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Exceedingly Cheap Perovskite Solar Cells Using Iron Pyrite Hole Transport Materials

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Methyl ammonium lead tri iodide perovskite solar cells attracted significant interest due to their high efficiency over 20% using polytriarylamine polymer (PTAA) and spiro-OMeTAD (Spiro). While the perovskite absorber material is relatively inexpensive to fabricate, the hole transport material is considerably expensive. Here we address the problem of cost by applying the vastly abundant mineral iron pyrite (FeS$_2$) as a hole transporting material in perovskite solar cells. We report a power conversion efficiency of 11.2% using n-i-p configuration where the perovskite is an intrinsic semiconductor, TiO$_2$ as an electron acceptor (n-type layer), and FeS$_2$ as hole transporter (p-type layer). We show through photoluminescence quenching studies that pyrite transfers holes at least as efficiently as Spiro. Cost analysis of the pyrite HTM and Spiro indicates that currently, pyrite is >300 times cheaper to produce for 1 m^2 modules.

In a matter of years, RNH$_3$PbI$_3$ (ammonium lead triiodide) and its analogs have emerged as a promising absorber for photovoltaics.[1–4] The materials have found other applications in photodetectors[5,6] and as emitters in LEDs. [7,8] The meteoric rise of perovskite solar cells efficiency has so far reached over 20% power conversion efficiency.[9] The exceptional performance of Pb perovskites has been attributed to several factors including strong absorption in the visible region,[10] carrier diffusion length in the μm range, low exciton binding energy,[11] a tunable band gap, [12–14] and a sharp optical band edge.

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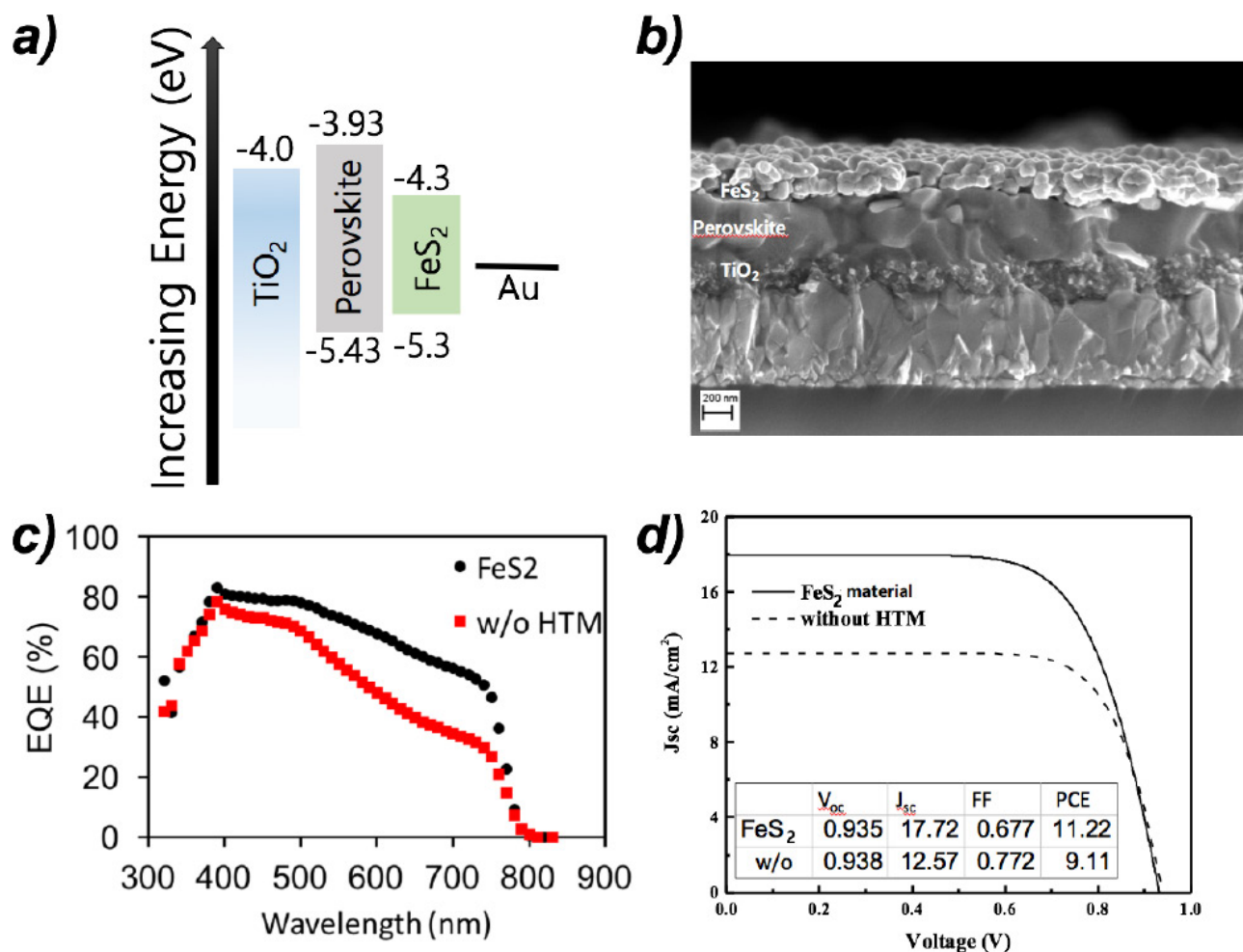Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/slct.201601378

