our group with combined experimental results and DFT calculations [1]. The presence of sp2 carbon in hydrogenated detonation ND allows the emission of solvated electrons in water under visible light (400 nm) according to ultrafast transient absorption spectroscopy. In addition, the diamond electronic structure can be strongly modified playing on its surface terminations (oxidized, hydrogenated, aminated) [2]. Combining these assets, ND becomes competitive to other semiconductors toward photoreactions. For instance, we recently evidenced H2 production under solar illumination from water dissociation in presence of oxidized ND [3].

The objective of this internship is to go further in the study of nanodiamonds for photo(electro)catalysis. A first aspect of the work will concern the optimization of their surface chemistry by exploring new functionalization methods, notably by sonochemistry. The later approach is new, not reported on ND. The challenge will be to confer NH2 terminations to ND which may prove interesting for the production of solvated electrons. Surface modifications will be probed by a panel of spectroscopic techniques (FTIR, Raman, XPS, etc.). Modified ND will be then dispersed in aqueous colloids and characterized by DLS and Zetametry. A second aspect will concern the fabrication of porous ND electrodes. We will use a home-made set-up allowing the co-deposition of nanoparticles in an aerodynamic jet produced from colloidal suspensions and a solid matrix of amorphous carbon or ITO by PVD [4]. After morphological and chemical characterizations of the ND-based porous structures by SEM, TEM, EDX and XPS, their electrochemical behavior will be investigated by cyclic voltammetry and capacitance measurements. Finally, photoelectrochemical measurements will be considered to evaluate the potentiality of the approach toward photoelectrocatalysis.

References

[1] F. Buchner, Early dynamics of the emission of solvated electrons from nanodiamonds in water, Nanoscale. 2022, 14,

17188. https://doi.org/ 10.1039/d2nr03919b
[2] C. Nebel, A source of energetic electrons, Nature Materials. 2013, 12, 780
[3] C. Marchal et al., Oxidized detonation nanodiamonds act as an efficient photocatalyst to produce hydrogen under solar irradiation, under review
[4] S. Lai et al., Aerosol-based functional nanocomposite coating process for large surface areas Sci. Rep. 13, 4709 (2023). https://doi.org/10.1038/s41598-023-31933-w

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Laboratory : CEA NIMBE, Nanometric Structures Laboratory (LEDNA)

Required skills: Nanomaterials, Colloids, Material characterizations, Photoelectrocatalysis

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Nanodiamond-based porous electrodes: towards photoelectrocatalytic production of solar fuels

Abstract:
The objective of this internship is to study nanodiamonds for photo(electro)catalysis, by building porous electrodes made of functionnalized diamond nanoparticles.

Subject :
Among nanoscale semiconductors, nanodiamonds (ND) were not really yet considered for photo(electro)catalytic reactions. This originates from the confusion with ideal monocrystalline diamond behaving a wide bandgap (5.5 eV) that requires a deep UV illumination to initiate photoreactivity. At nanoscale, ND enclose native defects (sp2 carbon, chemical impurities) that can create energetic states in the diamond band gap decreasing the light energy needed to initiate the charge separation. This is supported by a recent study that involved our group with combined experimental results and DFT calculations [1]. The presence of sp2 carbon in hydrogenated detonation ND allows the emission of solvated electrons in water under visible light (400 nm) according to ultrafast transient absorption spectroscopy. In addition, the diamond electronic structure can be strongly modified playing on its surface terminations (oxidized, hydrogenated, aminated) [2]. Combining these assets, ND becomes competitive to other semiconductors toward photoreactions. For instance, we recently evidenced H2 production under solar illumination from water dissociation in presence of oxidized ND [3].

The objective of this internship is to go further in the study of nanodiamonds for photo(electro)catalysis. A first aspect of the work will concern the optimization of their surface chemistry by exploring new functionalization methods, notably by sonochemistry. The later approach is new, not reported on ND. The challenge will be to confer NH2 terminations to ND which may prove interesting for the production of solvated electrons. Surface modifications will be probed by a panel of spectroscopic techniques (FTIR, Raman, XPS, etc.). Modified ND will be then dispersed in aqueous colloids and characterized by DLS and Zetametry. A second aspect will concern the fabrication of porous ND electrodes. We will use a home-made set-up allowing the co-deposition of nanoparticles in an aerodynamic jet produced from colloidal suspensions and a solid matrix of amorphous carbon or ITO by PVD [4]. After morphological and chemical characterizations of the ND-based porous structures by SEM, TEM, EDX and XPS, their electrochemical behavior will be investigated by cyclic voltammetry and capacitance measurements. Finally, photoelectrochemical measurements will be considered to evaluate the potentiality of the approach toward photoelectrocatalysis.

References

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