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Tin oxide as an emerging electron transport medium in perovskite solar cells

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ABSTRACT

Electron transport medium (ETM) is one of the most important components determining the photovoltaic performance of organic-inorganic halide perovskite solar cells (PSCs). Among the metal oxide semiconductors, anatase (TiO_2) is the most common material used as ETM in PSCs to facilitate charge collection as well as to support a thin perovskite absorber layer. Production of conductive crystalline TiO_2 requires relatively higher temperatures (400–500 °C) which limits its application to glass substrates coated with fluorine tin oxide (FTO) as other tin oxides (e.g. indium tin oxide) degrade at temperatures above 300 °C. Furthermore, this renders it unsuitable for flexible devices, often based on low-temperature flexible plastic substrates. Pure tin oxide, one of the earliest metal oxide semiconductors, is often used in myriad electronic devices and has shown outstanding characteristics as an ETM in PSC systems. Thus, tin oxide can be considered a viable alternative to TiO_2 due to its excellent electron mobility and higher stability than other alternatives such as zinc oxide. This review article gives a brief history of ETMs in PSC systems and reviews recent developments in the use of tin oxide in both pure and composite form as ETMs. Efficiencies of up to 21% have been reported in tin oxide based PSCs with photovoltages of up to ~1214 mV.

1. Introduction

Almost every convenient and consumable lifestyle item relies at some stage on electrical energy; therefore, the quality of life cannot be improved without development of cheap and clean energy resources. Consequently, the production of clean and sustainable energy at relatively low prices is one of the most important issues faced by the modern world. The development of solution-processable perovskite solar cells (PSCs) with photovoltaic conversion efficiencies (PCEs) in excess of ~22% is a significant leap towards achieving this goal. Central to PSC performance is the constituent photoactive material, which is an organic-inorganic hybrid with an ABX_3-type perovskite crystal lattice, where A is an organic cation, which may be either MA^+ (methyl ammonium, $CH_3NH_3{}^+$) or FA+ (formamidinium, $CH_3(NH_2)_2{}^+$), or inorganic cations such as cesium Cs^+ [1–6], or mixed cations with an appropriate Cs/MA, Cs/FA, Cs/FA/MA ratio [7–13]; B is a divalent metal cation such as Pb^{2+} or Sn^{2+} [14], and X is normally a halide anion such as I^-, Cl^-, Br^-, or F^-, shown in Fig. 1a [15]. The ideal perovskite structure has the B cation in 6-fold X coordination (i.e., at the corners of the parallelepiped) forming a BX_6 octahedron (Fig. 1b) and the A cation has 12-fold X coordination (Fig. 1c) [16,17]. The 'A' cation is larger in size than the 'B' cation and is selected such that; (i) the total charge on the crystal is balanced, and (ii) the sizes are such that the perovskite structure is stable as shown in Fig. 1a).

An absorber material suitable for solar cells must offer a set of optical and electrical properties, for example; (i) a smaller optical band gap such that a considerable fraction of solar light can be absorbed and converted into electrons, (ii) sufficiently crystalline to ensure a high absorption coefficient, and (iii) a lattice capable of holding the excited electrons for a longer time (electron lifetime). The best known organic–inorganic hybrid perovskite, i.e., methylammonium lead halide, offers all these characteristics, and consequently, interest in PSCs has grown sufficiently, particularly around improvements in photovoltaic conversion efficiency as highlighted in Fig. 1d). Efficiency values up to 22.1% have been reported in recent works [18]. This efficiency is at par with the current world-leading solar cells technologies at lab scale.

Solar cells can be typically split into two categories: n-i-p and p-i-n. In the n-i-p category, light shines on the intrinsic n-type material and the generated electrons and holes are collected by the n-type and p-type materials, respectively, whereas in the p-i-n configuration, the reverse is true. Perovskite crystals are most commonly nucleated from a solution on a substrate surface (typically titanium oxide - TiO_2) which acts as a medium on which the organometallic halide perovskite can crystallize. In addition, the solar photoelectrons are to be selectively

