FULL PAPER

On the Way to Optoionics

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Dedicated to Prof. *Michael Grätzel* on the occasion of his 75th birthday

Based on the recent finding of significant ion conduction enhancement in iodide perovskites upon illumination, the potential of an emerging field 'opto-ionics' – that we define in parallelism to 'opto-electronics' – is explored. We emphasize that the major prerequisite is the identification of appropriate stable materials which can act as light-tunable electrolytes, permeation membranes, or electrodes. In this way, classic, but light-tunable electrochemical devices would be in reach. We also touch upon related issues such as sensing, switching, and catalysis, in which light effects on ionic charge carriers are also expected to be important.

Keywords: optoionics, ion conductivity, solid state ionics, lead halide perovskites, photoelectrochemical devices, materials science.

Introduction

When thinking about light-matter interactions, electronic excitations – and their effect on electrical transport properties – come immediately to mind. Less obvious is the connection between light and compositional changes in materials and compounds, despite this also being part of our daily life; think of irreversible phenomena such as bleaching or yellowing. The classic example in this context is the old way of doing photography, namely, to decompose silver halides with visible light of sufficient energy to exceed the material's decomposition energy. The halogen escapes the system, leaving behind silver clusters. The image resolution obtained with this method is still unmatched even by the newest camera developments. For the photographic picture to form, mobility of silver ions is necessary; however, light does not directly affect this ion transport. Light effects on ion conductivity have been invoked for AgI, but the lack of a clear separation between ionic and electronic contributions makes these conclusions doubtful.[1] Conductivity effects induced by gamma irradiation in NaCl have been attributed to modified concentrations of cation and anion vacancies, however without direct experimental proof.[2] A very clear – but rather indirect – photo-effect on ion conduction was observed in the field of optogenetics, which deals with the biological consequences of optically influencing the conductivity of biochemical ion channels.[3]

The ability to significantly enhance ionic conductivity by illumination of the material under concern would in principle enable influencing or even tuning typical electrochemical functions that rely on ion transport. We will show in this contribution that important first steps in this direction have already been made. By analogy to optoelectronics, we term this emerging topic *optoionics*, which – as we will sketch – might become a field of its own right at the interface of photovoltaics and electrochemistry. The term optoionics has been sporadically used in the literature (see, for example, [4–6]), mostly in a wider sense that also includes optical effects of electrochemical variations. Here we will use it to categorize those phenomena that are concerned with optical effects on ion motion; this includes ion transport, transfer, redistribution and hence also storage. (In this sense optoionics relates to optoelectronics as solid

state ionics does to solid state electronics, or nano-ionics to nanoelectronics.) In a broader sense, also structural effects such as light-induced phase transformations or reactions belong to this topic (for example, Ref. [7]; also note a recent report on photo-modulated proton conductivity through isomerization in Ref. [8]).

To achieve such a light-enhanced ion conduction in solid compounds, one would want to change the ionic charge carriers' mobility (influencing the transition state, that is, the activation energy for ionic jumps) or their concentration (for example, of mobile interstitials and vacancies) without however decomposing the material. Still, the direct (through momentum transfer) influence on ion mobility or on the creation of ionic carriers requires (because of the large mass of the ions) energies that are far from the visible range and way above any decomposition energy. Such bombardment effects are rather of interest to the field of radiation damage, and they have been used to introduce metastable exotic defects in crystals (for example, F-, H-, V_K-centers, discussed in the next section).

Recently, clear evidence for an enhancement of the iodide conductivity in methylammonium lead triiodide ($CH_3NH_3PbI_3$, or MAPI) by several orders of magnitude was established in our laboratory.[9] (First indications were reported by *Yang et al.*,[10] and then by *Zhao et al.*,[11] yet both not based on unambiguous evidences.) This effect is truly surprising, and as mentioned above, has various potentially promising implications (see also Ref. [12]).

Here we will *1)* briefly give an account on the special case of MAPI, *2)* discuss the possibility of finding similar effects in other materials, *3)* outline the significance of the phenomenon for existing and novel devices, and *4)* connect the finding to related phenomena in crystals (photodecomposition, photostriction, photodemixing).

