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Invited Review

Surface-enhanced Raman spectroscopy toward application in plasmonic photocatalysis on metal nanostructures

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ABSTRACT

Among photothermal, photovoltaic and photochemical techniques, photochemistry is superior in energy storage and transportation by converting photons into chemical fuels. Recently plasmonic photocatalysis, based on localized surface plasmon resonance (LSPR) generated from noble metal nanostructures, has attracted much attention. It promotes photochemical reaction efficiency by optimizing the solar spectrum absorption and the surface reaction kinetics. The deeper understanding is in urgent need for the development of novel plasmonic photocatalysts. Surface-enhanced Raman spectroscopy (SERS), which is also originated from the LSPR effect, provides an excellent opportunity to probe and monitor plasmonic photoreactions in situ and in real-time, with a very high surface sensitivity and energy resolution. Here, fundamentals of plasmonic photocatalysis and SERS are first presented based on their connections to the LSPR effect. Following by a validity analysis, latest studies of SERS applied for the plasmon mediated photochemical reaction are reviewed, focusing on the reaction kinetics and mechanism exploration. Finally, limitations of the present study, as well as the future research directions, are briefly analyzed and discussed.

Contents

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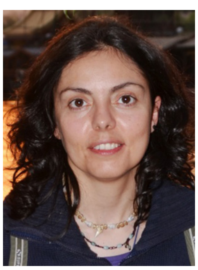
Xue-Jiao Chen received her BSc in 2007 at Southwest University and obtained her PhD in Physical Chemistry in 2013 with Prof. Lin Zhuang at Wuhan University. Now she is working as a postdoc fellow in Professor Zhong-Qun Tian's Group at Xiamen University. Her present interest focuses on the mechanistic research of the artificial-photosynthetic reactions, especially of the carbon dioxide reduction process, with the aid of the in-situ spectro-electrochemical method and the further development of efficient plasmonic photocatalyts toward artificial photosynthesis.



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De-Yin Wu received his BSc at Shaanxi's Normal University in 1992 and his PhD in Physical Chemistry at Sichuan University in 1998. Now he is a full professor of Department of Chemistry, College of Chemistry and Chemical Engineering (2006–) and State Key Laboratory of Physical Chemistry of Solid Surface (2007–), Xiamen University. His research area focuses on theories of Surface-enhanced Raman Spectroscopy, adsorption and electron transfer in electrochemical interfaces and charge transport in molecular electronics. Recently, his research interest is a mechanistic insight into surface plasmon-enhanced chemical reactions on noble metal nanostructures.

Zhong-Qun Tian has been a full professor at Xiamen University since 1992. He is a Member of Chinese Academy of Sciences, Fellow of the Royal Society of Chemistry and a Member of the International Society of Electrochemistry and a member of the advisory board of eleven international journals including JACS, Chem. Sci., Chem-Comm Anal. Chem, PCCP and an associate editor of Chem. Soc. Rev. and J. Raman Spectroscopy. His main research interests are surface-enhanced Raman spectroscopy, spectro-electrochemistry, nanochemistry, and plasmonic photocatalysis.

1. Introduction

The substitution of the traditional fossil fuels by renewable energies, which are abundant, cost-effective, and safe, is the only way to solve the problem of the rapid natural-resources depletion and the continuing environment deterioration. Solar energy is one of the most important renewable energies. It has been estimated that only with 0.02% of the solar energy arrived at the earth every hour, the entire energetic needs of all humans for a year can be satisfied [1]. Nevertheless, the efficiency of the solar energy conversion is far from satisfactory which makes this aim a long way to realize [2–5].

The common way of the solar energy conversion (utilization) is to convert the sunlight into heat, electricity, and/or chemical fuels. To make these conversions as efficient as possible, the R&D of novel materials for photothermal, photoelectric, and photochemical processes is of critical importance. Since the first report of the water splitting into H_2 and O_2 under UV-light illumination on the TiO_2 by Honda and Fujishima [6], the development of materials, including semiconductors [7–10] metal-nanostructures [11–13], molecule-assemblies [14–16], and combinations between them [17–21], has been under constant and vigorous study for the past 40 years. The improvement of the materials does not only depend on the numerous trial-and-error screening, but also relies on the microscopic understanding down to the molecule-level to provide the structure-to-activity relation for further improvements.

Among many other analytical techniques, surface-enhanced Raman spectroscopy (SERS) is highly attractive to surface scientists as it can in principle provide much insight into a variety of chemical, physical and biological surfaces and interfaces at the molecular level. It can be applied to in situ investigation of solid–liquid, solid–gas and solid–solid interfaces and processes, to which many surface techniques are not applicable [22]. These advantages profoundly benefit the real time study of the concomitant temperature variation, charge transfer, and/or reaction dynamics during the solar energy conversion on the active materials. Considering the recent fast-growing enthusiasm of studying the photochemical process by SERS and the scope of this tutorial review, we would like to limit our discussion in the field of photochemistry. The photothermal and photoelectric conversions studied by SERS can be found in literature [23–28] and [29–31], respectively.

In the following sections, a discussion of the localized surface plasmon resonance (Section 2.1) will be first presented before a brief introduction of SERS (Section 2.2). Then, the emerging plasmonic photochemistry and its light-harvesting principles will be discussed (Section 2.3). Based on the same origin, SERS applied to plasmonic photocatalysis will be discussed and analyzed allowing for the generality and reliability concerns (Section 2.4). Prototypical SERS studies of the plasmon-mediated photochemical (PMPC) reactions will be presented in Sections 3–6. Finally, conclusions and outlook of SERS toward application in the solar energy conversion will be summarized in Section 7.