

Water Oxidation at N-Doped Graphene Oxides – Structure Property Relationships and PCET Dynamics

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The generation of energy with resource-friendly materials has become one of the central challenges in modern material design and chemistry. One key process of particular interest in this field is the photoinduced proton-coupled electron-transfer (PCET) that concludes the first step of the water-oxidation reaction.¹ By applying theoretical model calculations it was proposed recently that graphitic carbon-nitrides, which are only composed of organic materials, are able to photo-catalyze this process.² Seeing how these graphitic carbon-nitrides have nitrogen as their reactive sites, we present here a similar study on the related fully-organic material family of N-doped graphene oxides (NGO) that has also been shown to catalyze water splitting under irradiation with light.³

Applying time-dependent density functional theory calculations for a large set of differently functionalized NGO model molecules, we find recurring designs that thermodynamically favor a PCET reaction using wavelengths closer and closer to the sunlight spectral maximum. Based on the relaxed reaction pathway for the hydrogen transfer from water towards the NGO model molecule, we estimate the necessary hydrogen transfer time and apply quantum dynamics calculations using the time-dependent configuration interaction scheme in its reduced density operator formulation (ρ -TDCI)⁴ to simulate the PCET dynamics upon laser excitation in the presence of thermal dissipation. By studying the importance of non-adiabatic coupling strengths we may find optimal thermalization life-times that may be helpful to design related devices.

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