New insights into the formation of multi-core–shell mesoporous SnO$_2$@SnS$_2$ nanostructures

Kinga Michalec, Anna Kusior, Andrzej Mikuła and Marta Radecka

Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Krakow, Poland

ABSTRACT
SnO$_2$@SnS$_2$ multi-core–shell heterostructures were synthesised via chemical conversion of mesoporous raspberry-like SnO$_2$ nanocrystals. In the syntheses, different concentrations of a sulphide precursor (thioacetamide) were applied. The samples were analysed using scanning and high-resolution transmission electron microscopy, X-ray diffraction, Raman spectroscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. The results revealed the presence of surface defects (Sn$^{2+}$, oxygen vacancies) on the raspberry-like surface, which play a crucial role in the chemical conversion reaction. With an increasing amount of thioacetamide, additional redox reactions occurred in the system (Sn$^{4+}$/Sn$^{2+}$, S$^2$−/S$^0$). The highest precursor concentration led to the microstructural disintegration and phase composition change.

IMPACT STATEMENT
This paper demonstrates the role of defects on the formation of SnO$_2$@SnS$_2$ multi-core–shell heterostructures in mesoporous SnO$_2$ nanomaterials.

Introduction
In recent years, semiconducting metal sulphides have attracted much attention as promising candidates for renewable energy-related applications [1]. Due to the narrow bandgap, they can work as visible-light-driven photocatalysts for solar hydrogen generation, CO$_2$ conversion into fuels, wastewater treatment, and air purification [1–3]. Among these compounds, tin disulphide (SnS$_2$) is a non-toxic, relatively inexpensive, layered n-type semiconductor with a band gap of 2.0–2.35 eV, and a conduction band edge enabling H$_2$ generation [2,4]. However, this material is vulnerable to photocorrosion, which hinders its long-term efficiency [4,5]. To date, various strategies have been investigated to suppress photocorrosion [5]. The formation of heterostructures with a wide-bandgap semiconductor and morphology control represent some of them. The former allows increasing the photostability due to the separation of charge carriers. Depending on the interface structure between coupled materials, core–shell configurations can be distinguished [5,6]. In these systems, the core material is typically a dense single sphere or connection of several small spheres. However, it can also possess 1D, 2D, or 3D morphology. Likewise, there are also different types of shell materials (i.e. continuous and discontinuous, porous and dense, and possessing various shapes) [7]. Herein, we demonstrate the formation of uncommon multi-core–shell heterostructures obtained via chemical conversion of SnO$_2$-based mesoporous hollow-sphere core material. In the literature, numerous synthetic routes of mesoporous SnO$_2$ using various structure-directing agents have been proposed [8–11]. The synthesis of
raspberry-like SnO2 hollow spheres for sensing applications was reported by Zhao et al. [11]. This mesoporous morphology of hollow nanospheres may also be advantageous for photocatalytic processes due to enhanced light harvesting and an increased number of active sites for surface redox reactions [12]. The combination of morphology design and SnO2@SnS2 type-II heterojunction may result in obtaining materials with enhanced photoactivity and photostability [2–5]. To obtain SnO2/SnS2 heterostructures, various approaches have been analysed. Overall, two main strategies can be distinguished. The first one is SnS2 oxidation, which can be conducted using heat treatment [4], ball-milling in the air [13], and hydrothermal route via self-hydrolysis [14], or with the addition of substances such as H2O2 [2], and ascorbic acid in the presence of HCO3− ions [15]. The second strategy is SnO2 conversion, which can be performed via solid-state reaction or hydrothermally using a sulphide precursor such as thioacetamide (TAA), thiourea, or Na2S [3,10,16]. Herein, we applied a hydrothermal SnO2-conversion approach using TAA as an SnS2 precursor. We aimed to synthesise mesoporous SnO2@SnS2 heterostructures composed of multi-core–shell particles.

To the best of our knowledge, this is the first time that a formation mechanism of such structures has been proposed. Our motivation for selecting the SnO2-conversion strategy was to utilise the SnO2 raspberry-like hollow spheres as a substrate stabilising SnS2. This well-defined morphology offers numerous active centres for adsorption/redox reactions, enhanced light harvesting, and the coverage of SnO2 with visible-light-driven SnS2. The proposed multi-core–shell SnO2@SnS2 combining the advantages of a mesoporous hollow-sphere morphology and type-II heterojunction, may be promising candidates for solar energy-related applications, such as hydrogen generation in photoelectrochemical cells, carbon dioxide conversion into fuels, and air/water purification. Moreover, they may also be applied as sensing materials in electrochemical and resistive-type sensors.

