Plasmonic Photocatalytic Oxidization of NH4⁺ in Micro Optical Fluidic Chip

Hung Ji Huang^{1,*}, Chih-Chung Yang¹, Po-Jui Chen¹, Chun-Ting Lin¹, Hai-Pang Chiang^{2,3}, Yuan-Fong Chou Chau⁴, and Chi-Hung Hwang¹

¹Instrument Technology Research Center, National Applied Research Laboratories, Hsinchu, Taiwan ²Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung, Taiwan

³Institute of Physics, Academia Sinica, Taipei 115, Taiwan

⁴Centre for Advanced Material and Energy Sciences, Universiti Brunei Darussalam, Negara Brunei Darussalam

* Email: hjhuang@narlabs.org.tw; Tel.: +886-3-5779911

This paper reports a new design of micro optofluidic chips in the application of plasmonic photocatalytic oxidization of Ammonium ions (NH_4^+) dissolved in water under light illumination, Fig. 1. In this report, the Au nanoparticles (NPs) replaced the typically used catalyst in typical artificial nitrogen cycle. The micro optical fluidic chip (MOFC) reactor is good with high mass transfer rate that can enhance processing efficiency of chemical reaction [1]. The UV light transmittable construction material, e.g. glass, Polydimethylsiloxane (PDMS), or NOA81 [1], makes the MOFC perfectly suitable for photocatalytic reaction.

Typically, artificial nitrogen cycle processes via the wet air oxidization (WAO) method oxidize and eliminate the dissolved NH₄⁺ from water with temperature higher than 150 °C and high pressure. The plasmonic heating in metal nanostructures and localized high temperature under light illumination enhances chemical reactions [2-5]. In this study, the pre-deposited layer of (3-Aminopropyl)trimethoxysilane (APTMS) fixed various sized Au NPs on the inner walls of the flow channel, Fig. 2. The pink color in the lower chip is coming from the scattering light of the fixed Au nanoparticles with size of 20 nm. Only the area of the rectangle fluidic channel, 2 cm (W) × 3 cm (L) × 58 μ m (H), deposited with APTMS layer can catch Au NPs, see SEM data in Fig. 3. No obvious depletion observed after the experiments of NH₄⁺ oxidization under alkaline conditions.

The MOFC reactor with or without fixed 20 nm Au nanoparticles presented oxidization of NH_{4}^{+} ions dissolved in water under light illumination, Fig. 1. Two array of profusion channels with 10 µm in width separated and limited the water flow-in speed from input-reservoir. External visible light supplied by halogen lamps illuminated the channel and induce surface plasmon resonances on Au nanoparticles. Two groups of experiments with various flow speed of test solution processed under alkaline condition with adding sodium hydroxide (NaOH). The pH adjustment increased the initial pH value to about 11.5 and supplied hydroxide ions (OH⁻) for oxidization of NH_{4}^{+} ions in water.

The reserved NH_4^+ ions in test solution after experiments with various water pumping flow speed was measured and depicted in Fig. 4. The experiments with fixed Au NPs had concentration of reserved NH_4^+ smaller than that with no Au NPs after 1 hr of processing time. The Au nanoparticles presented plasmonic enhancement of the chemical catalytic oxidization of NH_4^+ ions in water in the MOFC reactor.

In conclusion, the plasmonic oxidation of NH_4^+ ions in water presented inside the MOFC reactor with Au NPs as photocatalyst. The MOFC reactor shows great potential for further investigation in the future.



Fig. 1. Schematics of the MOFC reactor.



Fig. 2. MOFC reactor with and without fixed Au NPs.



Fig. 3. Au NPs fixed on glass substrate.



Fig. 4. Reserved NH_4^+ after treatment for various water pumping flow speed with and without Au NPs fixed in MOFC reactor.

REFERENCES:

- L. Lei, N. Wang, X. M. Zhang, Q. Tai, D. P. Tsai, and H. L. W. Chan, "Optofluidic Planar Reactors for Photocatalytic Water Treatment Using Solar Energy," Biomicrofluidics, 2010, 4, 043004.
- [2] H. J. Huang, B.-H. Liu, and J. A. Yeh, "Ammonium oxidization at room temperature and plasmonic photocatalytic enhancement," Catal. Comm., 2013, 36, 16-19.
- [3] H. J. Huang and B.-H. Liu, "Plasmonic energy transformation in the photocatalytic oxidation of ammonium," Catal. Comm., **2014**, 43, 136-140.
- [4] S. Mukherjee, F. Libisch, N. Large, O. Neumann, L. V. Brown, J. Cheng, J. B. Lassiter, E. A. Carter, P. Nordlander, and N. J. Halas, "Hot electrons do the impossible: plasmon-induced dissociation of H₂ on Au," Nano Lett., **2013**, 13, 240-7.
- [5] H. J. Huang, B.–H. Liu, C.–T. Lin, and W. S. Su, "Plasmonic photocatalytic reactions enhanced by hot electrons in a onedimensional quantum well," AIP Advances, 2015, 5, 117224.

ACKNOWLEDGE

The authors are grateful to the Ministry of Science and Technology of Taiwan, Republic of China for supporting this research under contract no. 105-2221-E-492-036