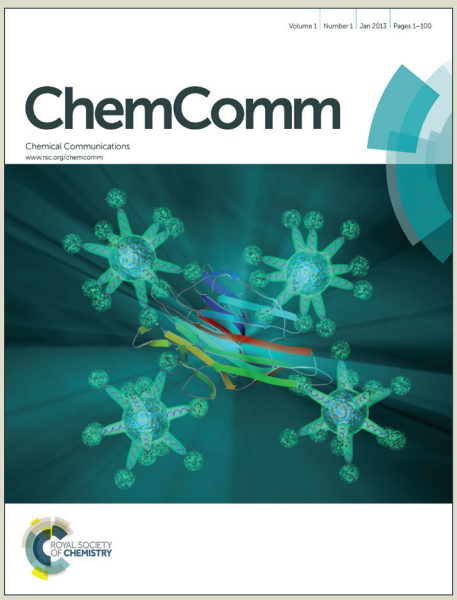
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

RSCPublishing

COMMUNICATION

Organohalide Lead Perovskite Based Photodetectors with Much Enhanced Performance

Cite this: DOI: 10.1039/xoxxoooooox

Hua-RongXia, [a,b]JiaLi,[a,c] Wen-Tao Sun[a,b*]and Lian-Mao Peng[a,b,c*]

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

$CH_3NH_3PbI_3$ based photodetectors were fabricated by a facile low-cost process with much enhanced performance. The rise time changed from 2.7s to 0.02s, the decay time from 0.5s to 0.02s, the ON/OFF ratio tripled with improved stability. The results indicate that perovskites are promising light-harvesting materials for photodetectors.

Organic-inorganic perovskites such as $CH_3NH_3PbX_3$ (X=Cl, Br, I) have attracted much attention as light-harvesting materials for mesoscopic solar cells with enhanced performance[1-7], since the pioneering work by Tsutomu Miyasaka et al[8]. Photodetectors have important applications in many fields and light-harvesting material is the key part of it. However, little work has been done on the research of perovskite based photodetectors. In this work, $CH_3NH_3PbI_3/TiO_2$ photodetectors were fabricated by a facile and low-cost process. Compared with the plain TiO_2 photodetector, the performance was significantly improved. The response speed is much faster with the rise time of the time response constants changed from 2.7 s to 0.02 s and the decay time from 0.5 s to 0.02s. At the same time, the ON/OFF ratio is about three times of that without t$CH_3NH_3PbI_3$, and the stability of the photodetector was also improved. The results indicate that perovskites are promising light-harvesting materials for photodetectors.

Organohalide lead perovskite ($CH_3NH_3PbI_3$) was prepared according to the procedure reported by Kim et al[9] (Details in SI, Supporting Information). And TiO_2 paste was made from P25 powder (TiO_2 nanoparticles with diameter of about 20 nm) with a procedure similar with the report of Gratzel's group[10]. In a typical process, the fabrication of perovskite based photodetectors includes three steps as shown in Figure 1. First, the electrodes for photodetectors were made as the following process: the FTO area used as electrodes were protected by tapes with others exposed, then the tape-protected FTO was coated with a layer of Zinc powder and immersed into 1 M hydrochloride solution to etch the FTO without tape protection (Details in SI). Second, TiO_2 paste was coated onto the etched area to link the two electrodes by a screen printing process and then annealed at 400 ℃ for 1 hour to form a mesoscopic film with a thickness of about 2 μm. By this way, a TiO_2-based photodetector was made indeed. Finally, the as-synthesized $CH_3NH_3PbI_3$ solution was spun onto the TiO_2 mesoscopic thin film and then dried at 115 ℃ for 15 min. Thus perovskite based photodetectors were successfully made. The performance of the photodetectors was measured by a CHI 660C electrochemical workstation under a solar simulator with AM 1.5 light. SEM (scanning electron microscope), XRD (X-ray diffraction spectrometer) and UV-Vis (ultraviolet-visible spectrometer) were also used to characterize the morphologies, structures and absorptions respectively.

