



Aero-ZnS prepared by physical vapor transport on three-dimensional networks of sacrificial ZnO microtetrapods

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Abstract

Aeromaterials represent a class of increasingly attractive materials for various applications. Among them, aero-ZnS has been produced by hydride vapor phase epitaxy on sacrificial ZnO templates consisting of networks of microtetrapods and has been proposed for microfluidic applications. In this paper, a cost-effective technological approach is proposed for the fabrication of aero-ZnS by using physical vapor transport with Sn₂S₃ crystals and networks of ZnO microtetrapods as precursors. The morphology of the produced material is investigated by scanning electron microscopy (SEM), while its crystalline and optical qualities are assessed by X-ray diffraction (XRD) analysis and photoluminescence (PL) spectroscopy, respectively. We demonstrate possibilities for controlling the composition and the crystallographic phase content of the prepared aerogels by the duration of the technological procedure. A scheme of deep energy levels and electronic transitions in the ZnS skeleton of the aeromaterial was deduced from the PL analysis, suggesting that the produced aerogel is a potential candidate for photocatalytic and sensor applications.

Introduction

Porous materials represent a class of solid-state networks widely used in adsorptive and photocatalytic removal of pollutants from the atmosphere and from water, in other catalytic processes, including photocatalytic water splitting, in energy

production and storage, in microfluidic systems, in drug delivery and other biomedical applications, in sensing, in electronic, photoelectronic, optoelectronic and nanophotonic devices, and in other specific applications, such as electromag-

netic interference shielding and microwave absorbing materials. Among inorganic porous materials, several groups predominate, such as metal halide perovskites (MHP) [1], Si and III–V semiconductors [2–6], chalcogenides [7–9], and metal oxides [1,9,10]. Metal oxides include TiO_2 , ZnO , Al_2O_3 , WO_3 , Cu_2O , CuO , SnO_2 , Fe_2O_3 , Bi_2O_3 , Ag_3PO_4 , BiWO_4 , BiVO_4 , BiFeO_3 , and SeTiO_3 , while chalcogenides are represented by ZnS , ZnSe , CdS , PbS , CdSe , SnS_2 , and Bi_2S_3 .

Among porous semiconductor materials, recently developed super-lightweight ones with ultrahigh degree of porosity, the so-called aeromaterials, are of special interest [11–18]. Aeromaterials are similar to aerogels, which are widely explored and used in various applications. Aerogels include inorganic [19–24], organic [21–25], and hybrid composite [26,27] materials.

Aeromaterials have been prepared on the basis of sacrificial nano/microstructured templates. Nanofibrillated cellulose has been used as a sacrificial template for the preparation of inorganic nanotube networks, such as titanium dioxide, zinc oxide, and aluminum oxide nanotube networks, by atomic layer deposition [20]. Another aeromaterial, so called aerographite, has been produced by a one-step chemical vapor deposition process with a simultaneous and complete removal of the template material consisting of highly porous 3D networks built from interconnected micrometer-thick ZnO rods with the shape of tetrapods [28]. This aerographite material is a tubular graphitic carbon mimicry of a sacrificial ZnO template architecture in which ZnO has been replaced by carbon from the toluene precursor.

Sacrificial porous ZnO networks of microtetrapods have also been used for the preparation of the abovementioned semiconductor-based aeromaterials. Most of these aeromaterials have been produced by hydride vapor phase epitaxy (HVPE) [11–18]. Particularly, an aero- ZnS material exhibiting hydrophilic properties under tension and hydrophobic properties when compressed against water was fabricated using HVPE of CdS on sacrificial ZnO microtetrapods through the simultaneous or subsequent transformation of CdS into ZnS and the removal of the sacrificial ZnO crystals [16]. Self-propelled liquid marbles have been demonstrated on the basis of this aeromaterial. However, HVPE is an expensive technology.

The goal of this paper is to demonstrate a cost-effective vapor transport approach for the preparation of ZnS aeromaterials.

