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Theory of materials for solar energy conversion

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The ability to generate energy in a renewable and sustainable way is rapidly becoming one of the key priorities both for science, technology and society. Solar energy is one such renewable resource, and nature harnesses it through the process of photosynthesis. Inspired by the natural photosynthesis, photovoltaics and photocatalysis are using sunlight to produce electricity or to drive chemical reactions.

The principles behind photocatalytic and photovoltaic processes are similar: both systems rely on absorption of light by the photoactive material (which can be either solid or a molecule) to create a bound electron-hole pair (exciton) [1-4]. The next essential step is the dissociation of the exciton to create a free electron and hole, while the recombination of the electron and hole – the loss process – should be avoided. The electron and the hole then will diffuse through the (heterogeneous) photocatalyst to reach the adsorbed reactant species [1,2], or diffuse through electron-transporting and hole-transporting media in solar cells to enter the electric circuit [3,4].

In heterogeneous photocatalysis, the photocatalytic material typically has both the function of absorbing light to create the electron-hole pair, and provides catalytic sites for oxidation and reduction reactions (although both processes can be assisted, e.g. by using adsorbed light-harvesting sensitisers [5] and by using co-catalysts for oxidation or reduction: molecular co-catalysts [5,6] or noble metals, such as Pt [6]). Similarly, in silicon solar cells the light-absorbing material (silicon) is also the electron- and hole-transporting medium [7]. In contrast, in third-generation solar cells (dye-sensitised [3], organic [4] and, most recently, perovskite-sensitised solar cells [8]), separate materials take the roles of light absorbers, electron- and hole-transporters. This removes the need to look for a single material with a combination of exceptional properties, but processes taking at the interface between the different components (e.g. interfacial charge separation and charge recombination) need to be taken into account [3,9].

Many of the properties that control the efficiency of materials for solar energy conversion firmly belong to the realm of condensed matter physics: structures of crystalline and amorphous solids; their surfaces and interfaces; light absorption; charge transport in bulk materials; electron and hole trapping; charge transfer and reactions at interfaces. Fundamental studies of these processes are essential for understanding materials' properties and designing new materials with better efficiencies.

Theoretical modelling plays an important role in materials research: on the fundamental level, it provides atomic-scale information which is often inaccessible to experiments, and helps identify key factors that control materials' behaviour. Computational design of materials can suggest new materials and thus new avenue for exploration. Increasingly, computational screening is a very useful tool for identifying promising materials, before time and effort are spent on synthesis [10,11].

This special issue brings together several computational studies which address some of the key challenges faced by the photocatalysis and photovoltaics community, such as the search for materials with good light absorption, separation and localisation of photogenerated charges, and mechanisms of photocatalysed reactions.

The paper by Guigliion et al. [12] sets the scene for this issue by providing a tutorial-style review of photocatalysis, with focus on the electronic properties which determine the efficiency of a photocatalyst (optical and fundamental band gaps, electron affinities and ionisation potentials, electron-hole separation). Current state-of-the-art approaches for calculating these properties are discussed, from the various flavours of Kohn-Sham density-functional theory (DFT) to time-dependent DFT (TD-DFT) and to the combination of GW and Bethe-Salpeter equation, together with some of the pitfalls of these methods. The discussion is illustrated with examples of calculations of the properties of TiO₂ and organic polymer photocatalysis.

TiO₂, the oldest reported photocatalyst [13], is still probably the most studied photocatalytic material [14], and three papers in this special issue deal with this material and address electron localisation [15], band positions and electron-hole separation [16] and photocatalytic reaction mechanisms [17]. Di Valentin [17] explores the mechanism of water splitting – one of the most important photocatalytic processes – focussing on the first steps of water oxidation on the anatase (101) surface. This study proposes a mechanism where photooxidation is triggered by a hole localised on a surface bridging oxygen: hole transfer from TiO₂ to an adsorbed water molecule takes place simultaneously with proton transfer from this water molecule to the surface, to form a reactive OH· radical species. The resulting OH· radical is likely to react with another hydroxyl radical to form hydrogen peroxide, H₂O₂, or react with other water molecules, with the outcome depending on the species' orientation.

The location and the extent of localisation of the photogenerated electrons and holes are very likely to influence the rates of charge transfer processes. Maggio et al. [15] explore the localisation of excess electron in TiO₂ where a positive counterion is present next to the surface (a charge-transfer exciton). This fundamental system is relevant both for photocatalysis (where the species being reduced is likely to be a cation) and for dye-sensitised solar cells, where the electrolyte solution contains dye cations, as well as other organic and metal cations. The DFT study finds that the excess electron is not fully localised: although a large fraction of the excess electron density is found on one surface or subsurface Ti atom, a noticeable fraction of the excess electron density is spread laterally over a large region. Therefore, a continuum model is introduced to complement DFT and access large areas; this model gives the exciton radius in TiO₂ of tens and even up to hundreds of Ångströms.

TiO₂ on its own may be not good enough as a photocatalyst, because of its lack of visible light absorption and significant electron-hole recombination; modification of this material may be needed to improve its performance. Fronzi et al. [16] give an overview of their recent work on modification of TiO₂ surfaces with metal oxide nanoclusters, such as TiO₂, SnO, SnO₂, PbO, PbO₂, NiO and CuO. The adsorbed nanoclusters modify the positions and the composition of the valence and conduction band edges (and therefore light absorption) of the parent TiO₂ system and, more importantly, can lead to spatial separation of photogenerated electrons and holes; however, the effect strongly depends on the nature of the nanocluster. Notably, the properties of “wet” (water-adsorbed) TiO₂/nanocluster systems are different from the properties of the same systems in vacuo.

Despite the popularity of TiO₂, a wide range of other promising materials are being explored [1,2]. In this issue, Poli et al. [18] present a study of imogolite (alumosilicate and alumogermanate) nanotubes and their properties as photocatalysts. Nanotubes have several attractive properties for photocatalysis: they are porous and therefore have a large surface area, and they are intrinsically polarised, offering different environment to reactant species adsorbed inside and outside the tube. The linear-scaling DFT study [18] finds that the valence and conduction bands of these nanotubes are spatially separated and are localised on the inner and outer nanotube surfaces, respectively, offering the possibility of photooxidation on the outside and hole scavenging on the inside of the tube. Interestingly, the energy

levels of adsorbed water are affected by tube wall polarisation: water adsorbed inside the tube has a higher propensity to be photo-oxidised, and outside the tube – photo-reduced.

Molecular systems are very attractive as a basis of organic photovoltaic devices, especially because plenty of molecular structures can be devised and their properties can be controllably tuned. Faced with this wealth of candidate materials, a fast screening technique is desirable, to weed out poor entries and to select few promising materials. Tortorella et al. [19] describe a search for a reliable and cost-efficient method for studying molecules for organic solar cells, focussing on a particular class of organic molecules – benzofulvene derivatives. Computational methods at different levels of complexity are explored, from semiempirical methods to DFT with a range of density functionals for structures and frontier orbital energies, and TD-DFT for excited states. The study identifies the best-performing method (i.e. the one providing the highest accuracy of the calculated optical gap) and shows that semiempirical methods can be efficiently used for fast but qualitatively reliable screening of large sets of molecules.

I would like to thank all the authors for their contributions, and I hope that the readers will enjoy this special issue.

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