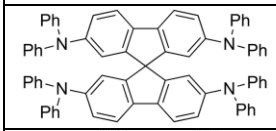
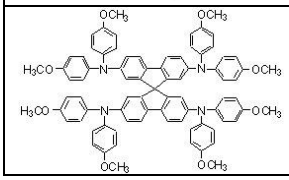
Perovskite Hybrid Solar Cell Reference (Selection of Steven Xiao) for the beginning of 2014

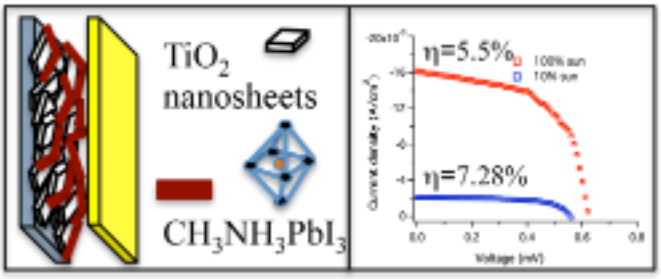
==========

1-Materials for your further advancement in PEROVSKITE Hybrid Solar Cell

Formula	CAS No.	Chemical Name	Specification	1M No.
$CH_3NH_3PbI_3$	69507-98-8	Methylammonium lead-iodide	Nano-powder	OS0998
			40% γ-butyrolactone	OS0998-40
CH3NH3I	14965-49-2	Methylammonium iodide	Crystal	IT0492
	189363-47-1	**Spiro-TAD** 2,2′,7,7′-Tetrakis(*N*,*N*-diphenylamino)-9,9-spirobifluorene	99%	HT0471
	207739-72-8	**Spiro-OMeTAD** 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluore	99%	HT0728

References selected by Steven Xiao on January 01, 2014.
(Reference No. 38 reported a PCE of 15.7%)

1. Mesoscopic CH3NH3PbI3/TiO2 Heterojunction Solar Cells
Etgar, Lioz; Gao, Peng; Xue, Zhaosheng; Peng, Qin; Chandiran, Aravind Kumar; Liu, Bin; Nazeeruddin, Md. K.; Gratzel, Michael, Journal of the American Chemical Society (2012), 134(42), 17396



We report for the first time on a hole conductor-free mesoscopic methylammonium lead iodide ($CH_3NH_3PbI_3$) perovskite/TiO_2 heterojunction solar cell, produced by deposition of perovskite nanoparticles from a soln. of CH_3NH_3I and PbI_2 in γ-butyrolactone on a 400 nm thick film of TiO_2 (anatase) nanosheets exposing (001) facets. A gold film was evapd. on top of the $CH_3NH_3PbI_3$ as a back contact. Importantly, the $CH_3NH_3PbI_3$ nanoparticles assume here simultaneously the roles of both light harvester and hole conductor, rendering superfluous the use of an addnl. hole transporting material. The simple mesoscopic $CH_3NH_3PbI_3$/TiO_2 heterojunction solar cell shows impressive photovoltaic performance, with short-circuit photocurrent d. 16.1 mA/cm^2, open-circuit photovoltage 0.631 V, and fill factor 0.57, corresponding to a light-to-elec. power conversion efficiency of 5.5% under std. air-mass 1.5 solar light of 1000 W/m^2 intensity. At a lower light intensity of 100 W/m^2, a power conversion efficiency of 7.3% was measured. The advent of such simple soln.-processed mesoscopic heterojunction solar cells paves the way to realize low-cost, high-efficiency solar cells.

2. Low-temperature processed meso-superstructured to thin-film perovskite solar cells
Ball, James M.; Lee, Michael M.; Hey, Andrew; Snaith, Henry J.
Energy & Environmental Science (2013), 6(6), 1739-1743

We have reduced the processing temp. of the bulk absorber layer in $CH_3NH_3PbI_{3-x}Cl_x$ perovskite solar cells from 500 to <150 °C and achieved power conversion efficiencies up to 12.3%. Remarkably, we find that devices with planar thin-film architecture, where the ambipolar perovskite transports both holes and electrons, convert the absorbed photons into collected charge with close to 100% efficiency.

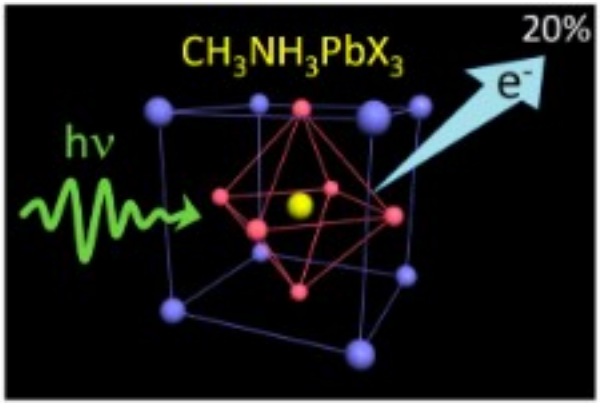
3. Comparative study on the excitons in lead-halide-based perovskite-type crystals CH3NH3PbBr3 CH3NH3PbI3
Tanaka, Kenichiro; Takahashi, Takayuki; Ban, Takuma; Kondo, Takashi; Uchida, Kazuhito; Miura, Noboru
Solid State Communications (2003), 127(9-10), 619-623.

Optical absorption and magnetoabsorption spectra of the Pb-halide-based perovskite-type crystals, $MeNH_3PbX_3$ (X = Br, I) have been studied. The lowest-energy excitons in these crystals are normal 3-dimensional Wannier-type excitons. Bohr radii, binding energies, reduced masses, effective g factors, and oscillator strengths of the excitons have been detd. with satisfactory accuracy. A larger bandgap and more tightly bound nature of the excitons in $MeNH_3PbBr_3$ compared to those in $MeNH_3PbI_3$ are a natural consequence of the halogen substitution.

4. Efficient inorganic-organic hybrid heterojunction solar cells containing perovskite compound and polymeric hole conductors
Heo, Jin Hyuck; Im, Sang Hyuk; Noh, Jun Hong; Mandal, Tarak N.; Lim, Choong-Sun; Chang, Jeong Ah; Lee, Yong Hui; Kim, Hi-jung; Sarkar, Arpita; Nazeeruddin, Md. K.; et al
Nature Photonics (2013), 7(6), 486-491

Inorg.-org. hybrid structures have become innovative alternatives for next-generation dye-sensitized solar cells, because they combine the advantages of both systems. Here, we introduce a layered sandwich-type architecture, the core of which comprises a bicontinuous three-dimensional nanocomposite of mesoporous (mp)-TiO2, with CH3NH3PbI3 perovskite as light harvester, as well as a polymeric hole conductor. This platform creates new opportunities for the development of low-cost, soln.-processed, high-efficiency solar cells. The use of a polymeric hole conductor, esp. poly-triarylamine, substantially improves the open-circuit voltage Voc and fill factor of the cells. Solar cells based on these inorg.-org. hybrids exhibit a short-circuit c.d. Jsc of 16.5 mA cm-2, Voc of 0.997 V and fill factor of 0.727, yielding a power conversion efficiency of 12.0% under std. AM 1.5 conditions.

5. Organometal Perovskite Light Absorbers Toward a 20% Efficiency Low-Cost Solid-State Mesoscopic Solar Cell
Park, Nam-Gyu
Journal of Physical Chemistry Letters (2013), 4(15), 2423-2429.

