Photon energy threshold in direct photocatalysis with metal nanoparticles – key evidence from action spectrum of the reaction

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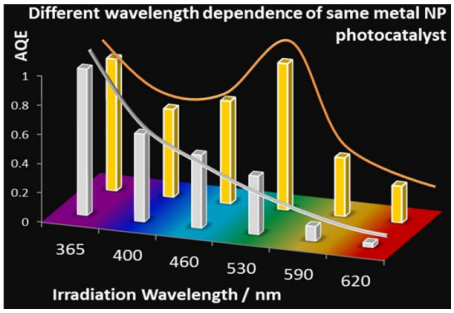
Abstract: *By investigating the action spectra - relationship between irradiation wavelength and apparent quantum efficiency of reactions under constant irradiance - of a number of reactions catalysed by nanoparticles including plasmonic metals, non-plasmonic metals and their alloys, we found that distinct action spectra were observed in the same type of reaction catalysed by the same catalyst. Demonstrating a photon energy threshold exists in each photocatalytic reaction: only photons with sufficient energy can initiate the reaction. These results indicate that photon-electron excitations play a dominant role in direct photocatalysis of metal nanoparticles.*



Keywords: Action spectra, Photon energy threshold, direct photocatalysis, metal nanoparticle.

1. Introduction

Nanoparticles (NPs) made from transition metals, such as Au, Ag, Cu; Pd, Pt, Rh, Ir, Ru and their alloys, dispersed on optically and catalytically inert materials (ZrO_2, Al_2O_3 etc) have been found as efficient photocatalysts. The NPs exhibit strong optical absorption over the entire solar spectrum, and efficiently channel the photon energy into molecules that are adsorbed on their surfaces and initiate chemical transformations. We note that an energy alignment is required for the reactions mediated by the hot electrons, which is different from reaction to reaction and depends closely on reaction conditions that influence the rate limiting step of the reaction. Since the energy state of the photoexcited electrons is mainly determined by irradiation wavelength, it is possible to gain insight into the mechanism of direct photocatalysis of metal NPs from analysis of the impact of irradiation wavelength on the photocatalytic reactions catalysed by metal nanoparticles.

2. Results and discussion

We analyse the dependence of photocatalytic activity in many photocatalytic reaction systems under illumination of different wavelengths, using seven catalysts in total (NPs made from six different metals, including Au, Ag, Pd, Pt, Rh, Ir and Au-Pd alloy). To avoid the interference from light absorption by the support solids, metal NPs were supported on photocatalytically inert support materials (such as ZrO_2, Al_2O_3 etc.) that have negligible light absorption at the wavelengths used. We use action spectra (the wavelength dependence of photocatalytic apparent quantum efficiency, AQE) in the present study to analyse the contribution of the different effects, as shown in Figure 1.