Irrespective of whether the enhancement of ionic conduction by UV or visible light occurs through increasing the ionic mobility or the ionic carrier concentration, it must be based on an initial electronic excitation, as a direct ionic photo-excitation can be discarded because of momentum arguments. For MAPI we have strong indications for increased ionic carrier (point defect) concentrations, therefore we will, before we start with the above points, discuss what is known about ionic point defect formation by light or other electromagnetic radiations. We will refer here to ionic halides, for which all these results have been reported.

Results and Discussion

Mechanisms of Defect Formation in Ionic Halides

It is well understood,[13,14] and well-described,[14] that in many types of solids high-energy particles (neutrons, protons, ions) can produce vacancy-interstitial pairs (*Frenkel* defects) through elastic collisions with the regular lattice atoms.[15,16] The host atoms are knocked out from their regular lattice sites and forced to occupy interstitial positions. Thus, it is momentum and energy transfer connected with these particles/electrons that result in the formation of spatially correlated pairs of vacancies and interstitials.[14,17,18] For wide band gap ionic crystals (for example, KCl, KBr), there exists another possibility of point defect generation, namely through electronic excitation using photons (excitonic mechanism).[17,19,20] It was already shown very early[21] that alkali halides (AH) can be colored by X-rays whose energies exceed the band gap. This color arises due to the formation of F centers (from the German *Farbzentrum*, or color center), that is, anion vacancies having captured an excess electron, which is then able to absorb light in the visible spectrum.[22] Detailed later experiments have shown that simultaneously with the electron-related F centers, the complementary hole H centers (split interstitial halogen atoms, X_2^- ions) also arise as metastable centers in AH after X-ray irradiation at low temperatures (below 40 K). Note that the optical, structural, vibrational properties of the H centers in AH are very close to the ones of the corresponding radicals in solutions.[13]

Besides neutral *Frenkel* defects (pairs of F and H centers), charged anion *Frenkel* defects are also observed. These are composed of pairs of anion vacancies (known as α-centers) and interstitial halogen ions (I centers).[13,23] Both charged and neutral halide interstitials are typically more mobile at room temperature than vacancies.[13,14,23] As the momentum and energy transferred to a crystal by X-rays are clearly insufficient to cause a knockout of ions from regular position to interstices, a more intricate defect formation mechanism should exist. *Lushchik et al.*[17] were the first to show for the wide bandgap NaCl that vacuum ultraviolet light produces excitons (a concept already suggested by *Frenkel*) and electron-hole pairs, which then results in the same radiation damage as under X-ray (or even γ-ray) irradiation. This has led to the fundamental conclusion that *Frenkel* pairs can be created as a result of non-radiative annihilation of self-trapped excitons (self-trapped hole X_2^- recombines with trapped electron in the excited state).[18,19]

The main criterion to realize the excitonic mechanism[14,19,20] is obviously that the width of the forbidden gap exceeds the defect formation energy (*ca.* 10 eV in AH) and that electronic carriers (small radius polarons) are localized and self-trapped on ions, such as holes on anions. This mechanism is well studied for anion defects in AH, alkaline earth halides (for example, MgF_2) and similar solids.[13,20] Creation and identification of defects involving the cation sublattice is more complicated, also due to higher cation defect formation energies.[14]

For ionic halides with a smaller band gap (for example, 2–3 eV), analogous defects could be created by photons in the visible energy range. An already mentioned example is the photolysis of AgBr and AgCl used in classic photography. Despite a long history of research of the latter materials, a complete understanding of the atomistic mechanism for the formation of these defects is still missing.

Very recent first principles calculations of $CsPbI_3$[24] and $CsPbBr_3$[25] (which have small band gaps around 1.5–2 eV) have shown that the formation energy of *Frenkel* defects is quite low and comparable with the band gap. Thus, the conditions for the possible

realization of the excitonic mechanism are met. In these systems, calculations show that halide interstitials tend to form either I_2^- dimer or Br_3^{2-} trimer ions,[24,25] similarly to what happens in AH crystals. Such self-trapping effects are certainly not restricted to ionic compounds, but they can also be found in organic compounds (see for example Ref. [26]).