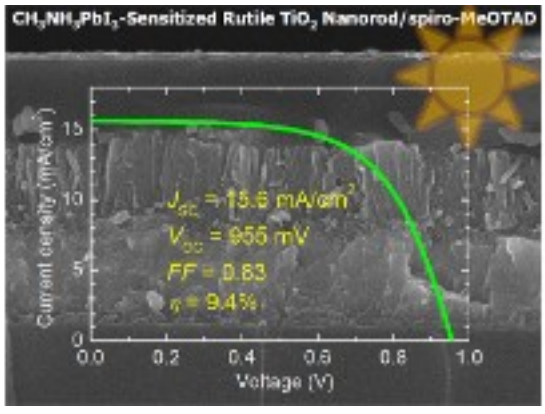


A review of recent progress in perovskite-sensitized solid-state mesoscopic solar cells. Recently, perovskite $CH_3NH_3PbI_3$ sensitizer has attracted great attention due to its superb light-harvesting characteristics. Organometallic or org. materials were mostly used as sensitizers for solid-state dye-sensitized solar cells at early stages. Inorg. nanocrystals have lately received attention as light harvesters due to their high light-absorbing properties. Metal chalcogenides have been investigated with solid-state dye-sensitized solar cells; however, the best power conversion efficiency was reported to be around 6%. $CH_3NH_3PbX_3$ (X = Cl, Br, or I) perovskite sensitizer made a breakthrough in solid-state mescoscopic solar cells, where the first record efficiency of ~10% was reported in 2012 using submicrometer-thick TiO_2 film sensitized with $CH_3NH_3PbI_3$. A rapid increase in efficiency approaching 14% followed shortly. On the basis of the recent achievements, a power conversion efficiency as high as 20% is expected based on optimized perovskite-based solid-state solar cells.

6. High Efficiency Solid-State Sensitized Solar Cells based on Submicrometer Rutile TiO2 Nanorods and CH3NH3PbI3 Perovskite Sensitizer

Kim, Hui-Seon; Lee, Jin-Wook; Yantara, Natalia; Boix, Pablo P.; Kulkarni, Sneha A.; Mhaisalkar, Subodh; Gratzel, Michael; Park, Nam-Gyu

Nano Letters (2013), 13(6), 2412-2417



The authors report a highly efficient solar cell based on a sub-micrometer (~0.6 μm) rutile TiO_2 nanorod sensitized with $MeNH_3PbI_3$ perovskite nanodots. Rutile nanorods were grown hydrothermally and their lengths were varied through the control of the reaction time. Infiltration of spiro-MeOTAD hole transport material into the perovskite-sensitized nanorod films demonstrated photocurrent d. of 15.6 mA/cm², voltage of 955 mV, and fill factor of 0.63, leading to a power conversion efficiency (PCE) of 9.4% under the simulated AM 1.5 G one sun illumination. Photovoltaic performance was significantly dependent on the length of the nanorods, where both photocurrent and voltage decreased with increasing nanorod lengths. A continuous drop of voltage with increasing nanorod length correlated with charge generation efficiency rather than

recombination kinetics with impedance spectroscopic characterization displaying similar recombination regardless of the nanorod length.

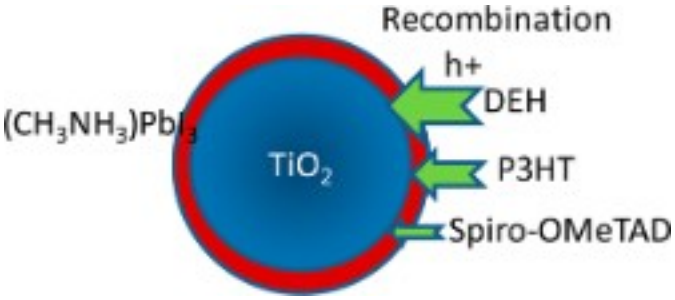
7. All-solid-state hybrid solar cells based on a new organometal halide perovskite sensitizer and one-dimensional TiO2 nanowire arrays
Qiu, Jianhang; Qiu, Yongcai; Yan, Keyou; Zhong, Min; Mu, Cheng; Yan, He; Yang, Shihe
Nanoscale (2013), 5(8), 3245-3248

A novel organometal halide perovskite ($CH_3NH_3PbI_2Br$) is synthesized and used as a visible light absorber to sensitize one-dimensional (1D) TiO_2 nanowire arrays (NWAs) for all-solid-state hybrid solar cells. It achieved a power conversion efficiency (PCE) of 4.87% and an open circuit voltage (V_{oc}) of 0.82 V, both higher than those of its analog $CH_3NH_3PbI_3$.

8. Structural study on cubic-tetragonal transition of CH3NH3PbI3
Kawamura, Yukihiko; Mashiyama, Hiroyuki; Hasebe, Katsuhiko
ournal of the Physical Society of Japan (2002), 71(7), 1694-1697

The cubic-tetragonal phase transition of $CH_3NH_3PbI_3$ was studied by single crystal x-ray diffractometry. The crystal structure was refined at five temps. in the tetragonal phase. The PbI_6 octahedron rotates around the c-axis alternatively to construct the $SrTiO_3$-type tetragonal structure. A methylammonium ion is partially ordered; 24 disordered states in the cubic phase are reduced to 8. With decreasing temp., the rotation angle of the octahedron increases monotonically, which indicates it is an order parameter of the cubic-tetragonal transition.

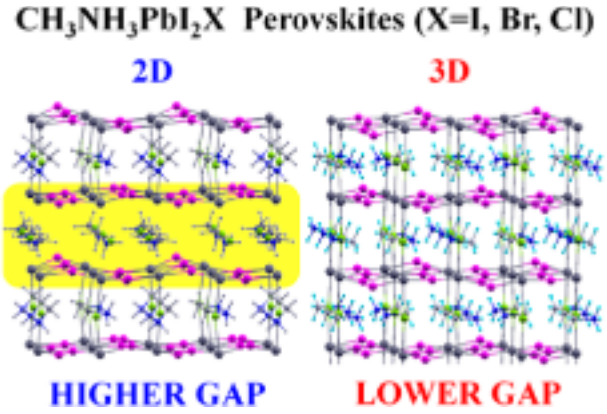
9. Effect of Different Hole Transport Materials on Recombination in CH3NH3PbI3 Perovskite-Sensitized Mesoscopic Solar Cells
Bi, Dongqin; Yang, Lei; Boschloo, Gerrit; Hagfeldt, Anders; Johansson, Erik M. J.
Journal of Physical Chemistry Letters (2013), 4(9), 1532-1536.



We report on perovskite $(CH_3NH_3)PbI_3$-sensitized solid-state solar cells using spiro-OMeTAD, poly(3-hexylthiophene-2,5-diyl) (P3HT) and 4-(diethylamino)benzaldehyde diphenylhydrazone (DEH) as hole transport materials with a light to electricity power conversion efficiency of 8.5%, 4.5%, and 1.6%, resp., under AM 1.5G illumination of 1000 W/m^2 intensity. Photoinduced absorption spectroscopy shows that hole transfer occurs from the $(CH_3NH_3)PbI_3$ to hole transport materials after excitation of $(CH_3NH_3)PbI_3$. The electron lifetime (τ_e) in these devices are in the order Spiro-OMeTAD > P3HT > DEH, while the charge transport time (t_{tr}) is rather similar. The difference in τ_e can therefore

explain the lower efficiency of the devices based on P3HT and DEH. This report shows that the nature of the hole transport material is essential for charge recombination and elucidates that finding an optimal hole transport material for the perovskite solar cell includes controlling the perovskite/hole transport material interaction. Design routes for new hole transport materials are suggested.

10. First-Principles Modeling of Mixed Halide Organometal Perovskites for Photovoltaic Applications
Mosconi, Edoardo; Amat, Anna; Nazeeruddin, Md. K.; Gratzel, Michael; De Angelis, Filippo
Journal of Physical Chemistry C (2013), 117(27), 13902-13913.