References

- Cui, Y.; Ge, P.; Chen, M.; Xu, L. *Catalysts* **2022**, *12*, 372. doi:10.3390/catal12040372
- Harraz, F. A. *Sens. Actuators, B* **2014**, *202*, 897–912. doi:10.1016/j.snb.2014.06.048
- Moretta, R.; De Stefano, L.; Terracciano, M.; Rea, I. *Sensors* **2021**, *21*, 1336. doi:10.3390/s21041336
- Monaico, E.; Tiginyanu, I.; Ursaki, V. *Semicond. Sci. Technol.* **2020**, *35*, 103001. doi:10.1088/1361-6641/ab9477
- Griffin, P. H.; Oliver, R. A. *J. Phys. D: Appl. Phys.* **2020**, *53*, 383002. doi:10.1088/1361-6463/ab9570
- Ngo, T. H.; Gil, B.; Shubina, T. V.; Damilano, B.; Vezeian, S.; Valvin, P.; Massies, J. *Sci. Rep.* **2018**, *8*, 15767. doi:10.1038/s41598-018-34185-1
- Mohan, J. L.; Arachchige, I. U.; Brock, S. L. *Science* **2005**, *307*, 397–400. doi:10.1126/science.1104226
- Irmer, G.; Monaico, E.; Tiginyanu, I. M.; Gärtner, G.; Ursaki, V. V.; Kolibaba, G. V.; Nedeoglo, D. D. *J. Phys. D: Appl. Phys.* **2009**, *42*, 045405. doi:10.1088/0022-3727/42/4/045405
- Wang, T.; Tian, B.; Han, B.; Ma, D.; Sun, M.; Hanif, F.; Xia, D.; Shang, J. *Energy Environ. Mater.* **2022**, *5*, 711–730. doi:10.1002/eem2.12229
- Mohd Kaus, N. H.; Rithwan, A. F.; Adnan, R.; Ibrahim, M. L.; Thongmee, S.; Mohd Yusoff, S. F. *Catalysts* **2021**, *11*, 302. doi:10.3390/catal11030302
- Tiginyanu, I.; Braniste, T.; Smazna, D.; Deng, M.; Schütt, F.; Schuchardt, A.; Stevens-Kalceff, M. A.; Raevschi, S.; Schürmann, U.; Kienle, L.; Pugno, N. M.; Mishra, Y. K.; Adelung, R. *Nano Energy* **2019**, *56*, 759–769. doi:10.1016/j.nanoen.2018.11.049
- Dragoman, M.; Braniste, T.; Iordanescu, S.; Aldrigo, M.; Raevschi, S.; Shree, S.; Adelung, R.; Tiginyanu, I. *Nanotechnology* **2019**, *30*, 34LT01. doi:10.1088/1361-6528/ab2023
- Braniste, T.; Zhukov, S.; Dragoman, M.; Alyabyeva, L.; Ciobanu, V.; Aldrigo, M.; Dragoman, D.; Iordanescu, S.; Shree, S.; Raevschi, S.; Adelung, R.; Gorshunov, B.; Tiginyanu, I. *Semicond. Sci. Technol.* **2019**, *34*, 12LT02. doi:10.1088/1361-6641/ab4e58
- Dragoman, M.; Ciobanu, V.; Shree, S.; Dragoman, D.; Braniste, T.; Raevschi, S.; Dinescu, A.; Sarua, A.; Mishra, Y. K.; Pugno, N.; Adelung, R.; Tiginyanu, I. *Phys. Status Solidi RRL* **2019**, *13*, 1900012. doi:10.1002/pssr.201900012
- Braniste, T.; Dragoman, M.; Zhukov, S.; Aldrigo, M.; Ciobanu, V.; Iordanescu, S.; Alyabyeva, L.; Fumagalli, F.; Ceccone, G.; Raevschi, S.; Schütt, F.; Adelung, R.; Colpo, P.; Gorshunov, B.; Tiginyanu, I. *Nanomaterials* **2020**, *10*, 1047. doi:10.3390/nano10061047
- Plesco, I.; Braniste, T.; Wolff, N.; Gorceac, L.; Duppel, V.; Cinic, B.; Mishra, K. Y.; Sarua, A.; Adelung, R.; Kienle, L.; Tiginyanu, I. *APL Mater.* **2020**, *8*, 061105. doi:10.1063/5.0010222
