SUMMARY OF THE DISSERTATION DONE

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Fundamentals and applications of photo-thermal catalysis

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Fundamentals and applications of photo-thermal catalysis

1. INTRODUCTION

Catalysis is an integral part of chemistry with large implications for the efficient production of everyday goods. Indeed, circa 95% of all chemical products are manufactured through catalytic routes. At the same time, many of these processes require an energy input that has, traditionally, been supplied by non-renewable sources.[1,2] In the last few decades, with the discovery of heterogeneous semiconductor-based photocatalysis, the possibility of catalyzing chemical transformations using light as a source of energy has become a reality. In a semiconductor, upon absorption of a photon with equal or higher energy than the band gap, electron–hole pairs are generated. Eventually these charge carriers can migrate to the semiconductor surface and be transferred to adsorbed molecules, thereby initiating reduction or oxidation processes. Since the seminal paper of Fujishima and Honda in 1972, tremendous advances in the field of photocatalysis have been reported. In spite of this, the efficiency of most photocatalytic processes remains insufficiently low (typically in the range of hundreds of $\mu mol\ g^{-1}\ h^{-1}$) mainly due to fast charge carrier recombination and low absorption and utilization of the solar spectrum by traditional wide band gap semiconductors.[3–8]

2. Localized surface Plasmon resonance and the photo-thermal effect

The localized surface plasmon resonance (LSPR) band in metallic nanoparticles (NPs) is an intense and broad absorption band along the UV-visible-NIR region of the electromagnetic spectrum. The physics behind this phenomenon has been traditionally explained by means of two theories: the Drude– Maxwell model and the theory developed by Gustav Mie in 1908.[9,10] Although it is beyond the scope of this review to contribute to a deep and extensive discussion of these theories, these models can provide insightful information to describe the LSPR phenomenon and its application to catalysis, so a brief overview of them will be addressed. As per these theories, inside metal NPs conducting free electrons can move when guided by external incident irradiation. This motion is dampened by electron inelastic collisions and the restoring force on the electron cloud created by the accumulation of surface charges (Fig. 1).

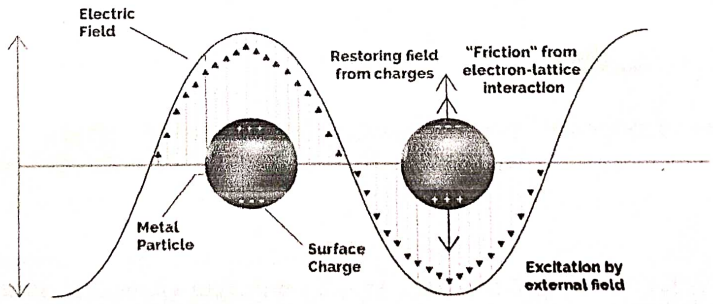

Fig. 1 Schematic illustration of the dynamics of an excited plasmonic nanoparticle

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3. Photo-thermal applications in catalysis

3.1. CO_2 conversion

The possibility of producing synthetic fuels or chemicals throughthe reaction between CO_2 and H_2O (or indirectly between CO_2 and H_2 derived from H_2O using green energy sources) is among themost promising alternatives to achieve CO_2 neutrality in transportationand the chemical industry. In general, the reduction of CO_2 can produce different chemicals and fuels, CO, CHOOH, CH_3OH or CH_4 among others, depending on the number of electrons thatcome into play. Over the last decade, the use of photothermal catalysis to speed up these processes has grown exponentially.

3.2. Artificial photosynthesis

Artificial photosynthesis is described as the most direct approach to reduce CO_2 and it tries to replicate the natural photosynthesis, one of the most important reactions on Earth.[11] The perfect route will employ CO_2 and water as reagents in a significant carbon recycling, producing hydrogen or carbon-based fuels by using ideally sunlight as a sustainable energy source.[12,13] This process is divided into two main reactions, the water splitting reaction that produces H_2, and CO_2 reduction, which produces carbon-based products such as CO, CH_3OH or CH_4.[14] The second reaction is much more challenging than the first one due to its requirement of the conduction banedge and multi-electron processes, depending on the product. On this basis, the main limitations of the photocatalytic methodology are the relatively low charge separation efficiency, light harvesting and reduction selectivity.[15,16] However, the cooperation between photo and thermocatalytic processes could be a solution.[17]

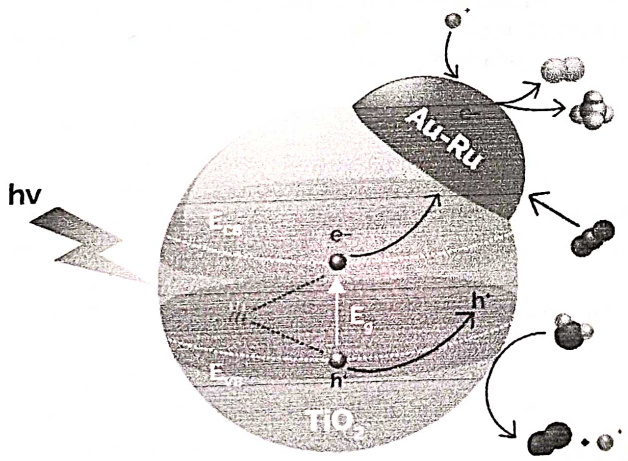

Fig. 2 Synergistic effects between photocatalysis and thermocatalysis in the direct thermophotocatalytic reduction of CO_2–H_2O over Au–Ru/TiO_2.

4. Conclusion

In this review, we have succinctly explained the physics behind the LPSR phenomenon and its direct influence on the photo-thermal effect displayed by plasmonic NPs. Upon light irradiation, nonradiative plasmon decay leads to the local heat generation and/or hot carrier formation in

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plasmonic structures. Individually or synergistically working together, thermal and photochemical contributions
of the photo-thermal effect in plasmonic or nonplasmonic nanostructures can be exploited to promote catalytic chemical transformations. A comprehensive analysis of the contribution of both approaches to the overall reaction rate is, however, crucial to further understand the reaction mechanisms, so an extensive revision of straightforward methodologies to successfully distinguish the dominant reaction pathway has been included in this review. Indeed, photo-thermal catalysis has proven to be an efficient strategy to perform a wide variety of high energydemanding catalytic processes including CO_2 hydrogenation, Fischer–Tropsch reaction, ammonia synthesis, methane activation or H_2 production. In order to improve catalytic performances and selectivity, a suitable material engineering is also advisable. In the last section of this review, we have included strategies for catalyst design in order to maximize the efficiency for a given photothermal- mediated pathway. The vast number of catalytic applicationsm together with the possibility of tailoring the thermal, optical and electronic properties of photocatalysts demonstrates the huge versatility and potential of photo-thermal catalysis.

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