The authors computationally study organometal $CH_3NH_3PbX_3$ and mixed halide $CH_3NH_3PbI_2X$ perovskites (X = Cl, Br, I), which are key materials for high efficiency solid-state solar cells. $CH_3NH_3PbX_3$ perovskites exhibited the expected absorption blue shift along the I → Br → Cl series. The mixed halide systems surprisingly showed the $CH_3NH_3PbI_3$ and the $CH_3NH_3PbI_2Cl$ (or $CH_3NH_3PbI_{3-x}Cl_x$) perovskites to have similar absorption onset at ~800 nm wavelength, whereas $CH_3NH_3PbI_2Br$ absorbs light ≲700 nm. To provide insight into the structural and electronic properties of these materials, in light of their application as solar cell active layers, the authors perform periodic DFT calcns. on the $CH_3NH_3PbX_3$ and $CH_3NH_3PbI_2X$ perovskites. A good agreement between the calcd. band structures and the exptl. trend of optical band gaps was found. For the mixed halide perovskites the authors' calcns. show the existence of two different types of structures with different electronic properties, whose relative stability varies by varying the X group. For these systems, the calcd. formation energies decrease in the order I > Br > Cl, in line with the obsd. miscibility of $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ compds., while suggesting a comparatively smaller Cl incorporation into $CH_3NH_3Pb(I_{1-x}Cl_x)_3$ compds. Also Cl atoms preferentially occupy the apical positions in the PbI_4X_2 octahedra, while Br atoms may occupy both apical and equatorial positions, consistent with reported lattice parameters. The interplay of the org. and inorg. components of the perovskites, possibly mediated by H bonding between the ammonium groups and the halides, seems to be the key to the obsd. structural variability.

11. Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH3NH3PbI3
Xing, Guichuan; Mathews, Nripan; Sun, Shuangyong; Lim, Swee Sien; Lam, Yeng Ming; Graetzel, Michael; Mhaisalkar, Subodh; Sum, Tze Chien
Science (Washington, DC, United States) (2013), 342(6156), 344-347.

Low-temp. soln.-processed photovoltaics suffer from low efficiencies because of poor exciton or electron-hole diffusion lengths (typically ~10 nm). Recent reports of highly efficient $CH_3NH_3PbI_3$ -based solar cells in a broad range of configurations raise a compelling case for understanding the fundamental photophys. mechanisms in these materials. By applying femtosecond transient optical spectroscopy to bilayers that interface this perovskite with either selective-electron or selective-hole extn. materials, the authors have uncovered concrete evidence of balanced long-range electron-hole diffusion lengths of at least 100 nm in soln.-processed $CH_3NH_3PbI_3$. The high photoconversion efficiencies of these systems stem from the comparable optical absorption length and charge-carrier diffusion lengths, transcending the traditional constraints of soln.-processed semiconductors.

12. High performance hybrid solar cells sensitized by organolead halide perovskites
Cai, Bing; Xing, Yedi; Yang, Zhou; Zhang, Wen-Hua; Qiu, Jieshan
Energy & Environmental Science (2013), 6(5), 1480-1485.

Solid state hybrid solar cells with hybrid organolead halide perovskites ($CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$) as light harvesters and p-type polymer poly[N-9-hepta-decanyl-2,7-carbazole-alt-3,6-bis(thiophen-5-yl)-2,5-dioctyl-2,5-di-hydropyrrolo[3,4-]pyrrole-1,4-dione] (PCBTDPP) as a hole transporting material were studied. The $CH_3NH_3PbBr_3$-sensitized hybrid devices display an outstanding open circuit voltage (V_{oc}) of ~1.15 V, and the $CH_3NH_3PbI_3$ -based cells exhibit a power conversion efficiency (PCE) of ~5.55% along with high stability. The present results show that PCBTDPP is superior to the model p-type polymer P3HT as a HTM in these hybrid solar cells to achieve remarkably high V_{oc} and high PCE. The possible mechanisms have been suggested.

13. Dielectric study of CH3NH3PbX3 (X = Cl, Br, I)
Onoda-Yamamuro, Noriko; Matsuo, Takasuke; Suga, Hiroshi
Journal of Physics and Chemistry of Solids (1992), 53(7), 935-9.

Complex dielec. permittivities of $CH_3NH_3PbX_3$ (X = Cl, Br, I) were measured at frequencies between 20 Hz and 1 MHz and at 20-300 K (15-350 K for the iodide). Discontinuities or a sharp bend of the real part of the dielec. permittivity occurred at the phase transitions, except at the tetragonal (I4/mcm)-cubic phase transition where the permittivity showed no apparent change. The dielec. behaviors in the cubic and tetragonal (I4/mcm) phases are described well by a modified Kirkwood-Froehlich equation. Dielec. dispersions were found in the orthorhombic phase of $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$ at 30-120 K.

14. CH3NH3PbI3 Perovskite/Fullerene Planar-Heterojunction Hybrid Solar Cells
Jeng, Jun-Yuan; Chiang, Yi-Fang; Lee, Mu-Huan; Peng, Shin-Rung; Guo, Tzung-Fang; Chen, Peter; Wen, Ten-Chin

Advanced Materials (Weinheim, Germany) (2013), 25(27), 3727-3732.

This paper presents a hybrid org. solar cell that uses a glass/ITO/PEDOT:PSS substrate as the pos. electrode, a planar heterojunction of $CH_3NH_3PbI_3$ perovskite/C_{60} fullerene structure as the active layer, a thin bathocuproine film as an exciton- or hole-blocking layer and an aluminum neg. electrode. The resulting solar cell demonstrates very promising photovoltaic performance with an open-circuit voltage of 0.55 V, a short-circuit c.d. of 5.21 mA/cm^2 and a fill factor of 0.57, corresponding to a power conversion efficiency of 1.6% under std. 1 sun air-mass 1.5 simulated solar irradn.

15. Morphological Control for High Performance, Solution-Processed Planar Heterojunction Perovskite Solar Cells
Eperon, Giles E.; Burlakov, Victor M.; Docampo, Pablo; Goriely, Alain; Snaith, Henry J.
Advanced Functional Materials (2014), 24(1), 151-157.

Organometal trihalide perovskite based solar cells have exhibited the highest efficiencies to-date when incorporated into mesostructured composites. However, thin solid films of a perovskite absorber should be capable of operating at the highest efficiency in a simple planar heterojunction configuration. Here, it is shown that film morphol. is a crit. issue in planar heterojunction $CH_3NH_3PbI_{3-x}Cl_x$ solar cells. The morphol. is carefully controlled by varying processing conditions, and it is demonstrated that the highest photocurrents are attainable only with the highest perovskite surface coverages. With optimized soln. based film formation, power conversion efficiencies of up to 11.4% are achieved, the first report of efficiencies above 10% in fully thin-film soln. processed perovskite solar cells with no mesoporous layer.

16. Excitonic bands in the photoconductivity spectra of some organic-inorganic hybrid compounds based on metal halide units
Papavassiliou, G. C.; Mousdis, G. A.; Koutselas, I. B.
International Journal of Modern Physics B: Condensed Matter Physics, Statistical Physics, Applied Physics (2001), 15(28, 29 & 30), 3727-3731.

The photocond. (PC) spectra of the compds. $CH_3NH_3PbI_3$, $[CH_3NH_3][CH_3C_6H_4CH_2NH_3]_2Pb_2I_7$, $[CH_3C_6H_4CH_2NH_3]_2PbI_4$, $[H_2NC(I)=NH_2]_3PbI_5$ as well as the spectra of similar compds. based on $C_{10}H_{21}SC(NH_2)_2$, $H_3N(CH_2)_6NH_3$, $C_{14}H_9CH_2SC(NH_2)_2$, SnI_4, $PbCl_xI_{4-x}$ and $PbBr_xI_{4-x}$ are described. The position, intensity and shape of the PC bands depend on the dimensionality (or size) of the inorg. network as well as on the nature of metal halide and the org. groups. Excitonic features are discussed.