Much research into tuning the perovskite absorber for high performance has paid off, namely through mixing organic and inorganic cations[9] or halides[15] in the perovskite structure. While this work has paid great dividends, the state-of-the-art devices reported today utilize n-i-p structure based on the perovskite as an intrinsic semiconductor, TiO$_2$ as the electron acceptor (n-type layer), and polytertiary aryl amine polymer (PTAA) as the hole transporter (p-type layer). However, the drawback of using PTAA polymers for solar cell applications is their reproducibility, and low purity inherent to their mass distribution and difficult characterization. For decades, the small organic molecule 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD) has been used as a hole transporting material in solid-state dye-sensitized solar cells, and recently in perovskite solar cells yielding power conversion efficiency of over 20%. Nevertheless, the Spiro-OMeTAD material is costly to purchase (> $170/gram). [16] By using a cheaper material, the overall price of the solar cell can be decreased, and the feasibility of large-scale implementation increased. Towards this end, we report the utilization *of the most abundant mineral in the earth's crust*, phase pure iron pyrite nanocrystals (FeS$_2$ NCs) as an HTM in perovskite solar cells. During our preliminary work, we became aware of a very recent paper where the authors also utilized pyrite. In that publication, the authors noted small (20 nm) FeS$_2$ particles could serve as HTM materials with good stability and performance (12.5%) that improved when also using Spiro in a "bilayer" approach (14.2%).[17]

A simplified energy level diagram of the perovskite cell with pyrite is illustrated in Figure 1a. The valence band (HOMO) and conduction band (LUMO) values for iron pyrite used here are those calculated by others[18] and used by some of us previously in constructing high efficiency CdTe solar cells using FeS$_2$ NC HTMs. [19] The cells followed a typical architecture, and the cross section of the device is shown in Figure 1b. From SEM measurements, the particles were observed to be ∼100 nm in width. Particle aggregation was an important factor in device preparation, as the deposition of a uniform film was exceedingly difficult, presumably due to strong aggregation and NCs being partially re-solubilized in necessary sequential depositions. From top-view SEM images (see Supporting Information), it is evident that the aggregated particles did not fully cover the perovskite layer even after five sequential depositions. Thus, while the fabricated devices performed well, we are actively working towards improving pyrite deposition.