Enhancement of Ionic Conductivity of Iodide Perovskites

Our present view of the phenomenon of light-enhanced ionic conductivity is depicted in *Figure 1,a* and *1,b*. The incoming light excites electrons from the valence band to the conduction band. Realizing that the band edges are predominantly formed by iodine and lead orbitals respectively, we face oxidation of I^- and reduction of Pb^{2+}. The valence band is narrow enough to allow for localization of the holes, yielding neutral iodine that can be further stabilized by displacing into interstitial sites and forming halide dimers or higher aggregates. This stabilization mode is also corroborated by atomistic considerations.[24] It is the outcome of a subtle balance of parameters including band-gap, band-width, and ion/atom polar-
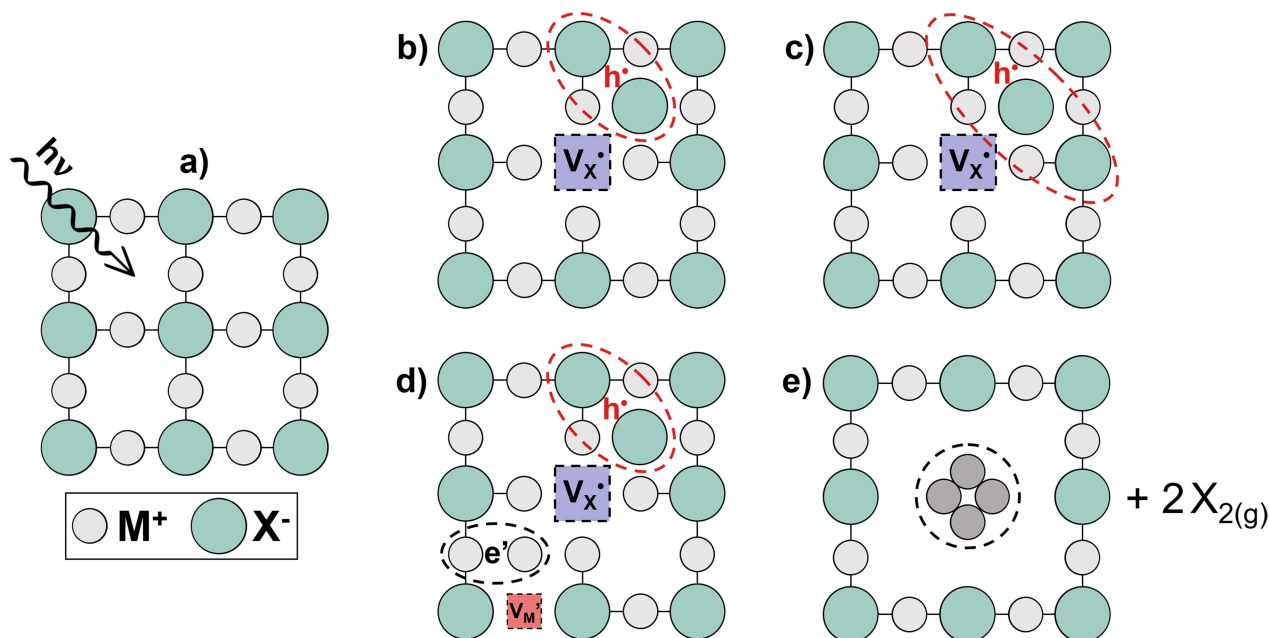

Figure 1. Relevant light-induced defect formation modes in a model halide MX as discussed in the text. a) Initial state, where the material absorbs a photon and generates an electron-hole pair. b) The hole localizes onto a halide ion, which is later displaced interstitially, forming a halide vacancy. Further relaxation of the structure is obtained upon sharing of the hole between two halide ions (X_2^- dimer named *H*-center). c) The hole localizes less than in case (b), and a loose trimer is instead formed (X_3^{2-}). d) Both hole and electron behave similarly, displacing an anion and a cation and forming pairs of vacancies and of dimers (anionic and cationic *Frenkel* defects). e) Holes localize onto halide atom, which leave the system as gas. Electrons localize on M sites forming metal clusters. This is the basis of the photographic process.

izability and size. In this way iodine vacancies are formed that can give rise to independent iodide motion. This mechanism agrees with several transport studies.[9,27] Along these lines, also mobility effects can be imagined by similar, but transient phenomena. Yet, so far, the studies favor a carrier concentration effect.[9,24] At any rate, a low diffusivity of the photo-generated neutral defects is important for the ionic conductivity enhancement to be sustainable.