17. The pressure-temperature phase relations of methylammonium haloplumbate CH3NH3PbX3 (X = chlorine, bromine, iodine) crystals
Onoda-Yamamuro, Noriko; Yamamuro, Osamu; Matsuo, Takasuke; Suga, Hiroshi
Journal of Physics and Chemistry of Solids (1992), 53(2), 277-81.

Pressure-temp. phase relations of $CH_3NH_3PbX_3$ (X = Cl, Br, I) crystals were studied by using a high pressure DTA app. in the range between 0.1 Pa and 200 MPa. A triple point was found in each compd. below 100 MPa. By pressurization, the low pressure phase disappeared at the triple point in the chloride and bromide while a new high-

pressure phase appeared in the iodide. The pressures and temps. of the triple points are 75.1 MPa, 175.7 K for $CH_3NH_3PbCl_3$, 43.2 MPa, 152.9 K for $CH_3NH_3PbBr_3$, and 84.8 MPa, 176.2 K for $CH_3NH_3PbI_3$. All the boundaries between the cubic and tetragonal phases are upward convex and that of the iodide has a max. at about 120 MPa. Other phase boundaries are essentially straight lines in the measured pressure and temp. ranges. By the use of the Clausius-Clapeyron equation, the transition vols. were calcd. from the slopes of the phase boundaries and the transition entropies obtained in a previously published calorimetric expt. (authors, 1990).

18. Displacive character of the cubic-tetragonal transition in CH3NH3PbX3
Mashiyama, H.; Kawamura, Y.; Magome, E.; Kubota, Y.
Journal of the Korean Physical Society (2003), 42(Suppl. Issue, Proceedings of the 4th Japan-Korea Conference of Ferroelectrics, 2002), S1026-S1029.

The cubic-tetragonal phase transition in $CH_3NH_3PbBr_3$ was studied from the detailed structural anal. The powder diffraction profiles, obtained with using a Debye-Scherrer camera installed at SPring-8, are analyzed by a Rietveld pattern fitting program. The lattice parameters change as if a 2nd order transition takes place, with accompanying superlattice reflections. In the cubic phase, the structure could be refined either by the displacive model or by the order-disorder model. But the latter model is not fully consistent throughout the transition. The former model gives the rotating angle of the $PbBr_6$ octahedron, which increases monotonically with decreasing temp. The angle is considered to be an order parameter, and the displacive character of the phase transition is concluded in $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$.

19. Depleted hole conductor-free lead halide iodide heterojunction solar cells
Laban, Waleed Abu; Etgar, Lioz
Energy & Environmental Science (2013), 6(11), 3249-3253.

Lead halide perovskite is an excellent candidate for use as a light harvester in solar cells. Our work presents a depleted hole conductor free $CH_3NH_3PbI_3$/TiO_2 heterojunction solar cell using a thick $CH_3NH_3PbI_3$ film. The $CH_3NH_3PbI_3$ formed large crystals which function simultaneously as light harvesters and as hole transport materials. We performed capacitance voltage measurements, which show a depletion region which extends to both n and p sides. The built-in field of the depletion region assists in the charge sepn. and suppresses the back reaction of electrons from the TiO_2 film to the $CH_3NH_3PbI_3$ film. This depleted hole conductor free $CH_3NH_3PbI_3$/TiO_2 heterojunction solar cell provides a power conversion efficiency of 8% with a c.d. of 18.8 mA cm^{-2}, the highest efficiency achieved to date for perovskite based solar cells without a hole conductor.

20. Nanostructured TiO2/CH3NH3PbI3 heterojunction solar cells employing spiro-OMeTAD/Co-complex as hole-transporting material
Noh, Jun Hong; Jeon, Nam Joong; Choi, Yong Chan; Nazeeruddin, Md. K.; Graetzel, Michael; Seok, Sang Il
Journal of Materials Chemistry A: Materials for Energy and Sustainability (2013), 1(38), 11842-11847.

For using 2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) as a hole conductor in solar cells, it is necessary to improve its charge-transport properties through electrochem. doping. With the aim of fabricating efficient mesoscopic TiO_2/$MeNH_3PbI_3$ heterojunction solar cells, the authors used tris[2-(1H-pyrazol-1-yl)-4-

(tert-butylpyridine)cobalt(III) tris(bis(trifluoromethylsulfonyl) imide)] (FK209) as a p-dopant for spiro-OMeTAD. The mixt. of spiro-OMeTAD, FK209, lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI), and 4-tert-butylpyridine (TBP) exhibited significantly higher performance than mixts. of pristine spiro-OMeTAD, spiro-OMeTAD, and FK209, and spiro-OMeTAD, Li-TFSI, and TBP. Such a synergistic effect between the Co-complex and Li-TFSI in conjunction with spiro-OMeTAD effectively improved the power conversion efficiency (PCE) of the fabricated solar cells. As a result, the authors achieved PCE of 10.4%, measured under std. solar conditions (AM 1.5 G, 100 mW/cm^2).

21. Using a two-step deposition technique to prepare perovskite (CH3NH3PbI3) for thin film solar cells based on ZrO2 and TiO2 mesostructures
Bi, Dongqin; Moon, Soo-Jin; Haeggman, Leif; Boschloo, Gerrit; Yang, Lei; Johansson, Erik M. J.; Nazeeruddin, Mohammad K.; Graetzel, Michael; Hagfeldt, Anders
RSC Advances (2013), 3(41), 18762-18766.

A two-step deposition technique is used for prepg. $CH_3NH_3PbI_3$ perovskite solar cells. Using ZrO_2 and TiO_2 as a mesoporous layer, we obtain an efficiency of 10.8% and 9.5%, resp., under 1000 W m^{-2} illumination. The ZrO_2 based solar cell shows higher photovoltage and longer electron lifetime than the TiO_2 based solar cell.

22. The origin of high efficiency in low-temperature solution-processable bilayer organometal halide hybrid solar cells
Sun, Shuangyong; Salim, Teddy; Mathews, Nripan; Duchamp, Martial; Boothroyd, Chris; Xing, Guichuan; Sum, Tze Chien; Lam, Yeng Ming
Energy & Environmental Science (2014), 7(1), 399-407.

This work reports a study into the origin of the high efficiency in soln.-processable bilayer solar cells based on methylammonium lead iodide ($CH_3NH_3PbI_3$) and [6,6]-phenyl-C_{61}-butyric acid Me ester ($PC_{61}BM$). Our cell has a power conversion efficiency (PCE) of 5.2% under simulated AM 1.5G irradn. (100 mW cm^{-2}) and an internal quantum efficiency of close to 100%, which means that nearly all the absorbed photons are converted to electrons and are efficiently collected at the electrodes. This implies that the exciton diffusion, charge transfer and charge collection are highly efficient. The high exciton diffusion efficiency is enabled by the long diffusion length of $CH_3NH_3PbI_3$ relative to its thickness. Furthermore, the low exciton binding energy of $CH_3NH_3PbI_3$ implies that exciton splitting at the $CH_3NH_3PbI_3$/$PC_{61}BM$ interface is very efficient. With further increase in $CH_3NH_3PbI_3$ thickness, a higher PCE of 7.4% could be obtained. This is the highest efficiency attained for low temp. soln.-processable bilayer solar cells to date.