Figure 1. A: Energy level diagram of perovskite device. B: Cross-section of the perovskite-pyrite NC solar cell. C: IPCE spectrum of the champion cell described here, with no HTM cell for comparison. D: Best cell current-voltage scans collected under AM 1.5G simulated sunlight for FeS_2 **NCs** and cell without HTM on mixed perovskite.

The perovskites were deposited on FTO/mesoporous TiO_2, followed by deposition of FeS_2 NC dispersion that were capped with tri-octylphosphine oxide (TOPO). [19,20] After evaporation of a gold back contact, measurements were conducted. The IPCE of the champion device incorporating the FeS_2 NCs is shown in Figure 1c, and the results are summarized in Table 1. The power

conversion efficiency of the perovskite device using pyrite FeS_2 NCs as HTM cells (11.2 %) outperformed the cells without an HTM (9.11 %), and the champion pyrite cell exhibited $J_{sc} = 17.72$ mA/cm$_2$, $V_{oc} = 0.937$ V, and FF = 0.677, hence with Voc and FF coming closer to those of cells using spiro (16.8 %) as shown in Figure 1d. From the IPCE spectrum, it is evident that high energy photons were utilized much more efficiently than low-energy photons. Notably for the pyrite cells, after three days of storage in dry air and without light the PCE was observed to decrease due to large fill factor losses, even though the J_{sc} increased from 17.72 to 18.95 mA/cm^2. Investigation into the nature of this increase in resistive losses is currently on-going.

After observing the IPCE spectrum, we hypothesized that perhaps the reason for the difference in the high and low energy regions of the spectrum was due to inefficient hole transport. To test this, we measured the photoluminescence spectrum of the Spiro and Pyrite NC devices by illuminating from either the perovskite side or the side with the HTM, shown in Figure 2. Illumination from the perovskite side provides the
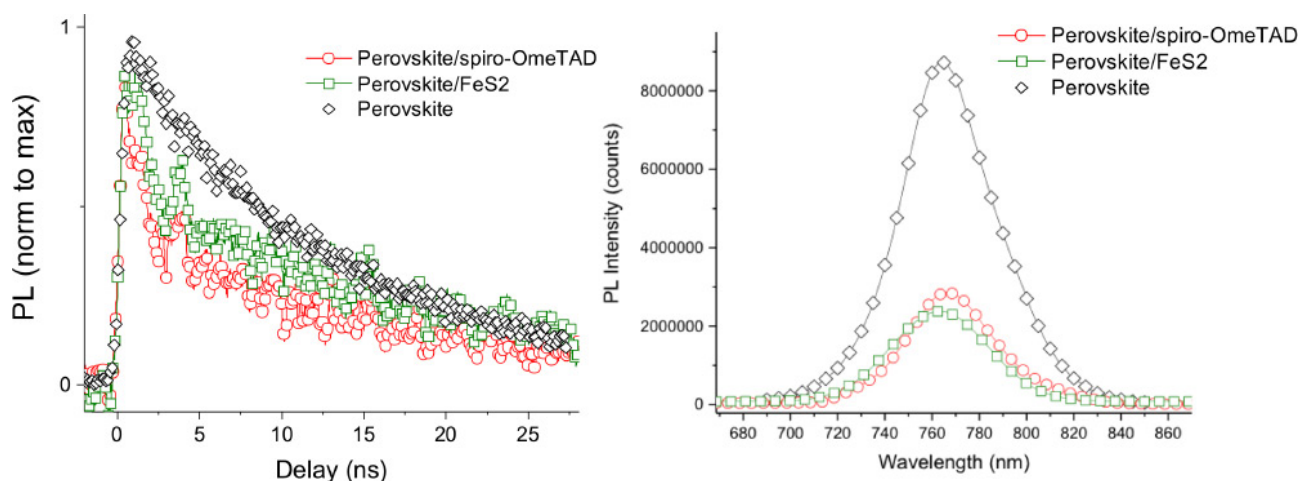
Table 1. Photovoltaic performance of solar cells including either Spiro or FeS_2 as HTM.[a]			
HTM	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η (%)
Spiro-OMeTAD	22.06	1.02	0.75	16.87
No HTM	12.57	0.936	0.772	9.11
FeS_2 Day 1	17.72	0.935	0.677	11.22
FeS_2 Day 3	18.95	0.91	0.53	9.13

[a] Devices constructed with the following architecture: glass/FTO/TiO_2/$FA_{0.98}MA_{0.02}PbI_{0.98}Br_{0.02}$/HTM/Au and measured under a simulated AM1.5G solar spectrum. Additional information can be found in Supporting Information.