In principle, such processes might also occur in AgI or PbI_2, but here the decomposition will be very fast because of the rather quick Ag^+ and Pb^{2+} motion,[28] so the effects will be hard to observe (see also *Figure 1,e*). What is more, the dark ion conductivity in these binaries is already high and the additional increase would not be so striking. In the ternary MAPI, decomposition requires ex-corporation of neutral iodine (like in the binaries, the surface step may be rate limiting and might be prevented by coating) and finally motion of at least two species. However, in the long run, MAPI photodecomposition will also take place, if special measures are not taken (for example, coating). The decomposition process is favored whenever the energy introduced by light (band gap) exceeds the thermochemical stability, and this is unfortunately rather the rule than the exception (see also the discussion below).

Searching for Other Materials

There might be other ways of translating the electronic excitation into an ionic effect. The most likely one would be reducing the activation barrier for ionic jumps by electronic effects such as size reduction of neighboring atoms due to valence changes (possible for cations and anions). A localization may even be induced by the ionic jump itself (reversible destruction and restoration of delocalization). As already mentioned, in the case of MAPI, all evidences so far point towards an increase of the iodide vacancy concentration as a cause for the photo-enhanced ion conduction (as discussed above and shown in *Figure 1,a* and *1,b*).[9,24] An important point is that the chemical diffusion coefficient (inversely proportional to the product of chemical resistance and chemical capacitance) for iodine in MAPI does not seem to markedly change under illumination. Indeed, in the event of a change in ionic carrier concentration, the influence on chemical resistance and chemical capacitance would be opposite and thus compensate. It is however not clear how relevant cation motion is for the transients in very thin films. A further argument is

that the Br-analogue ($CH_3NH_3PbBr_3$) does not show any significant photo-enhancement of ion transport. This is in agreement with a lower tendency of the hole towards self-trapping (as sketched in *Figure 1,c*).[25,29] The same situation is found for the fully inorganic halide perovskites, with $CsPbI_3$ showing a large photo-enhancement of ion conduction and $CsPbBr_3$ only presenting a negligible increase.[25,29] For the proposed mechanism to work, it is vital that the interstitial defect (displaced neutral iodine trapping a hole) is stabilized and relatively immobile. It is also important that the excess electrons are themselves sufficiently stabilized to prevent recombination. From the pure standpoint of ion conduction, the ideal situation would be a self-trapping of both electronic carriers, as then the electronic excitation could be completely converted into cation and anion vacancies (and corresponding neutral interstitial species). This process is sketched in *Figure 1,d* and might be particularly favored if the cation and anion interstitials stabilize each other. As far as the stability of the self-trapped electronic carrier is concerned, iodides are advantageous, but chalcogenides or pnictides may also show similar effects given their bonding properties. Oxides might be promising for many optoionic applications due to their high stability and wide non-stoichiometry range accessible, but the rather low mobility of the oxygen vacancy demands elevated temperatures. The stability issue is a particularly relevant criterion in the search of appropriate materials, as the photo-enhanced ionic conduction itself has severe consequences for photo-decomposition.[9] Unfortunately, many binaries with high carrier mobilities such as silver, copper and lead compounds are not very stable. Multinary compounds are more likely to work in terms of stability, as here one component might be inert and stabilize the lattice. The requirements of a reasonably low band gap imply usually a small electrochemical stability window which reduces the phase compatibility of potential electrochemical cells.

