RESEARCH ARTICLE

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Synthesis and Nanostructure Investigation of Hybrid β-Ga_2O_3/$ZnGa_2O_4$ Nanocomposite Networks with Narrow-Band Green Luminescence and High Initial Electrochemical Capacity

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The material design of functional "aero"-networks offers a facile approach to optical, catalytical, or and electrochemical applications based on multiscale morphologies, high large reactive area, and prominent material diversity. Here in this paper, the synthesis and structural characterization of a hybrid β-Ga_2O_3/$ZnGa_2O_4$ nanocomposite aero-network are presented. The nanocomposite networks are studied on multiscale with respect to their micro- and nanostructure by X-ray diffraction (XRD) and transmission electron microscopy (TEM) and are characterized for their photoluminescent response to UV light excitation and their electrochemical performance with Li-ion conversion reaction. The structural investigations reveal the simultaneous transformation of the precursor aero-GaN(ZnO) network into hollow architectures composed of β-Ga_2O_3 and $ZnGa_2O_4$ nanocrystals with a phase ratio of ≈1:2. The photoluminescence of hybrid aero-β-Ga_2O_3/$ZnGa_2O_4$ nanocomposite networks demonstrates narrow band ($\lambda_{em} = 504$ nm) green light emission of $ZnGa_2O_4$ under UV light excitation ($\lambda_{ex} = 300$ nm). The evaluation of the metal-oxide network performance for electrochemical application for Li-ion batteries shows high initial capacities of ≈714 mAh g^{-1} at 100 mA g^{-1} paired with exceptional rate performance even at high current densities of 4 A g^{-1} with 347 mAh g^{-1}. This study provides is an exciting showcase example of novel networked materials and demonstrates the opportunities of tailored micro-/nanostructures for diverse applications a diversity of possible applications.

1. Introduction

In the past, significant research effort has been devoted to the design, fabrication, and characterization of engineered hollow nanomaterial structures to examine new functionalities based on their high-surface area.[1–3] Such hollow micro- and nanostructures introduce well-defined geometrical boundaries and meso- to nanoscale open volumes to allow for hierarchical material architectures with increasing compositional and morphological design complexity, especially in the field of metal oxides.[4,5] Their structural features, such as a low density and high surface to volume ratio, as well as permeable and porous shells, promote many unique physiochemical properties advertising complex hollow nanostructures for energy-related applications including storage and conversion,[6–9] catalysis,[10,11] gas sensing[12,13] or biomedical applications.[14] Among this class of hollow material structures, highly porous and ultra-lightweight 3D networks

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offer outstanding high surface to volume ratios and design flexibility for diverse functionalities.[15–19]

In this respect, interpenetrating sacrificial tetrapodal ZnO (T-ZnO) networks provide a rigid framework encouraging the design of hollow-tube “aero”-networks with tailored porosities of 50–94% and variable densities of $< 2–5$ mg cm^{-3} offering high functionality and functionalization capabilities. The introduced template approach successfully interconnects nanoscopic physical phenomena of microscale building units to the macroscale, which is required for many applications. The high diversity of this approach opens up a vast exploration space in which manifold functional aero-materials based, for example, on carbon species, metal nitrides or glass and polymers are under investigation. Up to date, numerous reports include aero-networks based on carbon species, for example, aero-graphite[20] and aero-graphene[18,21] nitride materials such as aero-GaN(ZnO)[22,23] and aero-BN[24] and many others including aero-Si,[25] aero-ZnS[26] and aero-Ga_2O_3.[27] Further, their modifications by functionalization with metallic nanoparticles during and after the synthesis have been demonstrated to improve the catalytic performance.[28,29] A wide range of possible applications becomes possible from microfluidics and pneumatic systems[18] to optical light diffusion[24] or photocatalysis[28,29] and can be extended to bio-scaffolds and hydrogel templates as well as supercapacitor structures.[30] This heterogeneity in the material selection and associated properties is driving fundamental research to identify fabrication routes and new applications of new ultralight weight and porous aero-networks.

In this work, a gallium oxide based aero-network structure containing the spinel-type phase zinc gallate ($ZnGa_2O_4$) as a majority component is developed based on the simple high-temperature oxidation of aero-GaN(ZnO).[23] Like β-Ga_2O_3, $ZnGa_2O_4$ belongs to the group of ultra-wide bandgap oxide semiconductors exhibiting a bandgap of 4.6–5.2 eV, paired with high chemical and thermal stability.[31–33] Therefore gallium oxide phases, especially $ZnGa_2O_4$, are investigated for their photocatalytic applications or as gas sensors.[34–36] For in-depth information on $ZnGa_2O_4$, the reader is referred to a review by Chen et al. highlighting all aspects from synthesis to applications.[37]

$ZnGa_2O_4$ crystallizes in the normal spinel-type structure ($Fd\bar{3}m$), in which octahedral sites are occupied by Ga, forming a network of edge-sharing GaO_6 octahedra, like in β-Ga_2O_3, and tetrahedral sites occupied by Zn. Due to their intrinsic band structure, phase pure $ZnGa_2O_4$ nanoparticle systems have been studied as platform for optoelectronic applications showing prominent phosphorescence of blue emission under ultraviolet (UV, $\lambda = 254$ nm) light excitation.[33] The emission spectrum can be tailored by introducing dopants on the tetrahedral sites of the host-lattice with rare earth[38] metal or Mn^{2+}, or Cr^{3+} ions[39] to achieve green or red emission, respectively. The morphology of the micro-/nanostructures is demonstrated to impact the device performance as well, as hollow architectures improve the photoluminescent/photocatalytic properties due to enhanced scattering and reflection of incident light, thereby increasing light harvesting efficiency.[40–43] With respect to energy applications, $ZnGa_2O_4$-based nanoparticles have also been characterized regarding their electrochemical performance for Li-ion batteries.[44,45] Using the here described networked material based on interconnected hollow metal oxide microstructures, an increase in the volumetric loading capacity of Li-ions and improvement of its cyclic stability by the reduction of diffusion pathways could potentially be facilitated.[8]

This work focuses on the investigation of the solid-state transformation reaction of aero-GaN(ZnO) networks into gallium oxide-based aero-Ga_2O_3/$ZnGa_2O_4$ networks and explores their photoluminescent and electrochemical performance. X-ray powder diffraction (XRPD) combined with Rietveld refinements, in situ XRPD heating experiments, and TEM investigations were carried out on selected samples of hybrid gallium oxide nanostructures composed of β-Ga_2O_3 and $ZnGa_2O_4$ phases. The growth of a $ZnGa_2O_4$ phase is a feature of the epitaxially and chemically stabilized thin layer of ZnO(-rich) phase on the interior wall of aero-GaN(ZnO) structures. The annealing experiments further demonstrate the possibility to tune the nanocrystalline structure by the choice of annealing temperature. Studies of the network's optical luminescence under UV light excitation demonstrate a transition from broadband visible light emission observed for aero-GaN(ZnO) toward narrow green emission bands centered around 504 nm for the hybrid aero-Ga_2O_3/$ZnGa_2O_4$ nanocomposite showing potential for application as high-temperature stable green phosphor. The electrochemical performance during cyclic voltammetry (CV) was tested and showed high initial capacities of ≈714 mAh g^{-1} at 100 mA g^{-1} and exceptional rate performance at high current densities of 4 A g^{-1} with 347 mAh g^{-1}, which is partially explained by the enhanced diffusion kinetics with highly accessible surface regions well connected in the 3D-structured network morphology with respect to nanoparticle agglomerates.

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