Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2018, **28**, 378–380

Mendeleev Communications

Electrodeposition of porous CuSCN layers as hole-conducting material for perovskite solar cells

Natalia N. Shlenskaya,[a] Andrey S. Tutantsev,[a] Nikolay A. Belich,[a] Eugene A. Goodilin,*[a,b,c] Michael Grätzel[d] and Alexey B. Tarasov*[a,b]

[a] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 0998; e-mail: goodilin@yandex.ru, alexey.bor.tarasov@gmail.com*

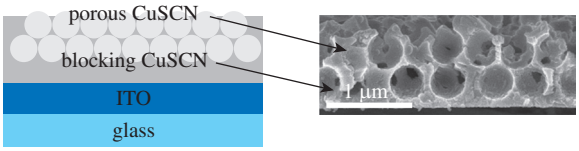
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

[c] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

[d] *Laboratory of Photonics and Interfaces, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, EPFL SB ISIC LPI, Station 6, 1015 Lausanne, Switzerland*

DOI: 10.1016/j.mencom.2018.07.012

One of the most promising among hole-conducting materials, CuSCN, was prepared for the first time in a form of porous layers for potential applications in inverted perovskite solar cells.



In the field of perovskite solar cells (PSCs), a notable amount of works has been performed to develop low-cost, stable, and effective inorganic hole-conducting materials (HTMs).[1,2] The most promising inorganic HTMs are CuI,[3] CuSCN,[4] and NiO_x[5] since they demonstrate high charge carrier mobilities, a thermal stability, and can be prepared *via* relatively simple synthetic procedures. The mesoscopic architecture of perovskite solar cells commonly gives higher conversion efficiencies than planar architectures due to a greater contact area with perovskite and a decreased carrier transport distance.[6] In the case of original *n-i-p* PSCs architecture, the electron-conducting material (TiO_2) is usually deposited on FTO/glass (FTO is the fluorine doped tin oxide) substrates as a blocking/mesoporous structure.[7] The same approach is desirable for the inverted *p-i-n* PSCs architecture, but the only reported[8,9] mesoscopic *p-i-n* PSCs are based on NiO_x. For copper-based HTMs (CuI, CuSCN, and Cu_2O), no mesoscopic inverted perovskite solar cells are known besides the fact that copper-based compounds are the most promising inorganic HTMs for PSCs.[10]

In order to fill this gap, we report a new preparation method of porous CuSCN based on electrodeposition[11] into a sacrificial polystyrene template.

Electrodeposition of CuSCN was conducted on ITO (indium doped tin oxide) substrates from water solution containing $CuSO_4$, Na_2EDTA, NaSCN (12, 12, and 24 mmol dm^{-3}, respectively) in a three-electrode cell (pH of working solution was 3–4). The corresponding cyclic voltammogram is shown in Figure 1, wherein the working region for CuSCN electrodeposition is highlighted in blue. The blocking CuSCN layer was potentiostatically deposited at –0.4 V, while the deposition of copper(I) thiocyanate into sacrificial polystyrene template was achieved at a lower potential of –0.1 V. CuSCN electrodeposition mechanism seems to be a nucleation and growth according to the current transient at E = const (see inset in Figure 1).

The CuSCN blocking layer (*b*-CuSCN) deposited onto the ITO substrate has a dense fine-crystalline morphology [Figure 2(*a*)]. The CuSCN layer thickness of about 40 nm was observed after deposition at –0.1 V for 5 min. An analysis of the CuSCN/ITO structure by X-ray diffraction (XRD) and Raman spectroscopy revealed the absence of any crystalline or amorphous phase impurities [Figure 2(*b*),(*c*)].

In the Raman spectrum, all sharp vibration modes correspond to CuSCN, and no Cu–O modes [*e.g.*, 411, 492, 633 cm^{-1} for Cu_2O, and 488 cm^{-1} for $Cu(OH)_2$][11] are present indicating the absence of oxidation during CuSCN electrodeposition. All Raman modes in copper(I) thiocyanate were fully assigned recently.[11]

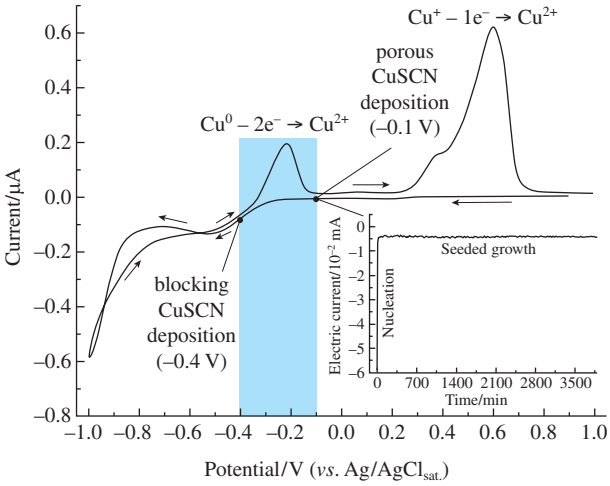


Figure 1 Cyclic voltammogram in the range from –1 to 1 V on the ITO electrode at the rate of 20 mV s^{-1}. The inset shows current transient at E = const during CuSCN electrodeposition into three layers on the polystyrene template.