The silver halides are certainly the best investigated ionic materials as far as photo effects are concerned. Here it is so that – fostered by the high Ag^+ mobility – trapped electrons are converted into Ag clusters while holes and halide ions quickly leave the system as halogen gas (see *Figure 1,e*).[30] Ref. [31] stresses the significance of the mobility of anion vacancies for this process. A possibly enhanced ionic conductivity in this system would – if it occurs – be measurable only for a very short time. Considering PbI_2, one has to realize that this compound is – unlike AgI – essentially an anionic conductor at room temperature.[32] Nonetheless, Pb

cations are also mobile, and become faster than the anions at high temperatures.[32] Also for this system, photodecomposition is assumed to be quick. It is also worth noting that a variety of seemingly rather robust photo-phenomena (for example, enhanced fluidity) have been reported for chalcogenide glasses.[33]

An additional interesting class are transition metal (or rare earth metal) oxides, where it may be assumed that oxygen vacancies are formed at the expense of a lowered valence state of the transition metal ion, leading to an oxygen deficit (*Figure 2*). This situation may be interesting for catalysis (for example, if oxygen vacancies are active sites) and will be discussed briefly below. A notable example of modified surface chemistry is the light-induced formation of surface oxygen vacancies in TiO_2, which has been related to a strongly increased hydrophilicity.[34] Kinetic and thermodynamic photo-ionic effects have also been considered for $SrTiO_3$. Here, electronic excitation lowers the surface barrier (accelerates the surface rate constant) for oxygen incorporation and thus for stoichiometry change.[35] This is primarily a kinetic effect. However, a residual steady state effect on the stoichiometry (detectable by color changes[35]) owing to light
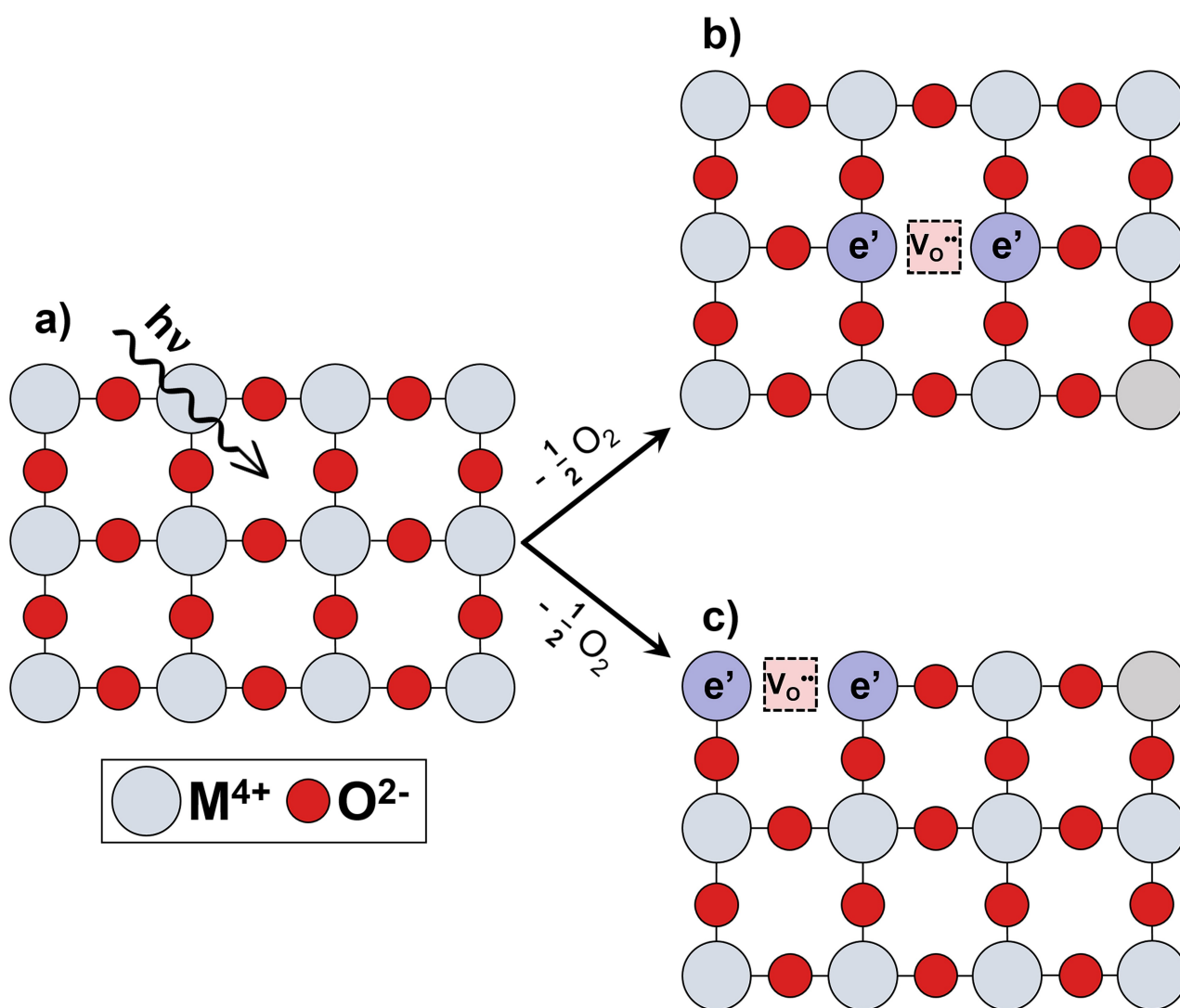