- Plesco, I.; Ciobanu, V.; Braniste, T.; Ursaki, V.; Rasch, F.; Sarua, A.; Raevschi, S.; Adelung, R.; Dutta, J.; Tiginyanu, I. *Materials* **2021**, *14*, 1985. doi:10.3390/ma14081985
- Ciobanu, V.; Ursaki, V. V.; Lehmann, S.; Braniste, T.; Raevschi, S.; Zalamai, V. V.; Monaico, E. V.; Colpo, P.; Nielsch, K.; Tiginyanu, I. M. *Crystals* **2022**, *12*, 1753. doi:10.3390/cryst12121753
- Ziegler, C.; Wolf, A.; Liu, W.; Herrmann, A.-K.; Gaponik, N.; Eychmüller, A. *Angew. Chem., Int. Ed.* **2017**, *56*, 13200–13221. doi:10.1002/anie.201611552
- Korhonen, J. T.; Hiekkataipale, P.; Malm, J.; Karppinen, M.; Ikkala, O.; Ras, R. H. A. *ACS Nano* **2011**, *5*, 1967–1974. doi:10.1021/nn200108s
- Mekonnen, B. T.; Ding, W.; Liu, H.; Guo, S.; Pang, X.; Ding, Z.; Seid, M. H. *J. Leather Sci. Eng.* **2021**, *3*, 25. doi:10.1186/s42825-021-00067-y
- Noman, M. T.; Amor, N.; Ali, A.; Petrik, S.; Coufal, R.; Adach, K.; Fijalkowski, M. *Gels* **2021**, *7*, 264. doi:10.3390/gels7040264
- Shah, N.; Rehan, T.; Li, X.; Tetik, H.; Yang, G.; Zhao, K.; Lin, D. *RSC Adv.* **2021**, *11*, 7187–7204. doi:10.1039/d0ra10275j
- Franco, P.; Cardea, S.; Taberner, A.; De Marco, I. *Molecules* **2021**, *26*, 4440. doi:10.3390/molecules26154440
- Romero-Montero, A.; Valencia-Bermúdez, J. L.; Rosas-Meléndez, S. A.; Núñez-Tapia, I.; Piña-Barba, M. C.; Leyva-Gómez, G.; Del Prado-Audelo, M. L. *Polymers (Basel, Switz.)* **2023**, *15*, 262. doi:10.3390/polym15020262
- Meti, P.; Mahadik, D. B.; Lee, K.-Y.; Wang, Q.; Kanamori, K.; Gong, Y.-D.; Park, H.-H. *Mater. Des.* **2022**, *222*, 111091. doi:10.1016/j.matdes.2022.111091
- Liu, Q.; Yan, K.; Chen, J.; Xia, M.; Li, M.; Liu, K.; Wang, D.; Wu, C.; Xie, Y. *Aggregate* **2021**, *2*, e30. doi:10.1002/agt2.30
- Mecklenburg, M.; Schuchardt, A.; Mishra, Y. K.; Kaps, S.; Adelung, R.; Lotnyk, A.; Kienle, L.; Schulte, K. *Adv. Mater. (Weinheim, Ger.)* **2012**, *24*, 3486–3490. doi:10.1002/adma.201200491
- Lin, M.-H.; Ho, C.-H. *ACS Omega* **2017**, *2*, 4514–4523. doi:10.1021/acsomega.7b00842
- Wei, Z.; Lu, Y.; Zhao, J.; Zhao, S.; Wang, R.; Fu, N.; Li, X.; Guan, L.; Teng, F. *ACS Omega* **2018**, *3*, 137–143. doi:10.1021/acsomega.7b01574
- McCarthy, G. J.; Welton, J. M. *Powder Diffr.* **1989**, *4*, 156–159. doi:10.1017/s0885715600016638
- Yoo, K. S.; Han, S. D.; Moon, H. G.; Yoon, S.-J.; Kang, C.-Y. *Sensors* **2015**, *15*, 15468–15477. doi:10.3390/s150715468
- Kim, J. H.; Rho, H.; Kim, J.; Choi, Y.-J.; Park, J.-G. *J. Raman Spectrosc.* **2012**, *43*, 906–910. doi:10.1002/jrs.3116
- Cheng, Y. C.; Jin, C. Q.; Gao, F.; Wu, X. L.; Zhong, W.; Li, S. H.; Chu, P. K. *J. Appl. Phys.* **2009**, *106*, 123505. doi:10.1063/1.3270401
- Saleh, M.; Lynn, K. G.; Jacobssohn, L. G.; McCloy, J. S. *J. Appl. Phys.* **2019**, *125*, 075702. doi:10.1063/1.5084738