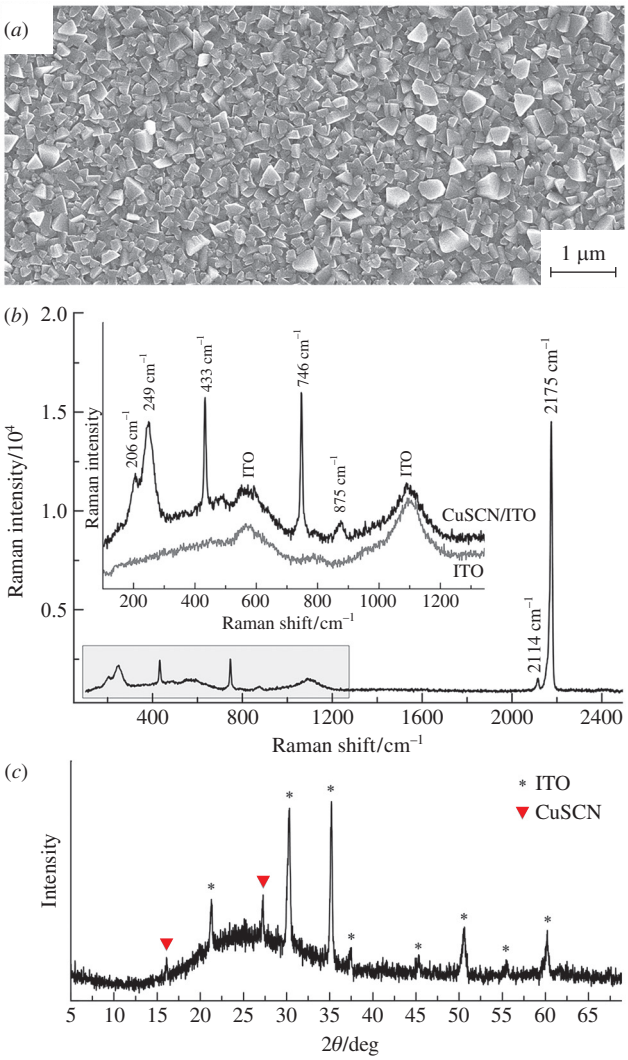


Figure 2 (*a*) SEM micrograph of the CuSCN blocking layer; (*b*) Raman spectra of CuSCN/ITO (black line) and pure ITO (gray line) substrates in the range of 100–2450 cm^{-1}; (*c*) XRD pattern of the CuSCN/ITO structure.

In the present work, we implemented electrodeposition of CuSCN into a sacrificial template[12] as an effective method of porous CuSCN preparation. Our approach includes several steps illustrated in Figure 3. The first step, electrodeposition of blocking

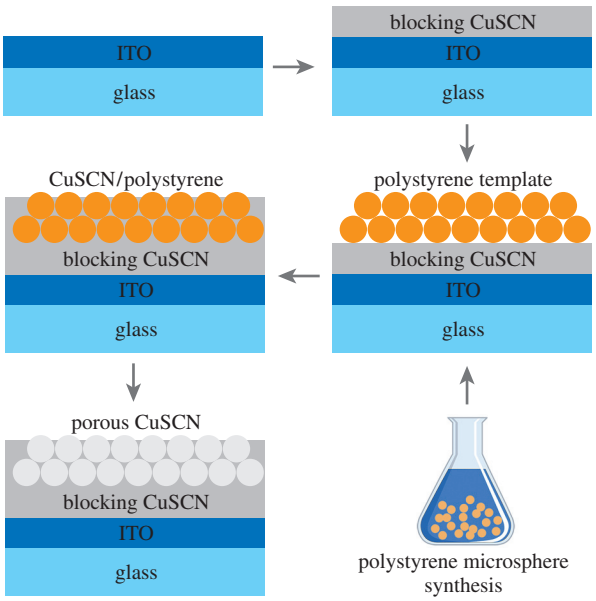


Figure 3 Step-by-step preparation scheme for porous CuSCN.

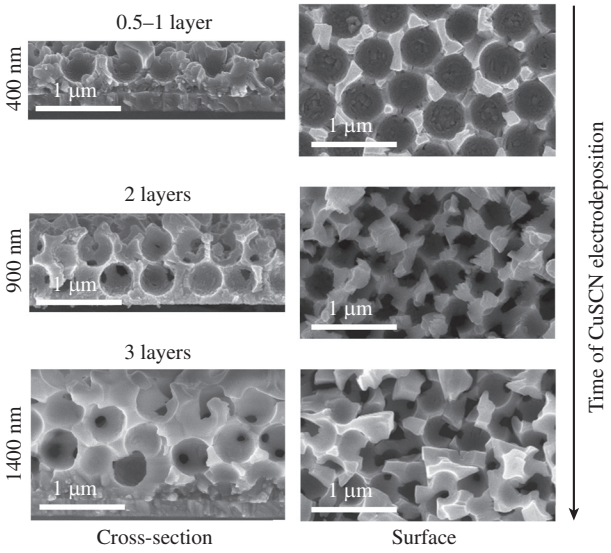


Figure 4 SEM micrographs of surfaces and cross-sections of CuSCN porous structures of different thicknesses.