Figure 2. Formation of light-induced oxygen deficiency in a transition metal oxide MO_2. a) Initial state, where the material absorbs photons and generates electron-hole pairs. b) The holes localize onto oxide ions, which leave the bulk of the material as oxygen gas and form an oxygen vacancy. Electrons are consumed by reduction of the transition metal cation. c) Same situation as for b), but the vacancy formation is (kinetically or thermodynamically) restricted to the surface layer. This occurrence affects surface properties (relevant for example for catalysis and sensors).

enhanced oxygen activity within the oxide has also been identified.[36]

Optoionic Devices and Applications

Here we speculate about possible optoionic devices or applications that could be realized given the availability of appropriate materials. As the only compounds in which a significant increase of ion conduction has been validated are at the moment MAPI and CsPbI$_3$, let us essentially refer to the conditions realized there. Here, light enhances both electronic and ionic conductivities and hence the ambipolar conductivity (harmonic mean of ionic and electronic conductivities). This yields a higher iodine flux through the bulk of the material (assuming the surface reaction is sufficiently fast). A direct application of such an effect is a *membrane for iodine permeation* (*Figure 3,a*). In fact, such a device showing an enhanced steady state iodine permeation rate, has been realized for demonstrating the occurrence of the optoionic effect.[9]

Unfortunately, in MAPI – just because the enhancement is due to an increase in carrier concentration – the chemical diffusion coefficient and hence the transient kinetics is not significantly varied. Yet, conditions may be found where this compensation between chemical resistance and chemical capacitance does not occur (see also Ref. [37]). In such cases, it could be possible to realize interesting light-triggered *resistive switches* or *electrochemical sensors/actuators.* The same would be true if the photo-ionic effect would be caused by an enhancement of ion mobility; then the chemical capacitance would remain unaffected, but chemical resistance and hence chemical diffusion coefficient would vary. In such a situation, the kinetics of mass storage of a material may be enhanced by illumination, and so the practical (not the theoretical) storage capacity of *battery electrodes* could be altered (*Figure 3,b*). (Photobatteries that have been reported so far[38] do not actually rely on an optoionic effect.) A light-triggered theoretical capacity enhancement (due to changes in stoichiometry) is also imaginable but may be rather small (this situation has been reported for SrTiO$_3$).[36,39] Additionally, situations where the light effect results in a pure ion conductivity enhancement would open up possibilities for tuning the functionality of *solid electrolytes* (for example for batteries and fuel cells). Such light-activated ion channels may also be realized in mixed conductors upon inserting electronically blocking phases (*Figure 3,c*).
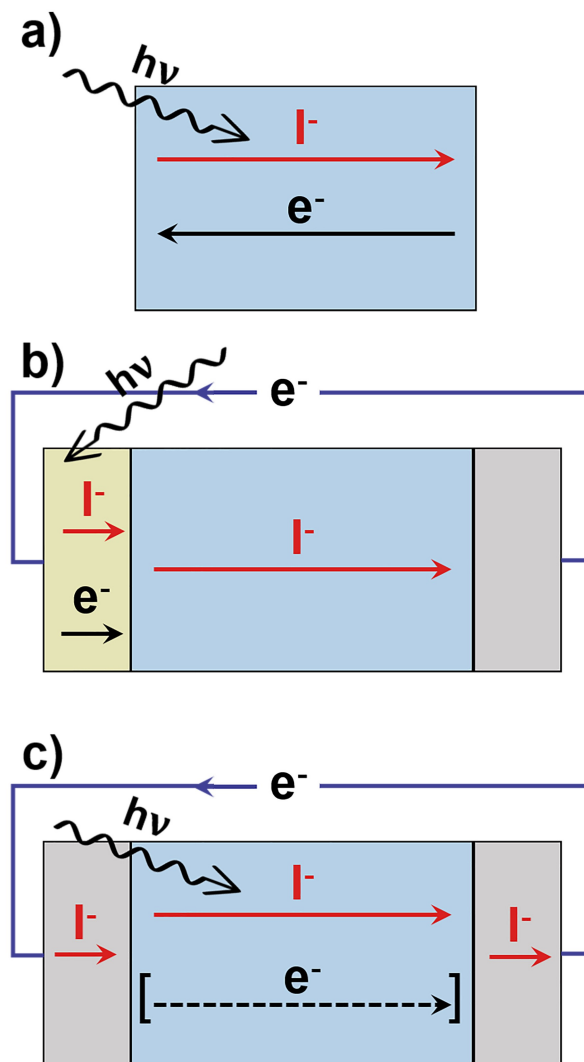