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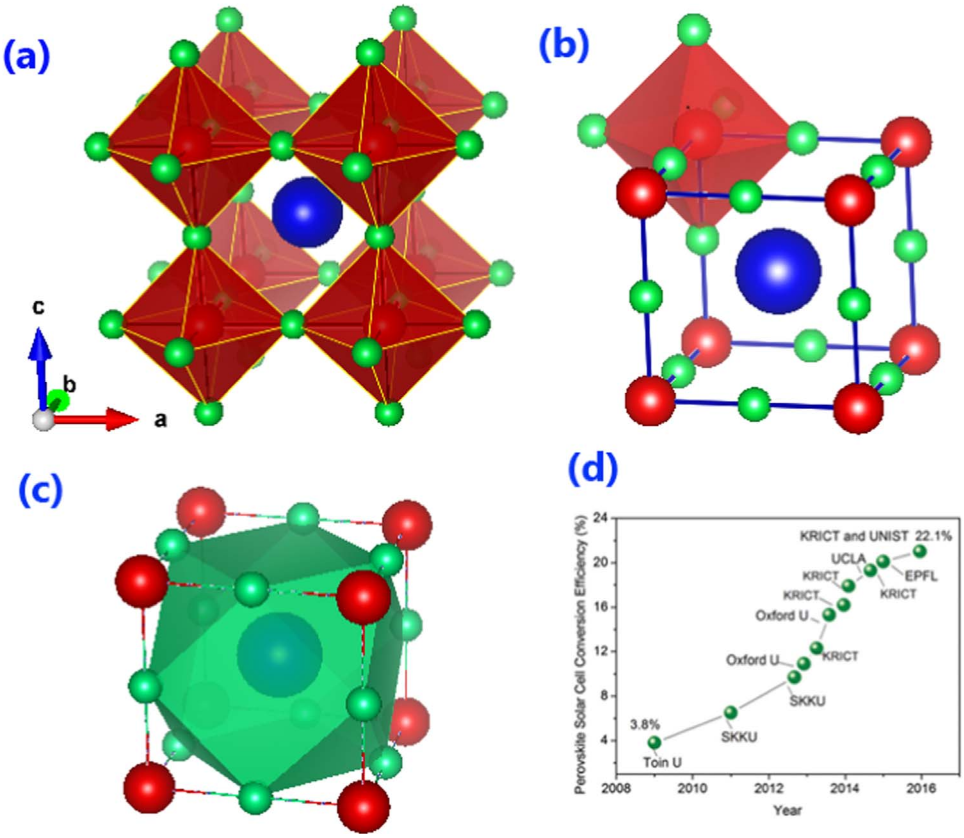

Fig. 1. (a) Crystal structure of organic-inorganic perovskite, (b) where central big atom is methyl ammonium while the Pb atom is surrounded by six halogen atoms, (c) A cation coordinated by X ions in12-fold cuboctahedral symmetry, and (d) progress made in PSCs in term of efficiency.

collected through this material which acts as a working electrode by working as an electron transport medium (ETM). The holes are collected at the counter electrode (the hole transport medium - HTM) where the hole selectivity is a property of the counter electrode material employed [19]. A number of materials can act as a medium for perovskite nucleation and selective electron collection, with the most commonly used for this purpose being TiO_2 [20–23]. An interesting innovation has been the development of PSC's that operate without a charge transport medium, as they are nucleated directly on the collecting transparent conducting oxide substrate.

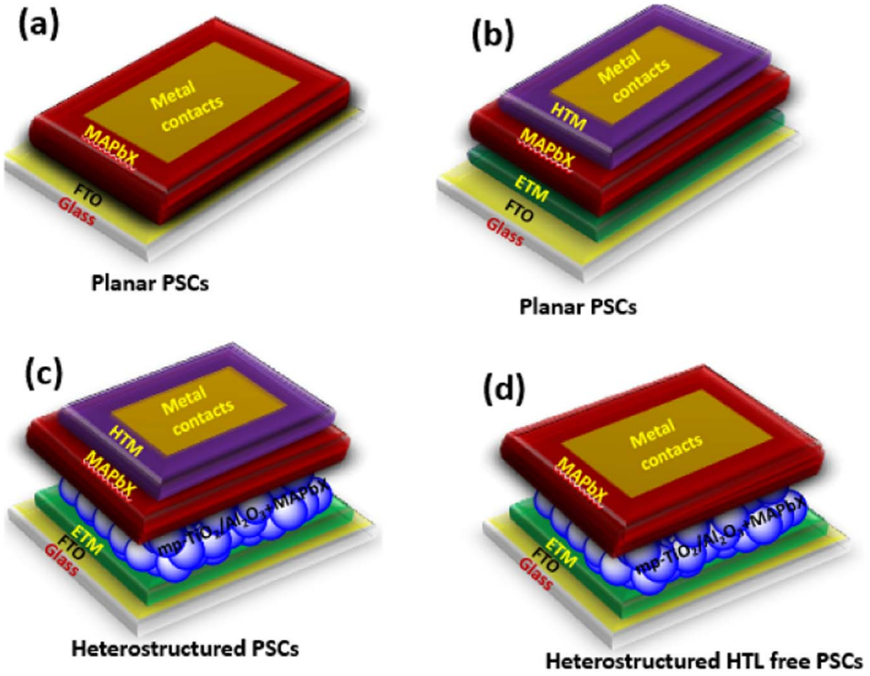

Fig. 2. Four common PSC device configurations: (a) Planar configuration without a HTM and ETM, (b) Planar configuration employing a thin ETM layer and a HTM, (c) mesostructured configuration employing m-TiO_2 or Al_2O_3 as an ETM, with a HTM and (d) HTM-free PSCs.