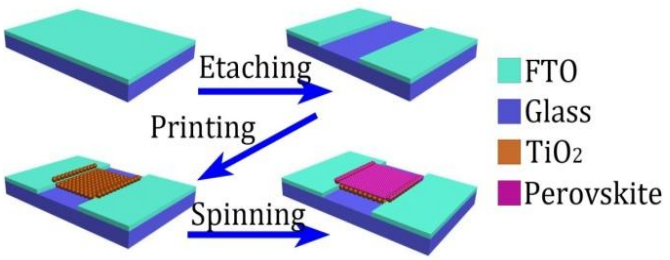


Figure 1. Scheme of the fabrication of organic-inorganic perovskite based photodetectors

The morphologies of the photodetectors were characterized by SEM with typical images shown in Figure 2a-c. Figure 2a shows an image of the conducting side of FTO glass, which is composed of large numbers of close-packed particles with the diameters from 10 to 100nm. Seen from Figure 2b, the mesoscopic TiO_2 thin film is made up of many interconnected TiO_2 nanoparticles with the diameter of about 20 nm. As there are lots of nanopores in the mesoscopic TiO_2 film, the organohalide lead perovskite solution can penetrate into them and form perovskite/TiO_2 heterojunctions. Figure 2c shows the images of $CH_3NH_3PbI_3/TiO_2$ film, with many perovskite penetrated into the film and others forming large flakes onto the film which is similar with the

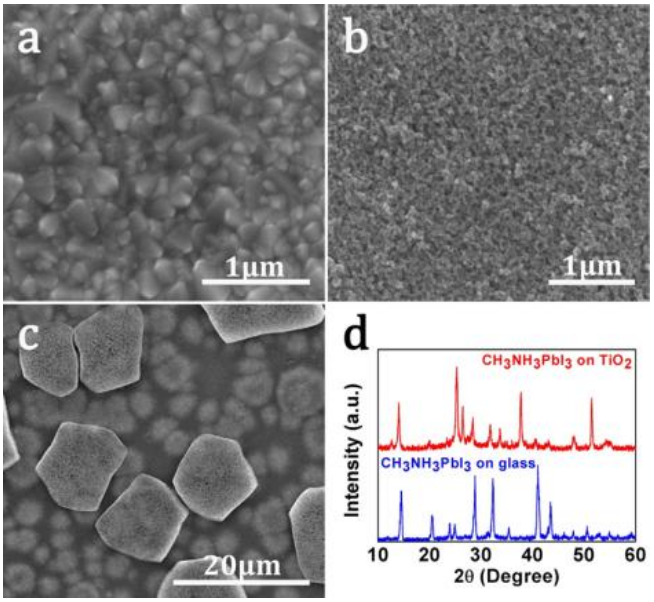


Figure 1. (a-c) SEM images of FTO glass, TiO_2mesoscopic thin film, and $CH_3NH_3PbI_3/TiO_2$ thin film respectively. (d)XRD patterns of $CH_3NH_3PbI_3/TiO_2$ film (red line) and pure $CH_3NH_3PbI_3$ on a glass substrate (blue line).

reference[4]. The XRD patterns of19.94, 28.42, 31.78, 40.48 and 43.04° are corresponding to the reflections from (110), (112), (220), (310), (224) and (314) crystal planes respectively, indicating a tetragonal perovskite structure with a=8.855 Å and c=12.659 Å (Figure 3a)[11]. No impurity peaks other than the ones attributed to $CH_3NH_3PbI_3$ and TiO_2/FTO are observed, suggesting that $CH_3NH_3PbI_3$ grown on the mesoporous TiO_2 thin film is phase pure.

Typical transmission spectra of the etched FTO glass (black line), TiO_2 on etched FTO glass (red line) and $CH_3NH_3PbI_3/TiO_2$ on etched FTO glass (blue line) are shown in Figure 3 b, with the corresponding photographs inset. The sharp absorption edge of the TiO_2-coated etched FTO glass has a red shift compared to that of the etched FTO glass, which may result from the smaller band gap of TiO_2 (3.2 eV) compared to SnO_2 (3.6 eV). And the significant enhanced absorption of $CH_3NH_3PbI_3/TiO_2$ mesoscopic thin film is ascribed to the large absorption coefficient of $CH_3NH_3PbI_3$[6]. Typical I-V curves of the TiO_2 photodetector and $CH_3NH_3PbI_3/TiO_2$ photodetector are shown in Figure 3c and 3d respectively. Clearly, I-V curves present linear dependence with the applied bias, indicating the formation of ohmic contact between TiO_2 and FTO electrode, which is crucial to photoconductive photodetectors. The dark currents at 3 V of the TiO_2 photodetector (1.34E-10 A) and the $CH_3NH_3PbI_3/TiO_2$ photodetector (1.36E-10 A) are similar, while the photocurrent at 3 V of the $CH_3NH_3PbI_3/TiO_2$ photodetector (9.75 E -9 A, corresponding responsivity 0.49 μA/W) is much larger than that of TiO_2 photodetector (3.27 E -9 A, corresponding responsivity 0.16 μA/W) showing that the introduction of $CH_3NH_3PbI_3$ into the TiO_2 mesoscopic photodetector improved the ON/OFF ratio (or gain) for about three times. The improvement can be attributed to the much enhanced light harvesting capability resulting from the addition of $CH_3NH_3PbI_3$ (shown in Figure 3b). The corresponding photocurrent time response were measured at 3V bias under a solar simulator ON/OFF switching irritation with the light intensity of 100 mW/cm^2 and an ON/OFF internal of 20 s. Ten cycle curves under ON/OFF illumination are shown in Figure 3e. It can