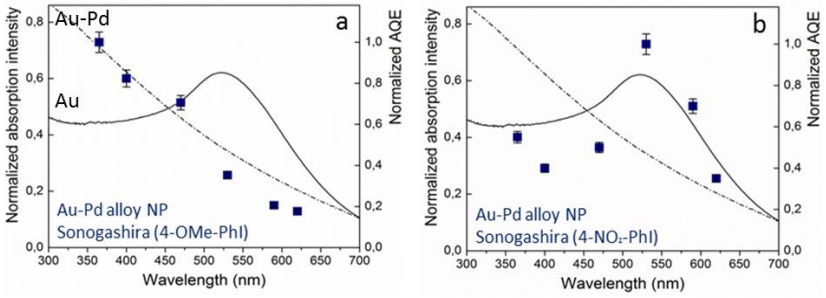
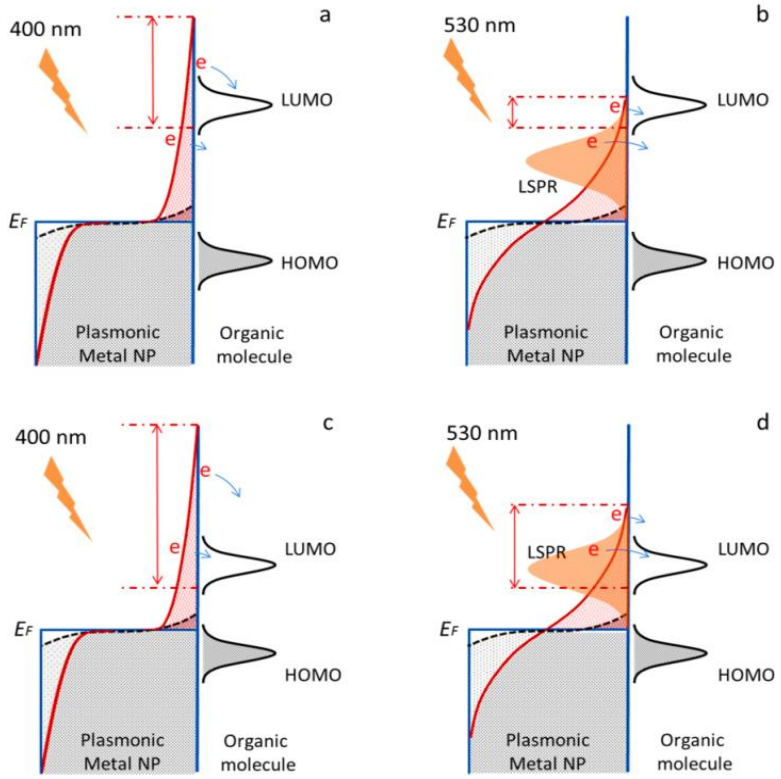


Figure 1. Different action spectra shown on Au-Pd alloy NP photocatalysts. The dash line is the light absorp-tion of Au-Pd alloy NP photocatalyst and solid line is the absorption of Au NPs a) Sonogashira coupling of phenylacetylene with 4-iodoanisole (4-OCH3-

PhI), show an action spectrum follows the light absorption of Au-Pd alloy NPs; b) So-nogashira coupling of phenylacetylene with 1-iodo-4-nitrobenzene (4-NO2-PhI), exhibits an action spectrum does not follow the light absorption of Au-Pd alloy NPs but follows absorption of Au NP.

By measuring the wavelength dependence of AQE we reveal the photon energy threshold; above which significant photocatalytic activity is observed. Analysis of the action spectra, the shape of the spectral dependence, allows us to distinguish reactions mediated by energetic electrons and those mediated by plasmon-induced heating.

Reactant molecules on the metal NP surface with different LUMO energy levels are indicated in the scheme: high energy LUMO (a and b) and low energy LUMO (c and d). The reactions are predominantly driven through interaction between the hot metal electrons with sufficient energy. By changing the position of the orbital that must be populated to drive the chemical reaction, the action spectra are significantly modified. Thus, one can see a molecular imprint on the action spectra.



Scheme 1. Hot electron distribution of metal NPs under irradiation of different wavelengths and their contribution to AQE in different reactions. a: metal NP irradiated with light of 400 nm wavelength. b: metal NP irradiated with its LSPR wavelength (e.g. 530 nm for the Au NPs in this study). c: metal NP irradiated with 400 nm wavelength and an organic molecule with lower LUMO. d: metal NP irradiated with its plasmon wavelength, the hot electrons able to contribute to AQE is the area above LUMO, involving hot electrons excited by both wavelengths.

4. Conclusions

The threshold is a feature of the photo-induced electron excitation driven reactions. The photon-electron excitation mechanisms are important as they can efficiently channel the photon energy into the chemical bonds to be activated. They also reveal opportunities to achieve efficient chemical transformations at near ambient conditions by tuning the wavelength and intensity of the irradiation as well as the reaction temperature. Such photocatalysis may lead to discoveries in the selective organic synthesis reactions driven by irradiation of solar spectrum.

References

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2. S. Sarina, H-Y. Zhu et al, J. Phys. Chem. Lett. 2017, 8, 2526−2534.