23. Mechanism of carrier accumulation in perovskite thin-absorber solar cells
Kim, Hui-Seon; Mora-Sero, Ivan; Gonzalez-Pedro, Victoria; Fabregat-Santiago, Francisco; Juarez-Perez, Emilio J.; Park, Nam-Gyu; Bisquert, Juan
Nature Communications (2013), 4, 3242/1-3242/7.

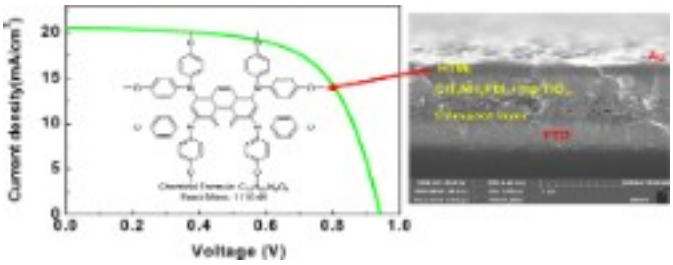
Photovoltaic conversion requires two successive steps: accumulation of a photogenerated charge and charge sepn. Detn. of how and where charge accumulation is attained and how this accumulation can be identified is mandatory for understanding the performance of a photovoltaic device and for its further optimization. Here we analyze the mechanism of carrier accumulation in lead halide perovskite, $CH_3NH_3PbI_3$, thin-absorber solar cells by means of impedance spectroscopy. A fingerprint of the charge accumulation in high d. of states of the perovskite absorber

material has been obsd. at the capacitance of the samples. This is, as far as we know, the first observation of charge accumulation in light-absorbing material for nanostructured solar cells, indicating that it constitutes a new kind of photovoltaic device, differentiated from sensitized solar cells, which will require its own methods of study, characterization and optimization.

24. Efficient Inorganic-Organic Hybrid Perovskite Solar Cells Based on Pyrene Arylamine Derivatives as Hole-Transporting Materials

Jeon, Nam Joong; Lee, Jaemin; Noh, Jun Hong; Nazeeruddin, Mohammad Khaja; Gratzel, Michael; Seok, Sang Il

Journal of the American Chemical Society (2013), 135(51), 19087-19090.



A set of three N,N-di-p-methoxyphenylamine-substituted pyrene derivs. have successfully been synthesized and characterized by $^{1}H/^{13}C$ NMR spectroscopy, mass spectrometry, and elemental anal. The optical and electronic structures of the pyrene derivs. were adjusted by controlling the ratio of N,N-di-p-methoxyphenylamine to pyrene, and investigated by UV/vis spectroscopy and cyclic voltammetry. The pyrene derivs. were employed as hole-transporting materials (HTMs) in fabricating mesoporous TiO_2/$CH_3NH_3PbI_3$/HTMs/Au solar cells. The pyrene-based deriv. Py-C exhibited a short-circuit c.d. of 20.2 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.886 V, and a fill factor of 69.4% under an illumination of 1 sun (100 mW/cm^2), resulting in an overall power conversion efficiency of 12.4%. The performance is comparable to that of the well-studied spiro-OMeTAD, even though the V_{oc} is slightly lower. Thus, this newly synthesized pyrene deriv. holds promise as a HTM for highly efficient perovskite-based solar cells.

25. Study on the stability of CH3NH3PbI3 films and the effect of post-modification by aluminum oxide in all-solid-state hybrid solar cells

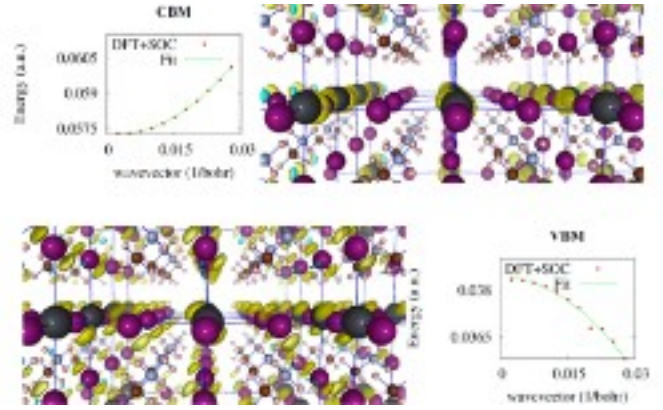
Niu, Guangda; Li, Wenzhe; Meng, Fanqi; Wang, Liduo; Dong, Haopeng; Qiu, Yong

Journal of Materials Chemistry A: Materials for Energy and Sustainability (2014), 2(3), 705-710.

Degrdn. of perovskite has been a big problem in all-solid-state perovskite solar cells, although many researchers mainly focus on the high efficiency of these solar cells. This paper studies the stability of $CH_3NH_3PbI_3$ films and finds that $CH_3NH_3PbI_3$ is sensitive to moisture. The degrdn. reaction is proposed according to UV-Vis spectra and XRD results. In order to improve the degrdn. of $CH_3NH_3PbI_3$, we introduce aluminum oxide as a post-modification material into all-solid-state perovskite solar cells for the first time. UV-Vis spectra show that Al_2O_3 modification could maintain the absorption of $CH_3NH_3PbI_3$ after degrdn. XRD results reveal that Al_2O_3 could protect perovskite from degrdn. Moreover, the device post-modified by Al_2O_3 has shown more brilliant stability than that without modification when

exposed to moisture. EIS results and dark current illustrate that the modification increased interface resistance in the dark, indicating the restrained electron recombination process.

26. Small Photocarrier Effective Masses Featuring Ambipolar Transport in Methylammonium Lead Iodide Perovskite: A Density Functional Analysis
Giorgi, Giacomo; Fujisawa, Jun-ichi; Segawa, Hiroshi; Yamashita, Koichi
Journal of Physical Chemistry Letters (2013), 4(24), 4213-4216.



Methylammonium lead iodide perovskite ($CH_3NH_3PbI_3$) plays an important role in light absorption and carrier transport in efficient org.-inorg. perovskite solar cells. In this Letter, the authors report the 1st theor. estn. of effective masses of photocarriers in $CH_3NH_3PbI_3$. Effective masses of photogenerated electrons and holes are $m_e^* = 0.23m_0$ and $m_h^* = 0.29m_0$, resp., including spin-orbit coupling effects. This result is consistent with the long-range ambipolar transport property and with the larger diffusion const. for electrons compared with that for holes in the perovskite, which enable efficient photovoltaic conversion.

27. High efficiency CH3NH3PbI(3-x)Clx perovskite solar cells with poly(3-hexylthiophene) hole transport layer
Di Giacomo, Francesco; Razza, Stefano; Matteocci, Fabio; D'Epifanio, Alessandra; Licoccia, Silvia; Brown, Thomas M.; Di Carlo, Aldo
Journal of Power Sources (2014), 251, 152-156.

We fabricate perovskite based solar cells using $CH_3NH_3PbI_{3-x}Cl_x$ with different hole-transporting materials. The most used 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene (Spiro-OMeTAD) has been compared to the poly(3-hexylthiophene-2,5-diyl) (P3HT). By tuning the energy level of P3HT and optimizing the device's fabrication, we reached 9.3% of power conversion efficiency, which is the highest reported efficiency for a solar cell using P3HT. This result shows that P3HT can be a suitable low cost hole transport material for efficient perovskite based solar cells.

28. Photoinduced processes in lead iodide perovskite solid-state solar cells
Marchioro, Arianna; Brauer, Jan C.; Teuscher, Joel; Gratzel, Michael; Moser, Jacques-E.
Proceedings of SPIE (2013), 8811(Physical Chemistry of Interfaces and Nanomaterials XII), 881108/1-881108/6.

