Is azo-coupling of p-nitrothiophenol a good reaction for the evaluation of plasmon catalysis mechanism?

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The excitation of plasmon resonance on noble metals nanostructures delvers practical outcome in sensorics, photocatalysis. In plasmon-induced transformationsm, plasmon exciation allows to overcome the limitations of classical catalysis, such as high temperatures, pressures, and the use of complex catalytic systems. A model reaction for studying the mechanistic aspects of the plasmon-induced catalysis is the azo coupling of nitro- or -aminothiophenols. However, the nature of bonding between thiols and plasmonic metals is considered as chemisorption, which may be reversibile – one thiophenols can be replaced by other molecules. Thiols can desorb from the substrate surface at elevated temperature and pressure, different pH values. This calls into question the validity of using the azo coupling reaction to assess the mechanism of plasmon catalysis. Therefore, we were faced with the task of evaluating the possibility of using this reaction in mechanistic studies.

We performed a detailed study about the stability of thiols-metal layer under the excitation of plasmon resonance. The elemental composition and chemical state (sulfur and nitrogen) were evaluated on the surface of nanoparticles during the azo coupling reaction. The azo coupling reaction of nitrothiophenol was carried out on the surface of gold nanoparticles with a size of 13 nm under excitation of plasmon resonance by illumination of 660 nm (corresponding to the maximum of plasmon resonance) for 1, 3, 6 hours. The reaction control was performed by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The elemental composition and chemical state of the atoms were verified by XPS. We found that during irradiation, the oxidation and desorption processes were observed on S2p XPS spectra. This calls into question the validity of using the azo coupling reaction to study the mechanistic aspects of plasmon catalysis.

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