Materials and methods

SnO2@SnS2 multi-core–shell mesoporous heterostructures were prepared via chemical conversion of SnO2 raspberry-like hollow spheres (RS). In the syntheses, three different concentrations of the sulphide precursor (thioacetamide, TAA) were applied. Depending on the molar ratio of TAA to RS, the samples were labelled RSS-1:2, RSS-1:1, and RSS-2:1. The obtained materials were characterised using scanning and high-resolution transmission electron microscopy (SEM, HRTEM), X-ray diffraction (XRD), Raman spectroscopy, BET/BJH analysis, energy dispersive spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and UV-Vis diffuse reflectance spectroscopy (DRS). The details are described in the Supplemental Material.

Results and discussion

The microstructural analysis was performed using SEM and TEM (Figure 1). SEM micrographs indicate that the RS sample consists of well-dispersed spherical nanoparticles with a diameter of about 78 nm. TEM analysis, in turn, revealed that RS are hollow-sphere structures. These nanospheres are composed of 12 nm elements that form a 0D–0D raspberry-like shape. In the case of SnO2@SnS2 hybrid materials, the core morphology is preserved in RSS-1:2 and RSS-1:1 samples. The latter is characterised by a slightly larger particle size than RSS-1:2 (87 and 79 nm, respectively). This may indicate that the sulphide layer is thicker for RSS-1:1. In the case of RSS-2:1, SEM images suggest that the raspberry-like core is fully covered with the shell material, forming a flower-like structure of about 167 nm in size. Surprisingly, TEM examination revealed that the core is completely disintegrated. It turned out that the sample is composed of hexagon-like plates with smaller elements randomly distributed on their surface.

The TEM images also suggest that the raspberry-like hollow spheres (RS, RSS-1:2, RSS-1:1) are mesoporous structures. To confirm this assumption, BET/BJH analysis was performed. The nitrogen adsorption−desorption isotherms (Figure S1), pore size distribution (Figure S2), calculated surface and pore parameters (Table S1), and the interpretation are given in the Supplemental Material.

Figure 2(a) presents the XRD patterns recorded for the obtained samples. For RS, all diffraction peaks can be assigned to tetragonal cassiterite SnO2 (PDF no. 98-016-9033). In the case of RSS-1:2, additional characteristic X-ray reflections related to (001), (101), and (102) facets of hexagonal SnS2 (PDF no. 98-065-9217) also appeared. Rietveld quantitative analysis revealed that the sample contains 97.4% of SnO2 and 2.6% of SnS2. With an increasing amount of TAA used in the synthesis, the intensity of the (001) diffraction peak from hexagonal SnS2 enhances continuously, and other characteristic peaks from this phase appear. This confirms the increasing SnS2 content from RSS-1:2 to RSS-2:1. The diffraction patterns of RSS-1:1 and RSS-2:1 also revealed the presence of SnS2 with two distinct preferred orientation directions ((001) and (110), respectively). The former contains 8.0 and 3.6% of differently oriented SnS2 phases (11.6% in total), and the latter – 19.0 and 13.9% (32.9% in total), respectively. In the case of RSS-2:1, diffraction peaks assigned to sulphur (PDF no. 00-013-0141) and...
Figure 1. (a-d) SEM and (e-h) TEM images of the obtained samples: (a, e) RS, (b, f) RSS-1:2, (c, g) RSS-1:1, and (d, h) RSS-2:1.

Figure 2. (a) XRD patterns and (b, c) Raman spectra of the analysed samples.

tin oxide sulphate Sn$_2$OSO$_4$ (PDF no. 98-003-5101) were also detected.