Org.-inorg. hybrid systems based on lead halide compds. have recently encountered considerable success as light absorbers in solid-state solar cells. Herein we show how fundamental mechanistic processes in mesoporous oxide films impregnated with $CH_3NH_3PbI_3$ can be investigated by time resolved techniques. In particular, charge sepn. reactions such as electron injection into the titanium dioxide film and hole injection into the hole transporting material spiro-OMeTAD as well as the corresponding charge recombination reactions were scrutinized. Femtosecond

transient absorption spectroscopy and time-resolved terahertz spectroscopy were applied to $CH_3NH_3PbI_3$ deposited either on TiO_2 or Al_2O_3 mesoporous films and infiltrated with the hole transporting material spiro-OMeTAD.

29. Efficient and stable CH3NH3PbI3-sensitized ZnO nanorod array solid-state solar cells
Bi, Dongqin; Boschloo, Gerrit; Schwarzmueller, Stefan; Yang, Lei; Johansson, Erik M. J.; Hagfeldt, Anders
Nanoscale (2013), 5(23), 11686-11691.

We report for the first time the use of a perovskite ($CH_3NH_3PbI_3$) absorber in combination with ZnO nanorod arrays (NRAs) for solar cell applications. The perovskite material has a higher absorption coeff. than mol. dye sensitizers, gives better solar cell stability, and is therefore more suited as a sensitizer for ZnO NRAs. A solar cell efficiency of 5.0% was achieved under 1000 W m^{-2} AM 1.5 G illumination for a solar cell with the structure: ZnO NRA/$CH_3NH_3PbI_3$ /spiro-MeOTAD/Ag. Moreover, the solar cell shows a good long-term stability. Using transient photocurrent and photovoltage measurements it was found that the electron transport time and lifetime vary with the ZnO nanorod length, a trend which is similar to that in dye-sensitized solar cells, DSCs, suggesting a similar charge transfer process in ZnO NRA/$CH_3NH_3PbI_3$ solar cells as in conventional DSCs. Compared to $CH_3NH_3PbI_3$ /TiO_2 solar cells, ZnO shows a lower performance due to more recombination losses.

30. The Raman Spectrum of the CH3NH3PbI3 Hybrid Perovskite: Interplay of Theory and Experiment
Quarti, Claudio; Grancini, Giulia; Mosconi, Edoardo; Bruno, Paola; Ball, James M.; Lee, Michael M.; Snaith, Henry J.; Petrozza, Annamaria; Angelis, Filippo De
Journal of Physical Chemistry Letters (2013), Ahead of Print. DOI:10.1021/jz402589q

We report the low-frequency resonant Raman spectrum of methylammonium lead-iodide, a prototypical perovskite for solar cells applications, on mesoporous Al_2O_3. The measured spectrum assignment is assisted by DFT simulations of the Raman spectra of suitable periodic and model systems. The bands at 62 and 94 cm^{-1} are assigned resp. to the bending and to the stretching of the Pb-I bonds, and are thus diagnostic modes of the inorg. cage. We also assign the librations of the org. cations at 119 and 154 cm^{-1}. The broad, unstructured 200-400 cm^{-1} features are assigned to the torsional mode of the methylammonium cations, which we propose as a marker of the orientational disorder of the material. Our study provides the basis to interpret the Raman spectra of organohalide perovskites, which may allow one to further understand the properties of this important class of materials in relation to their full exploitation in solar cells.

31. Formation of a passivating CH3NH3PbI3/PbI2 interface during moderate heating of CH3NH3PbI3 layers
By Supasai, T.; Rujisamphan, N.; Ullrich, K.; Chemseddine, A.; Dittrich, Th.
Applied Physics Letters (2013), 103(18), 183906/1-183906/3.

Layers of $CH_3NH_3PbI_3$ were studied by modulated surface photovoltage spectroscopy (SPV) during heating in vacuum. As prepd. $CH_3NH_3PbI_3$ layers behave as a p-type doped semiconductor in depletion with a band gap of 1.5 eV. After heating to 140° the sign of the SPV signals of $CH_3NH_3PbI_3$ changed concomitant with the appearance of a 2nd band gap at 2.36 eV ascribed to PbI_2, and SPV signals related to charge sepn. from defect states were reduced after moderate heating.

32. A perspective of mesoscopic solar cells based on metal chalcogenide quantum dots and organometal-halide perovskites
Rhee, Jae Hui; Chung, Chih-Chun; Diau, Eric Wei-Guang
NPG Asia Materials (2013), 5(Oct.), e68.

We review two types of inorg. nanomaterials-metal chalcogenide quantum dots (QDs) and lead halide perovskites-that serve as prospective light harvesters in hybrid mesoscopic solar cells. Metal chalcogenide QDs are introduced in three parts: chalcogenides of cadmium (CdS, CdSe and CdTe), chalcogenides of lead (PbS and PbSe) and chalcogenides of antimony (Sb_2S_3 and Sb_2Se_3). The devices made using these chalcogenide QDs in a liq.-type electrolyte showed the best cell efficiencies, ranging from 3 to 6%. For solid-state QD-sensitized solar cells (QDSCs), the device performances were generally poor; only devices made of Sb_2S_3 and PbS QDs attained cell efficiencies approaching ~7%. In contrast, nanocryst. lead halide perovskites have emerged since 2009 as potential photosensitizers in liq.-type sensitized TiO_2 solar cells. In 2012, the efficiencies of the all-solid-state perovskite solar cells were enhanced to 9.7 and 10.9% using anodes of TiO_2 and Al_2O_3 films, resp., with 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD) as a hole-transporting material. In 2013, the performance of a TiO_2 solar cell sensitized with lead iodide perovskite ($CH_3NH_3PbI_3$) was optimized further to attain an overall power conversion efficiency η=15%, which is a new milestone for solar cells of this type having a device structure similar to that of a dye-sensitized solar cell.

33. Excitonic bands in the photoconductivity spectra of some organic-inorganic hybrid compounds based on metal halide units
Papavassiliou, G. C.; Mousdis, G. A.; Koutselas, I. B.; Papaioannou, G. J.
Edited By:Cho, Kikuo; Matsui, Atsuo
Excitonic Processes in Condensed Matter, Proceedings of International Conference, 4th, Osaka, Japan, Aug. 22-25, 2000 (2001), 159-163.

The photocond. (PC) spectra of the compds. $CH_3NH_3PbI_3$, $[CH_3NH_3][CH_3C_6H_4CH_2NH_3]_2Pb_2I_7$, $[CH_3C_6H_4CH_2NH_3]_2PbI_4$, $[H_2NC(I)=NH_2]_3PbI_5$ as well as the spectra of similar compds. based on $C_{10}H_{21}SC(NH_2)_2$, $H_3N(CH_2)_6NH_3$, $C_{14}H_9CH_2SC(NH_2)_2$, SnI_4, $PbCl_xI_{4-x}$ and $PbBr_xI_{4-x}$ are described. The position, intensity and shape of the PC bands depend on the dimensionality (or size) of the inorg. network as well as on the nature of metal halide and the org. groups. Excitonic features are discussed.

34. Planar Heterojunction Perovskite Solar Cells via Vapor-Assisted Solution Process
By Chen, Qi; Zhou, Huanping; Hong, Ziruo; Luo, Song; Duan, Hsin-Sheng; Wang, Hsin-Hua; Liu, Yongsheng; Li, Gang; Yang, Yang
Journal of the American Chemical Society (2013), Ahead of Print. DOI:10.1021/ja411509g

Hybrid org./inorg. perovskites (e.g., $CH_3NH_3PbI_3$) as light absorbers are promising players in the field of third-generation photovoltaics. Here we demonstrate a low-temp. vapor-assisted soln. process to construct polycryst. perovskite thin films with full surface coverage, small surface roughness, and grain size up to microscale. Solar cells based on the as-prepd. films achieve high power conversion efficiency of 12.1%, so far the highest efficiency based on $CH_3NH_3PbI_3$ with the planar heterojunction configuration. This method provides a simple approach to perovskite

film prepn. and paves the way for high reproducibility of films and devices. The underlying kinetic and thermodn. parameters regarding the perovskite film growth are discussed as well.