CuSCN, was discussed above. The next step is a formation of a porous polymer template from polystyrene microspheres (with radius of ~400–500 nm) previously synthesized in a standard way.[13] Thin films of polystyrene microspheres were spin-coated on *b*-CuSCN/ITO substrates from a water/ethanol suspension in the presence of Triton X-100 surfactant, which allows one to obtain a denser and more regular template. The second CuSCN electrodeposition into the template was performed at –0.1 V and the time of potentiostatic deposition defined the final thickness of porous copper(I) thiocyanate film (Figure 4). After this step, polystyrene was dissolved in toluene to open the porous CuSCN/ITO heterostructure making it ready for applications in the inverted mesoscopic PSCs based on inorganic HTM.

Our approach makes it possible to obtain the porous copper(I) thiocyanate structures of various thicknesses starting from a half of the preceding polystyrene microspheres layer and up to much larger thickness, which depends on the applied polymer template. In this work, the CuSCN structures were prepared with 0.5–1, 2, and 3 layers of thicknesses (see Figure 4). The hole sizes in the porous structure can be themselves controlled, evidently, by varying the radii of polystyrene microspheres.

It is worth pointing out that an application of CuSCN porous layers in the PSCs demands an optimal thickness of the porous HTM and the corresponding hybrid perovskite layer should be in the range of 300–500 nm. Thicker layers show a worse efficiency due to the increased charge carrier distances.

Therefore, the effective electrochemical preparation of porous CuSCN structures *via* the sacrificial template method has been implemented for the first time. This approach allows one to obtain porous copper(I) thiocyanate layers possessing a various thickness and controlled microstructure. This porous CuSCN structure might be potentially applied in the inverted perovskite solar cells as a transparent inorganic hole-conducting material.

This work was supported by the Ministry of Education and Science of the Russian Federation (grant no. RFMEFI61316X0053). N.N.Sh. and A.S.T. made the equal contribution to this study.

References

1 A. S. Subbiah, A. Halder, S. Ghosh, N. Mahuli, G. Hodes and S. K. Sarkar, *J. Phys. Chem. Lett.*, 2014, **5**, 1748.
2 M.-H. Li, J.-H. Yum, S.-J. Moon and P. Chen, *Energies*, 2016, **9**, 331.
3 M. Huangfu, Y. Shen, G. Zhu, K. Xu, M. Cao, F. Gu and L. Wang, *Appl. Surf. Sci.*, 2015, **357**, 2234.

4 N. Arora, M. I. Dar, A. Hinderhofer, N. Pellet, F. Schreiber, S. M. Zakeeruddin and M. Grätzel, *Science*, 2017, **358**, 768.
5 H. Zhang, J. Cheng, F. Lin, H. He, J. Mao, K. S. Wong, A. K.-Y. Jen and W. C. H. Choy, *ACS Nano*, 2016, **10**, 1503.
6 Z. Song, S. C. Watthage, A. B. Phillips and M. J. Heben, *J. Photonics Energy*, 2016, **6**, 22001.
7 Z. Ku, Y. Rong, M. Xu, T. Liu and H. Han, *Sci. Rep*., 2013, **3**, 3132.
8 Z. Liu, M. Zhang, X. Xu, L. Bu, W. Zhang, W. Li, Z. Zhao, M. Wang, Y.-B. Cheng and H. He, *Dalton Trans*., 2015, **44**, 3967.
9 K.-C. Wang, J.-Y. Jeng, P.-S. Shen, Y.-C. Chang, E. W.-G. Diau, C.-H. Tsai, T.-Y. Chao, H.-C. Hsu, P.-Y. Lin, P. Chen, T.-F. Guo and T.-C. Wen, *Sci. Rep*., 2014, **4**, 4756.
10 R. Rajeswari, M. Mrinalini, S. Prasanthkumar and L. Giribabu, *Chem. Rec*., 2017, **17**, 681.
11 D. Ramírez, G. Riveros, K. Álvarez, B. González, C. J. Pereyra, E. A. Dalchiele, R. E. Marotti, D. Ariosa, F. Martín and J. R. Ramos-Barrado, *Mater. Sci. Semicond. Process*, 2017, **68**, 226.
12 A. S. Poyraz, C.-H. Kuo, S. Biswas, C. K. King'ondu and S. L. Suib, *Nat. Commun*., 2013, **4**, 2952.
13 E. V. Parkhomchuk, V. S. Semeykina, K. A. Sashkina, A. G. Okunev, A. I. Lysikov and V. N. Parmon, *Top. Catal*., 2017, **60**, 178.

Received: 28th December 2017; Com. 17/5445