36. Ursaki, V. V.; Tiginyanu, I. M.; Zalamai, V. V.; Rusu, E. V.; Emelchenko, G. A.; Masalov, V. M.; Samarov, E. N. *Phys. Rev. B* **2004**, *70*, 155204. doi:10.1103/physrevb.70.155204
37. Prasad, N.; Karthikeyan, B. *J. Phys. Chem. C* **2018**, *122*, 18117–18123. doi:10.1021/acs.jpcc.8b05164
38. Tiginyanu, I. M.; Ursaki, V. V.; Karavanskii, V. A.; Sokolov, V. N.; Raptis, Y. S.; Anastassakis, E. *Solid State Commun.* **1996**, *97*, 675–678. doi:10.1016/0038-1098(95)00677-x
39. Meyer, B. K.; Alves, H.; Hofmann, D. M.; Kriegseis, W.; Forster, D.; Bertram, F.; Christen, J.; Hoffmann, A.; Straßburg, M.; Dworzak, M.; Habocek, U.; Rodina, A. V. *Phys. Status Solidi B* **2004**, *241*, 231–260. doi:10.1002/pssb.200301962
40. Ursaki, V. V.; Tiginyanu, I. M.; Zalamai, V. V.; Masalov, V. M.; Samarov, E. N.; Emelchenko, G. A.; Briones, F. *Semicond. Sci. Technol.* **2004**, *19*, 851–854. doi:10.1088/0268-1242/19/7/012
41. Ursaki, V. V.; Tiginyanu, I. M.; Zalamai, V. V.; Masalov, V. M.; Samarov, E. N.; Emelchenko, G. A.; Briones, F. *J. Appl. Phys.* **2004**, *96*, 1001–1006. doi:10.1063/1.1762997
42. Chen, W.; Wang, Z.; Lin, Z.; Lin, L. *J. Appl. Phys.* **1997**, *82*, 3111–3115. doi:10.1063/1.366152
43. Qin, X.; Cui, L.; Shao, G. *J. Nanomater.* **2013**, 428419. doi:10.1155/2013/428419
44. Mahajan, J.; Jeevanandam, P. *ChemistrySelect* **2019**, *4*, 12580–12591. doi:10.1002/slct.201903544
45. Fu, Q.; Guo, L. *AIP Adv.* **2022**, *12*, 015201. doi:10.1063/5.0073968
46. Mishra, Y. K.; Kaps, S.; Schuchardt, A.; Paulowicz, I.; Jin, X.; Gedamu, D.; Freitag, S.; Claus, M.; Wille, S.; Kovalev, A.; Gorb, S. N.; Adlung, R. *Part. Part. Syst. Charact.* **2013**, *30*, 775–783. doi:10.1002/ppsc.201300197

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