35. Iodide solar cell with perovskite structure manufactured by solid-liquid reaction
Cui, Guanglei; Pang, Shuping; Liu, Zhihong; Lv, Siliu; Hu, Hao; Xu, Hongxia; Zhang, Chuanjian
Faming Zhuanli Shenqing (2013), CN 103346018 A 20131009,

On the basis of FTO\dense TiO_2\mesoporous layer, iodide perovskite ABI_3 is prepd., wherein AI is a monovalent org. salt, BI_2 is a divalent salt, perovskite phase ABI_3 contains $CH_3NH_3PbI_3$, NH_2:$CHNH_3PbI_3$, $CH_3NH_3SnI_3$, NH_2:$CHNH_3SnI_3$, etc. it has good absorption, photoelec. conversion, hole transport capability. The invention introduces electron transport layer (TiO, ZnO, NbO) and hole transport layer to interface between the active material and the electrode, can construct perovskite ABI_3-based solar cell device. The material has simple synthesis and low cost, and the device has high stability and service life.

36. Relativistic solar cells
Umari, Paolo; Mosconi, Edoardo; De Angelis, Filippo
arXiv.org, e-Print Archive, Condensed Matter (2013), 1-16, arXiv:1309.4895v1 [cond-mat.mtrl-sci].

Hybrid AMX_3 perovskites (A = Cs, CH_3NH_3; M = Sn, Pb; X = halide) have revolutionized the scenario of emerging photovoltaic technologies. Introduced in 2009 by Kojima et al., a rapid evolution very recently led to 15% efficient solar cells. $CH_3NH_3PbI_3$ has so far dominated the field, while the similar $CH_3NH_3SnI_3$ has not been explored for photovoltaic applications, despite the reduced band-gap. Replacement of Pb by the more environment-friendly Sn would facilitate the large uptake of perovskite-based photovoltaics. Despite the extremely fast progress, the materials electronic properties which are key to the photovoltaic performance are relatively little understood. Here we develop an effective GW method incorporating spin-orbit coupling which allows us to accurately model the electronic, optical and transport properties of $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$, opening the way to new materials design. The different $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$ properties are discussed in light of their exploitation for solar cells, and found to be entirely due to relativistic effects.

37. Density functional theory analysis of structural and electronic properties of orthorhombic perovskite CH3NH3PbI3
By From Physical Chemistry Chemical Physics (2014), 16(4), 1424-1429.

The org.-inorg. hybrid perovskite $CH_3NH_3PbI_3$ is a novel light harvester, which can greatly improve the solar-conversion efficiency of dye-sensitized solar cells. In this article, a first-principle theor. study is performed using local, semi-local and non-local exchange-correlation approxns. to find a suitable method for this material. Our results, using the non-local optB86b + vdWDF functional, excellently agree with the exptl. data. Thus, consideration of weak van der Waals interactions is demonstrated to be important for the accurate description of the properties of this type of org.-inorg. hybrid materials. Further anal. of the electronic properties reveals that I 5p electrons can be photo-excited to Pb 6p empty states. The main interaction between the org. cations and the inorg. framework is through the ionic bonding between CH_3 and I ions. Furthermore, I atoms in the Pb-I framework are found to be chem. inequivalent because of their different chem. environments.

38. Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques
Liu, Dianyi; Kelly, Timothy L.
Nature Photonics (2013), Ahead of Print. DOI:10.1038/nphoton.2013.342

Org.-inorg. hybrid solar cells that combine a mesoporous scaffold, a perovskite light absorber and an org. hole transporter have emerged at the forefront of soln.-processable photovoltaic devices; however, they require processing temps. of up to 500 °C to sinter the mesoporous metal-oxide support. Here, we report the use of a thin film of ZnO nanoparticles as an electron-transport layer in $CH_3NH_3PbI_3$ -based solar cells; in contrast to mesoporous TiO_2, the ZnO layer is both substantially thinner and requires no sintering. We took advantage of these facts to prep. flexible solar cells with power-conversion efficiencies in excess of 10%. The use of ZnO also results in improvements to device performance for cells prepd. on rigid substrates. Solar cells based on this design exhibit power-conversion efficiencies as high as **15.7%** when measured under AM1.5G illumination, which makes them some of the highest-performing perovskite solar cells reported to date.

39. Impedance Spectroscopic Analysis of Lead Iodide Perovskite-Sensitized Solid-State Solar Cells
Dualeh, Amalie; Moehl, Thomas; Tetreault, Nicolas; Teuscher, Joel; Gao, Peng; Nazeeruddin, Mohammad Khaja; Gratzel, Michael
ACS Nano (2013), Ahead of Print. DOI:10.1021/nn404323g

Mesoscopic solid-state solar cells based on the inorg.-org. hybrid perovskite $CH_3NH_3PbI_3$ in conjunction with the amorphous org. semiconductor spiro-MeOTAD as a hole transport material (HTM) are investigated using impedance spectroscopy (IS). A model to interpret the frequency response of these devices is established by expanding and elaborating on the existing models used for the liq. and solid-state dye-sensitized solar cells. Furthermore, the influence of changing the additive concns. of tert-butyl-pyridine and LiTFSI in the HTM and varying the HTM overlayer thickness on top of the sub-micrometer thick TiO_2 on the extd. IS parameters is investigated. The internal elec. processes of such devices are studied and correlated with the overall device performance. In particular, the features in the IS responses that are attributed to the ionic and electronic transport properties of the perovskite material and manifest as a slow response at low frequency and an addnl. RC element at intermediate frequency, resp., are explored.

40. Efficient panchromatic inorganic-organic heterojunction solar cells with consecutive charge transport tunnels in hole transport material
Chen, Haiwei; Pan, Xu; Liu, Weiqing; Cai, Molang; Kou, Dongxing; Huo, Zhipeng; Fang, Xiaqin; Dai, Songyuan
Chemical Communications (Cambridge, United Kingdom) (2013), 49(66), 7277-7279.

A simple soln.-processing method was employed to fabricate panchromatic mp-TiO_2/$CH_3NH_3PbI_3$ /P3HT-MWNT/Au solar cells. MWNTs in a P3HT-MWNT composite acted as efficient nanostructured charge transport tunnels and induce crystn. of P3HT, hence significantly enhancing the cond. of the composite. The fill factor of the hybrid solar cells was greatly enhanced by 26.7%.

41. Efficient organometal trihalide perovskite planar-heterojunction solar cells on flexible polymer substrates
Docampo Pablo; Ball James M; Darwich Mariam; Eperon Giles E; Snaith Henry J
Nature communications (2013), 42761,
Organometal trihalide perovskite solar cells offer the promise of a low-cost easily manufacturable solar technology, compatible with large-scale low-temperature solution processing. Within 1 year of development, solar-to-electric power-conversion efficiencies have risen to over 15%, and further imminent improvements are expected. Here we show that this technology can be successfully made compatible with electron acceptor and donor materials generally used in organic photovoltaics. We demonstrate that a single thin film of the low-temperature solution-processed organometal trihalide perovskite absorber CH3NH3PbI3-xClx, sandwiched between organic contacts can exhibit devices with power-conversion efficiency of up to 10% on glass substrates and over 6% on flexible polymer substrates. This work represents an important step forward, as it removes most barriers to adoption of the perovskite technology by the organic photovoltaic community, and can thus utilize the extensive existing knowledge of hybrid interfaces for further device improvements and flexible processing platforms.