Figure 3. Schematics of possible optoionic devices (see text). a) Light-triggered iodine permeation through a MAPI membrane. The driving force is given by a difference in iodine partial pressure of both sides of the membrane. b) Light-enhanced storage capacity in a photo-battery, obtained by inducing optoionic effects on the electrode. c) Light-induced enhancement of the transport function of solid electrolytes. In the case of a mixed conducting inner phase, electron-blocking interphases are to be used.

In addition to the above bulk effects, *surface functions* may also be greatly altered by light (see sketch in *Figure 2,c*). Examples are the light-induced oxygen deficiency in transition metal oxides addressed above,[35] and the photo-induced generation of surface oxygen vacancies in TiO$_2$; they are held responsible for superhydrophilicity,[34] and are possibly also involved in the material's disinfection properties. If the modifications of the surface functions are characteristic,

they can be exploited to tune for example *sensing properties*. Accelerated surface reaction kinetics would also have important implications for *catalysis*. A variety of materials comes into question here such as transition metal oxides.

Related Optoionic Phenomena

Many further phenomena may be caused by optoionic effects. These include optical effects on *ion transfer*,[35] but also on *ion redistribution* (as for example within ionic double layers[40,41]). In a wider sense, one also might refer to *optical properties* (color centers and irreversible bleaching/yellowing reactions), as well as variations of *mechanical properties* (e.g. changes in dislocation charge or volume variations associated with self-trapping of electronic carriers, that is, ionically caused photostriction), all of which depend on point defects.

An additional phenomenon is the *photodemixing* reported for mixed anion halide perovskites such as $CH_3NH_3Pb(Br_xI_{1-x})_3$. As pure $CH_3NH_3PbBr_3$ does not show a significant self-trapping effect, but MAPI does, demixing of a Br/I mixture on illumination would be expected in order to capitalize the related *Gibbs* energy change.[29] Indeed such phase separation has been frequently observed in this systems[42] but ascribed to various different reasons.[43,44] For chalcogenide glasses, various effects have been reported (photo-anisotropy, photo-alloying) that may be also related to optoionic phenomena.[33]

As mentioned in the introduction the term 'optoionics' may also be useful in a wider sense as to include optical property variations by solid state ionics (for example, electrochromic windows).[45–47]

Conclusions

Variation of ion transport by illumination such as the conversion of light into ionic defects enabled by photo-excited electronic carriers opens the possibility of realizing a great variety of light-triggered electrochemical devices. A necessary condition for optoionics to become a field of practical interest is the identification of stable materials of relevance. Unfortunately, lead halide perovskites – for which the phenomenon has been established – are chemically and thermally rather unstable, and this limits the applicability of their optionic behaviour. Intensive research will be needed to advance this novel field, starting with the exploration of the relevant materials space.

Author Contribution Statement

A. S., *E. K.*, and *J. M.* jointly discussed and wrote the paper.

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