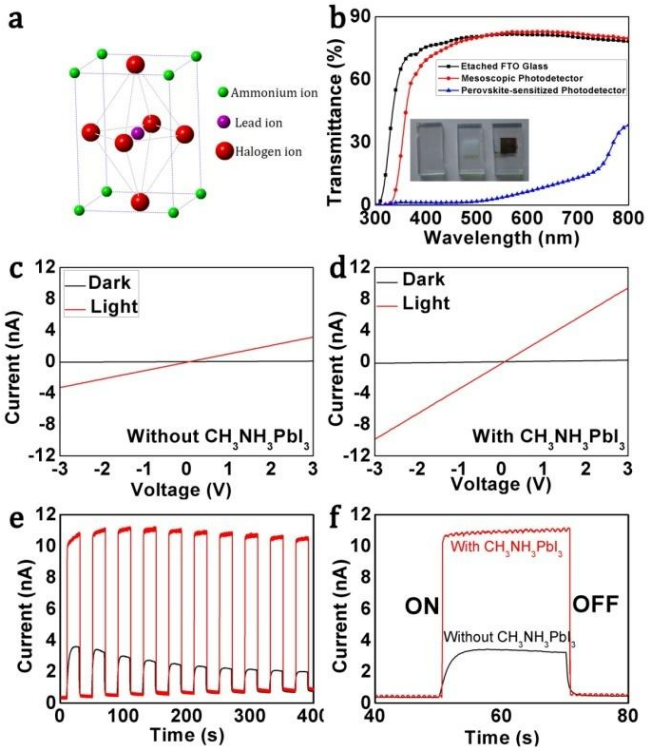


Figure 2. (a) Crystal structures of organohalide leadperovskite compounds. (b) Transmission spectra of etached FTO (black line), mesoscopic TiO_2 thin film (red line) and $CH_3NH_3PbI_3/TiO_2$ thin film (blue line) with the corresponding photographs inset. (c)(d) I-V cures of the photodetectors without/with $CH_3NH_3PbI_3$. (e)(f) Time response behaviors of the photodetectors with (red line)/without (black line) $CH_3NH_3PbI_3$.

be seen that the photocurrent of $CH_3NH_3PbI_3/TiO_2$ photodetector (red line) is consistent and repeatable while that of TiO_2 photodetector (black line) decays significantly, which is consistent with the report[12]. An enlarged typical ON/OFF cycle is shown in Figure 3f, from which it can be seen that the $CH_3NH_3PbI_3/TiO_2$ photodetector switches much faster. To quantitatively extract the time response constant, the well accepted quantitative criterion is introduced. That is, the rise time is the time to reach 90% of the stable photocurrent, and the decay time is the time to reach 1/e (37%) of the original photocurrent[13]. According to this criterion, the rise time and decay time of the TiO_2 photodetector are about 2.7 s and 0.5 s respectively, which is comparable with the best performance of TiO_2 photodetectors reported elsewhere[14, 15]. While the rise time and decay time of the $CH_3NH_3PbI_3/TiO_2$ photodetector are about 0.02 s and 0.02 s respectively.

The mechanism of the significantly shorten rise and decay time of the CH3NH3PbI3/TiO2 based photodetectors compared with the TiO2 based ones may be described as follows. For a pure TiO2 photodetector, it is generally accepted that the oxygen adsorption/desorption at the TiO2 surface plays an important role and the photoresponse rate is mainly determined by the rate of oxygen adsorption/desorption.[16-18] For a perovskite/TiO_2 heterojunction photodetector, band-bending at the interface makes it fast for the

separation of electron-hole pairs. Upon illumination, large numbers of electrons are injected into TiO_2 rapidly which increase the photoconductivity of the TiO_2 film. While when the light is switched off, the sudden absence of electron injection results in the decrease of the conductivity rapidly. Since the light-induced carrier concentration modulation is much faster than the one controlled by the oxygen adsorption/desorption process, the time response speed of the perovskite/TiO_2 photodetector is much faster than that of pure TiO_2 photodetector (Figure 5f). Besides, as the oxygen adsorption/desorption process is susceptible to the atmosphere, the cycle stability of perovskite/TiO_2 photodetector is better than that of pure TiO_2 photodetector (Figure 5e).