42. High Performance Perovskite-Polymer Hybrid Solar Cells via Electronic Coupling with Fullerene Monolayers
Abrusci Agnese; Stranks Samuel David; Docampo Pablo; Yip Hin-Lap; Jen Alex K-Y; Snaith Henry J
Nano letters (2013), ,
A plethora of solution processed materials have been developed for solar cell applications. Hybrid solar cells based on light absorbing semiconducting polymers infiltrated into mesoporous TiO2 are an interesting concept, but generating charge at the polymer:metal oxide heterojunction is challenging. Metal-organic Perovskite absorbers have recently shown remarkable efficiencies but currently lack the range of color tunability of organics. Here, we have combined a fullerene self-assembled monolayer (C60SAM) functionalised mesoporous titania, a perovskite absorber (CH3NH3PbI3-xClx) and a light absorbing polymer hole-conductor, P3HT, to realise a 6.7% hybrid solar cell. We find that photoexcitations in both the perovskite and the polymer undergo very efficient electron transfer to the C60SAM. The C60SAM acts as an electron acceptor, but inhibits further electron transfer into the TiO2 mesostructure due to energy level misalignment and poor electronic coupling. Thermalized electrons from the C60SAM are then transported through the perovskite phase. This strategy allows a reduction of energy loss, whilst still employing a "mesoporous electron acceptor", representing an exciting and versatile route forward for hybrid photovoltaics incorporating light absorbing polymers. Finally, we show that we can use the C60SAM functionalization of mesoporous TiO2 to achieve an 11.7% perovskite-sensitized solar cell using Spiro-OMeTAD as a transparent hole transporter.

43. Yttrium-substituted nanocrystalline TiO2 photoanodes for perovskite based heterojunction solar cells
Qin Peng; Domanski Anna L; Chandiran Aravind Kumar; Berger Rudiger; Butt Hans-Jurgen; Dar M Ibrahim; Moehl Thomas; Tetreault Nicolas; Gao Peng; Ahmad Shahzada; et al
Nanoscale (2013),

We report the use of Y(3+)-substituted TiO2 (0.5%Y-TiO2) in solid-state mesoscopic solar cells, consisting of CH3NH3PbI3 as the light harvester and spiro-OMeTAD as the hole transport material. A power conversion efficiency of 11.2% under simulated AM 1.5 full sun illumination was measured. A 15% improvement in the short-circuit current density was obtained compared with pure TiO2, due to the effect of Y(3+) on the dimensions of perovskite

nanoparticles formed on the semiconductor surface, showing that the surface modification of the semiconductor is an effective way to improve the light harvesters' morphology and electron transfer properties in the solid-state mesoscopic solar cells.

44. Flexible, low-temperature, solution processed ZnO-based perovskite solid state solar cells
Kumar Mulmudi Hemant; Yantara Natalia; Dharani Sabba; Graetzel Michael; Mhaisalkar Subodh; Boix Pablo P; Mathews Nripan
Chemical communications (Cambridge, England) (2013), 49(94), 11089-91,

A ZnO compact layer formed by electrodeposition and ZnO nanorods grown by chemical bath deposition (CBD) allow the processing of low-temperature, solution based and flexible solid state perovskite CH3NH3PbI3 solar cells. Conversion efficiencies of 8.90% were achieved on rigid substrates while the flexible ones yielded 2.62%.

45. Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber
Stranks Samuel D; Eperon Giles E; Grancini Giulia; Menelaou Christopher; Alcocer Marcelo J P; Leijtens Tomas; Herz Laura M; Petrozza Annamaria; Snaith Henry J
Science (New York, N.Y.) (2013), 342(6156), 341-4,

Organic-inorganic perovskites have shown promise as high-performance absorbers in solar cells, first as a coating on a mesoporous metal oxide scaffold and more recently as a solid layer in planar heterojunction architectures. Here, we report transient absorption and photoluminescence-quenching measurements to determine the electron-hole diffusion lengths, diffusion constants, and lifetimes in mixed halide (CH3NH3PbI(3-x)Cl(x)) and triiodide (CH3NH3PbI3) perovskite absorbers. We found that the diffusion lengths are greater than 1 micrometer in the mixed halide perovskite, which is an order of magnitude greater than the absorption depth. In contrast, the triiodide absorber has electron-hole diffusion lengths of ~100 nanometers. These results justify the high efficiency of planar heterojunction perovskite solar cells and identify a critical parameter to optimize for future perovskite absorber development.

46. High efficiency electrospun TiO2 nanofiber based hybrid organic-inorganic perovskite solar cell
Dharani Sabba; Mulmudi Hemant Kumar; Yantara Natalia; Thu Trang Pham Thi; Park Nam Gyu; Graetzel Michael; Mhaisalkar Subodh; Mathews Nripan; Boix Pablo P
Nanoscale (2013),

The good electrical and morphological characteristics of TiO2 nanofibers and the high extinction coefficient of CH3NH3PbI3 perovskite are combined to obtain a solar cell with a power conversion efficiency of 9.8%. The increase of the film thickness dramatically diminishes the performance due to the reduction in porosity of the TiO2 nanofiber framework. The optimum device (~413 nm film thickness) is compared to a planar device, where the latter produces higher Voc but lower Jsc, and consequently lower efficiency at all measured light intensities.

47. Density functional theory analysis of structural and electronic properties of orthorhombic perovskite CH3NH3PbI3
Wang Yun; Gould Tim; Dobson John F; Zhang Haimin; Yang Huagui; Yao Xiangdong; Zhao Huijun
Physical chemistry chemical physics : PCCP (2013), 16(4), 1424-9,

The organic-inorganic hybrid perovskite CH3NH3PbI3 is a novel light harvester, which can greatly improve the solar-conversion efficiency of dye-sensitized solar cells. In this article, a first-principle theoretical study is performed using local, semi-local and non-local exchange-correlation approximations to find a suitable method for this material. Our results, using the non-local optB86b + vdWDF functional, excellently agree with the experimental data. Thus, consideration of weak van der Waals interactions is demonstrated to be important for the accurate description of the properties of this type of organic-inorganic hybrid materials. Further analysis of the electronic properties reveals that I 5p electrons can be photo-excited to Pb 6p empty states. The main interaction between the organic cations and the inorganic framework is through the ionic bonding between CH3 and I ions. Furthermore, I atoms in the Pb-I framework are found to be chemically inequivalent because of their different chemical environments.

48. Mechanism of carrier accumulation in perovskite thin-absorber solar cells
Kim Hui-Seon; Mora-Sero Ivan; Gonzalez-Pedro Victoria; Fabregat-Santiago Francisco; Juarez-Perez Emilio J; Park Nam-Gyu; Bisquert Juan
Nature communications (2013), 42242,

Photovoltaic conversion requires two successive steps: accumulation of a photogenerated charge and charge separation. Determination of how and where charge accumulation is attained and how this accumulation can be identified is mandatory for understanding the performance of a photovoltaic device and for its further optimization. Here we analyse the mechanism of carrier accumulation in lead halide perovskite, CH3NH3PbI3, thin-absorber solar cells by means of impedance spectroscopy. A fingerprint of the charge accumulation in high density of states of the perovskite absorber material has been observed at the capacitance of the samples. This is, as far as we know, the first observation of charge accumulation in light-absorbing material for nanostructured solar cells, indicating that it constitutes a new kind of photovoltaic device, differentiated from sensitized solar cells, which will require its own methods of study, characterization and optimization.