To determine the structural changes of the raspberry-like SnO$_2$ and its heterostructures, Raman spectroscopy was applied (Figure 2(b,c)). This technique allows the analysis of the materials' vibrational modes. However, in the case of SnO$_2$, it can be used to designate the presence of lattice defects and disclose the surface-related ones. In nature, bulk SnO$_2$ exhibits three main vibrational modes: $E_g$ (474 cm$^{-1}$), $A_1g$ (627 cm$^{-1}$), and $B_2g$ (768 cm$^{-1}$) [17]. With an increased surface area, an additional Raman band may appear in the range of 542–575 cm$^{-1}$ [17,18] assigned to the presence of surface-related defects (oxygen vacancies). The second
characteristic band may appear at about 693 cm$^{-1}$ and is associated with the occurrence of the local lattice disorder [17,18]. All five vibrational modes can be detected for RS (Figure 2(c)). The mesoporous structure of RS characterises a large surface area. Moreover, the raspberry-like shape comprises 0D elements of about 12 nm in diameter. These two factors may affect the formation of surface and lattice defects, which act as high-energy active centres. During the synthesis of RSS, the ion exchange mechanism starts after the adsorption of $S_2^{2-}$ ions on the selenium. Therefore, the intensity of the defect-related bands decreases (RSS-1:2). For RSS-1:1 and RSS-2:1, the band at 317 cm$^{-1}$ assigned to SnS$_2$ appeared (Figure 2(b)). It is worth noting that for RSS-1:1, the intensity of the defect-related band at 565 cm$^{-1}$ increased (compared to RSS-1:2). This behaviour may be attributed to the growth of SnS$_2$ in two distinct preferred orientation directions or/and weakening the bonds that connect the individual elements forming a raspberry-like structure, as also evidenced by the shift of the aforementioned band toward higher wavenumbers. This bond-weakening results in complete structural disintegration of RSS-2:1, which is also related to the presence of accessible surface area.

More detailed microstructural and structural studies were performed using high-resolution transmission electron microscopy (HRTEM) and a PDF database. Figure 3(a, b) presents HRTEM images of RS. The observed lattice fringes of about 3.35 Å (marked in white) can be attributed to the (110) crystal facet of tetragonal SnO$_2$, which is consistent with the XRD results. Differently oriented (110) facets come from smaller elements that form hollow-sphere structures. Moreover, two additional lattice spacings of about 3.45 and 2.72 Å (marked in blue) can be observed. These lattice spacings may correspond to the (0–11) and (030) facets of mixed-valence anorthic Sn$_2$O$_3$, or the (−120) and (210) ones of anorthic Sn$_3$O$_4$, respectively. The amount of these intermediate phases in the samples is below the detection limit of XRD. Thus, the HRTEM results confirm the presence of defects (Sn$^{2+}$) on the RS surface. Figure 3(c, d) presents HRTEM images of RSS-1:1. For this sample, the d-spacing values that correspond to SnO$_2$ and intermediate tin oxide phases can also be observed. Moreover, HRTEM examination confirms the presence of 5.88 and 3.17 Å lattice fringes (marked in yellow) that can be ascribed to (001) and (100) facets of hexagonal SnS$_2$, respectively. The lattice spacing of about 3.32 Å (marked in orange) may correspond to (222) facet of monoclinic sulphur, which presence in the case of this sample was also not detected using XRD analysis. During the synthesis, the $S^{2-}$ ions may be oxidised to $S^0$ due to the reduction of Sn$^{4+}$ to Sn$^{2+}$ ions on the raspberry-like surface.

The distribution of chemical elements in the samples was analysed using energy-dispersive X-ray (EDX) mapping (Figure 4(a,b)). The results reveal that tin, oxygen, and sulphur are homogeneously distributed in the raspberry-like SnO$_2$/SnS$_2$ heterostructures (RSS-1:2, RSS-1:1). The surface chemistry of the selected elements and surface defects were studied by XPS. Figure 4(c-e) presents the Sn 3$d_{5/2}$, S 2$p$, and O 1$s$ high-resolution spectra. The peak of Sn 3$d_{5/2}$ exhibits two components at 486.5 and 484.8 eV that are assigned to Sn$^{4+}$ and Sn$^{2+}$, respectively. For the RS, RSS-1:2, and RSS-1:1 samples, the Sn$^{2+}$ contribution is insignificant and amounts to about 1.2–1.9%. Starkly different results were obtained for the sample synthesised using the highest molar ratio.
of TAA to SnO₂ (RSS-2:1), for which the Sn²⁺ contribution is close to 22%. The higher amount of Sn²⁺ is related to the presence of Sn₂OSO₄ phase. For RSS-1:2, the S 2p peak is fitted by two components at 162.58 and 161.38 eV, which are ascribed to S²⁻ in SnS₂. In the case of RSS-1:1 and RSS-2:1, two more components with higher binding energy corresponding to elemental sulphur (S⁰) are fitted. For the O 1s spectra, the XPS peak is deconvoluted into two components. The lower-energy component is related to the lattice oxygen in tin dioxide (530.3 eV), while the higher-energy one is associated with surface defects. According to the literature reports [19],