Conclusions

In conclusion, $CH_3NH_3PbI_3/TiO_2$ photodetectors were accomplished by a facile and low-cost all-solution method. The as-prepared organohalide lead perovskite ($CH_3NH_3PbI_3$) based photodetector has significantly enhanced performance on the time response constants and the ON/OFF ratio. The rise time changes from 2.7 s to 0.02 s and the decay time from 0.5 s to 0.02s. At the same time, the ON/OFF ratio is about three times of that without $CH_3NH_3PbI_3$. ON/OFF cycle experiments also indicate that the photocurrent of $CH_3NH_3PbI_3/TiO_2$ photodetector is more consistent and repeatable than that of plain TiO_2 photodetector. The results suggest that perovskite materials may have a promising application in photodetectors.

Acknowledgements

This work was supported by the Ministry of Science and Technology (Grant No. 2011CB933002 and 2012CB932702) and the National Science Foundation of China (Grant No. 61306079, 61171023).

Notes and references

[a]Key Laboratory for the Physics and Chemistry of Nanodevices, Peking University, Beijing 100871,China
[b]Department of Electronics, Peking Uniersity, Beijing 100871, China
[c]Academy for Advanced Interdisciplinary Studies, Peking University, Beijing 100871, China
*Email: wtaosun@pku.edu.cn; lmpeng@pku.edu.cn.

† Electronic Supplementary Information (ESI) available: Experimental details of $CH_3NH_3PbI_3$ synthesis, preparation of TiO_2 paste, and fabrication of FTO electrodes on glass, Photographs of the $CH_3NH_3PbI_3$ solution, TiO_2 paste and FTO electrodes. See DOI: 10.1039/c000000x/

1 M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643.
2 J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Gratzel, *Nature*, 2013, **499**, 316.
3 H.-S. Kim, I. Mora-Sero, V. Gonzalez-Pedro, F. Fabregat-Santiago, E. J. Juarez-Perez, N.-G.Park and J. Bisquert, *Nat Commun*, 2013, **4**, 2242.
4 M. Liu, M. B. Johnston and H. J. Snaith, *Nature*, 2013, **501**, 395.
5 S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, **342**, 341.
6 G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar and T. C. Sum, *Science*, 2013, **342**, 344.
7 V. Gonzalez-Pedro, E. J. Juarez-Perez, W.-S.Arsyad, E. M. Barea, F. Fabregat-Santiago, I. Mora-Sero and J. Bisquert, *Nano Letters*, 2014, **14**, 888.
8 A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *Journal of the American Chemical Society*, 2009, **131**, 6050.
9 H. S. Kim, C. R. Lee, J. H. Im, K. B. Lee, T. Moehl, A. Marchioro, S. J. Moon, R. Humphry-Baker, J. H. Yum, J. E. Moser, M. Gratzel and N. G Park, *Scientific Reports*, 2012, **2**, 591.
10 S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Pechy and M. Gratzel, *Progress in Photovoltaics*, 2007, **15**, 603.
11 Y. Zhao and K. Zhu, *The Journal of Physical Chemistry Letters*, 2013, **4**, 2880.
12 G. H. Liu, N. Hoivik and K. Y. Wang, *Electrochemistry Communications*, 2013, **28**, 107.
13 Y. R. Xie, L. Wei, Q. H. Li, G. D. Wei, D. Wang, Y. X. Chen, J. Jiao, S. S. Yan, G. L. Liu and L. M. Mei, *Applied Physics Letters*, 2013, **103**, 261109.
14 C. H. Feng, H. F. Zhang, Y. Wang, W. Li, J. R. Zhou, L. H. Chen, L. X. Yu and S. P. Ruan, *Journal of the American Ceramic Society*, 2012, **95**, 1980.
15 J. Zou, Q. Zhang, K. Huang and N. Marzari, *The Journal of Physical Chemistry C*, 2010, **114**, 10725.
16 S. Zhang, C. Xie, Z. Zou, L. Yang, H. Li and S. Zhang, *The Journal of Physical Chemistry C*, 2012, **116**, 19673.
17 W. Zhang, J.-K.Huang, C.-H.Chen, Y.-H.Chang, Y.-J.Cheng and L.-J.Li, *Advanced Materials*, 2013, **25**, 3456.
18. G. H. Liu, N. Hoivik, X. M. Wang, S. S. Lu, K. Y. Wang and H. Jakobsen, *Electrochimica Acta*, 2013, 93, 80-86.