Figure 2. *Left:* PL Quenching study of pyrite-HTM (green) and Spiro-HTM (red) perovskite solar cells. *Right:* PL Lifetime Quenching study of pyrite-HTM (green) and Spiro-HTM (red) perovskite solar cells.

"baseline" perovskite PL signal, while illumination from the HTM side provides indication of PL quenching.

In these studies, diminished luminescence intensity after illuminating through the HTM side is evidence of emission quenching due to hole injection from the perovskite to the HTM, which is the phenomenon observed. We also observed the photoluminescence emission kinetics of pristine perovskite thin films and compared this photoluminescent lifetime with devices utilizing either Spiro or FeS_2. The two quenching studies indicate hole transport is comparable to that observed when using Spiro.

Thus, as the rate of PL quenching is comparable in the two materials, we suggest one reason for the lower performance observed with pyrite might be due to defect-mediated recombination at the perovskite-pyrite interface, perhaps due to the capping ligand (TOPO). Because TOPO is electron deficient, the valence band edge (HOMO) is expected to be stabilized, which could increase the recombination rate[21] if the valence band is stabilized too much. Studies into precise effects of capping ligands on the observed IPCE is currently ongoing.

To substantiate our claims that pyrite, while being the most abundant mineral in the earth's crust, is also cheap to synthesize as 100 nm NCs, we undertook a cost analysis study as has previously been conducted by others (See SI). [22–24] This analysis has indicated that while Spiro performed better (16.87%), it was considerably more expensive ($92/gram) than were the pyrite NCs ($0.76/gram), which translates into material cost per m^2 of $39.46 and $0.12 respectively. To cement the difference in cost, the cost per peak watt ($/$W_p$) cells using Spiro at 16.87% is 1.088 $/$W_p$,[23] while for similar cells using 100 nm pyrite NCs it is is 0.012 $/$W_p$, nearly a two order of magnitude difference. For description of the cost-analysis procedure, see the Supporting Information. Thus, because of their high performance and very low cost, pyrite NCs are better positioned to allow for large-scale perovskite solar cells than those including Spiro, even though on mass scale production the cost of spiro could likely still be decreased.

In an attempt to lower the cost of lead perovskite solar cells, which often incorporate an expensive HTM material, Spiro-OMeTAD, we applied *the most abundant mineral in the earth's crust*, iron pyrite (FeS_2), as an HTM material in these solar cells. Using this configuration, we observed device efficiencies up to 11.2%, which outperformed cells with no HTM (9.11%) and performed comparably, particularly in V_{OC} and FF, with Spiro (16.87%). Cost-analysis of the HTM materials indicated that the phase pure pyrite nanocrystals are much cheaper to incorporate in large scale devices than Spiro when materials cost was compared. Further efforts into developing pyrite NCs should include more comprehensive cost-analysis techniques, but this (currently) state of the art analysis clearly illustrates how pyrite NCs are much cheaper to produce than Spiro.

While luminescence quenching was observed to be somewhat more efficient than the benchmark Spiro HTM, the device efficiencies were not as high. This was evident in the IPCE spectrum, where low energy photons were left largely unutilized. This could potentially be due to non-productive recombination events between the perovskite and HTL, or possibly because of inefficient hole collection stemming from the inhomogeneous HTL layer. Work towards resolving these issues3 and improving device stability by NC modification is currently ongoing.

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