**Figure 5.** Formation mechanism of SnO₂@SnS₂ multi-core-shell mesoporous heterostructures.
this binding energy close to 531.35–531.75 eV can be attributed to oxygen vacancies in the oxide lattice. Based on the analysis of the area ratio of S, Sn, and O species from the fitted components, the fraction of Sn$^{2+}$, S$^0$, and surface defects is the highest for RSS-2:1. The XPS results confirm the presence of Sn$^{2+}$, S$^0$ and oxygen vacancies that were detected by Raman spectroscopy and HRTEM (Sn$^{2+}$, S$^0$).

The UV-Vis DRS measurements were performed to study the optical properties of the materials, as they are potential candidates for photocatalysts (Figure S3). The results are described in the Supplemental Material.

Based on the obtained results, the growth mechanism of multi-core–shell SnO$_2$@SnS$_2$ heterostructures can be proposed (Figure 5). The surface of mesoporous raspberry-like SnO$_2$ is characterised by the presence of defects, such as Sn$^{2+}$ cations and oxygen vacancies. These defects play a crucial role as high-energy active sites in the chemical conversion process. In aqueous solutions, TAA undergoes hydrolysis (CH$_3$CSNH$_2$ ↔ CH$_3$CONH$_2$ $\rightarrow$ H$_2$S). The released S$^{2-}$ ions adsorb on the defective surface centres of RS. Thereafter, the exchange of ions occurs. RSS-1:2 contains 2.6% of SnS$_2$. As the concentration of TAA increases, the SnS$_2$ content in the samples is higher. In the case of RSS-1:1, HRTEM and XPS measurements also revealed the presence of elemental sulphur. For RSS-2:1, an increased amount of S$^0$ and Sn$^{2+}$ was detected. This may indicate that with an increasing amount of TAA, Sn$^{4+}$ cations are reduced to Sn$^{2+}$, while S$^{2-}$ ions are oxidised to S$^0$. For RSS-2:1, some elemental sulphur was further oxidised to S$^{6+}$ in Sn$_2$O$_5$SO$_4$. Moreover, the growth of two distinctly oriented SnS$_2$ phases and bond-weakening between the individual elements forming mesoporous SnO$_2$ result in the complete disintegration of the raspberry-like shape. In this sample, SnS$_2$ exhibits the morphology of hexagon-like layers surrounded by smaller SnO$_2$ crystals.

Conclusions

The multi-core–shell structure of SnO$_2$@SnS$_2$ is determined by the defective surface of the mesoporous core SnO$_2$ materials, which comprise very small (12 nm) individual elements that form the raspberry-like shape. The RSS-1:2 and RSS-1:1 samples (with the SnS$_2$ content of 2.6% and 11.6%, respectively) exhibit multi-core–shell structure, while the raspberry-like shape of RSS-2:1 (32.9% of SnS$_2$) was completely disintegrated. In addition to the ion exchange, the reduction of Sn$^{4+}$ cations and the oxidation of S$^{2-}$ anions occur during the chemical conversion of SnO$_2$ to SnS$_2$. The higher the sulphide precursor (TAA) concentration used in the synthesis, the increased amount of Sn$^{2+}$ and S$^0$ was detected in the samples. The examination of (micro)structural, surface, and optical properties revealed that the proposed multi-core–shell SnO$_2$@SnS$_2$ are promising candidates for visible-light-driven photocatalysts in various devices, adsorbents and sensing materials.

Disclosure statement

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ORCID

Kinga Michalec http://orcid.org/0000-0002-1654-1800
Anna Kasior http://orcid.org/0000-0002-1730-7610
Andrzej Mikula http://orcid.org/0000-0002-8067-996X
Marta Radecka http://orcid.org/0000-0001-7912-6340

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