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Microwave-Assisted Synthesis of Perovskite SrSnO₃ Nanocrystals in Ionic Liquids for Photocatalytic Applications

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Supporting Information

ABSTRACT: Nanosized SrSnO₃ photocatalysts have been successfully synthesized by microwave synthesis in various ionic liquids (ILs) followed by a heat treatment process to optimize the materials' crystallinity. The influence of the ILs with various cations such as 1-butyl-3-methylimidazolium ($[C_4mim]^+$), 6-bis(3-methylimidazolium-1-yl)hexane ($[C_6(mim)_2]^{2+}$), butyl-pyridinium ($[C_4Py]^+$), and tetradecyltrihexylphosphonium ($[P_{66614}]^+$) and bis(trifluoromethanesulfonyl)amide ($[Tf_2N]^-$) as the anion on the structure, crystallization, and morphology of the products was investigated. The samples were characterized by X-ray diffraction (XRD), thermogravimetry (TG), scanning electron microscopy (SEM), surface area analysis by gas adsorption, X-ray photoelectron spectroscopy (XPS), diffuse reflectance UV-vis spectroscopy, and Raman and IR spectroscopy all samples



crystallized phase-pure in the orthorhombic GdFeO₃ perovskite structure type. SEM reveals that, on the basis of the IL, the obtained SrSnO₃ nanoparticles exhibit different morphologies and sizes. Rod-shaped particles are formed in $[C_4mim][Tf_2N]$, $[C_6(mim)_2][Tf_2N]_2$, and $[P_{66614}][Tf_2N]$. However, the particle dimensions and size distribution vary depending on the IL and range from quite thin and long needlelike particles with a narrow size distribution obtained in $[P_{66614}][Tf_2N]$ to relatively larger particles with a broader size distribution obtained in $[C_6(mim)_2][Tf_2N]_2$. In contrast, in $[C_4Py][Tf_2N]$ nanospheres with a diameter of about 50 nm form. For these particles the highest photocatalytic activity was observed. Our investigations indicate that the improved photocatalytic activity of this material results from the synergistic effect of the relatively large surface area associated with nanosize and an appropriate energy band structure.

■ INTRODUCTION

Strontium stannate, $SrSnO_3$, adopts the orthorhombic $GdFeO_3$ -type perovskite structure under ambient conditions and undergoes structural transitions to the archetypal cubic perovskite structure at elevated temperatures (1295 K).¹ $SrSnO_3$ has gained increasing academic and technological interest in recent years due to its electronic structure and associated photophysical properties. Because of its properties $SrSnO_3$ is of interest for a wide range of applications for example as a dielectric material for use in capacitors with small temperature coefficient of capacitance, single-flux quantum circuits, lithium ion batteries, high-temperature humidity sensors, and many others, the most important probably being photocatalysis.² There is a high and tremendously growing demand for primary fuels. The worldwide increasing primary fuel consumption has led to continuous worsening of environmental pollution. For that reason, the replacement of nonsustainable fossil fuels with sustainable, safe, and clean fuel supplies and pollution-free technologies is desirable.³ Producing hydrogen by photocatalytic water splitting represents one of the most promising technologies among the wide variety of green and renewable energy projects.⁴ Water splitting using semiconductor photoelectrodes and photocatalysts has been extensively studied since the Honda–Fujishima effect, the splitting of water into H₂ and O₂, was reported in 1972 using a rutile TiO₂ semiconductor anode coupled with a platinum dark cathode.⁶ Suitable photocatalysts for water splitting have to meet several requirements regarding the semiconducting and electrochemical properties to achieve overall water splitting.

Received: February 10, 2017 Published: June 5, 2017 First of all, the photocatalyst has to possess a suitable band gap. Moreover, it has to be stable against photocorrosion in the aqueous environments of the reaction. The backward reaction has to be suppressed. Once the photoexcited electrons are formed, the photocatalytic system has to be able to separate them from the holes. Furthermore, energy losses associated with charge transport and electron-hole recombination have to be minimized and proper electron transfer from the photocatalyst surface to the water molecules has to be achieved. In addition, simplicity and reproducibility in the preparation and low preparation cost are needed.^{5,6} It has been shown that SrSnO₃ is well-suited to split water into hydrogen and oxygen with UV light, because of its proper valence (2.69 eV) and conduction (-1.37 eV) band edge positions.³⁷ However, a reliable synthetic route for the manufacturing of photocatalytically active SrSnO₃ nanomaterial is needed.

Microwave heating is a fast and environmentally friendly method for chemical synthesis. It is emerging as an efficient technology for the preparation of oxide materials, replacing other synthetic methods such as the conventional hightemperature solid-state reaction of SrCO₃ and SnO₂ requiring temperatures of 1000–1200 °C,⁷ solvothermal, combustion,⁸ sol-gel, coprecipitation methods using water as the solvent, polymeric precursor methods,¹⁰ and pyrolytic techniques. These latter methods have one or more drawbacks such as requiring relatively long reaction times, high pressures and/or high temperatures, toxic and expensive raw materials including volatile compounds as starting materials, and capping agents which also can adversely affect the photocatalytic performance. In contrast to conventional methods, microwave heating shows the advantage of not only being more cost-effective and shortening the reaction time but also increasing the yield of product¹¹ and leading to products with small particle sizes and high surface area, especially in combination with ionic liquids.

Ionic liquids (ILs) are commonly defined as salts with melting points below 100 °C.12 They headed a new green chemical revolution, due to their interesting and unique physical-chemical properties. For example, ILs can be designed to have a negligible volatility, low toxicity, high electrochemical and thermal stability, and high ionic conductivity.¹³ The physical and chemical properties of ILs can be influenced by their cationic and anionic moieties; for their tunable properties they are often addressed as designed liquids. The application of ILs as nonaqueous green solvents, reactants, and structuredirecting agents or stabilizing agents for preparing inorganic functional materials is a rather new development which has only emerged during the last years.¹⁴ The IL-assisted microwave method is considered to be an environmentally friendly synthetic method because ILs have been demonstrated to be an excellent medium for efficiently absorbing microwave radiation. This is because they are composed of large ions with high polarizability and conductivity, leading to fast, effective heating.^{15,16} This results in a high nuclei formation being favorable for nanoparticle formation. Due to the short heating times, particle growth is not supported as with conventional synthetic methods.

To the best of our knowledge, there have been no reports on the preparation of $SrSnO_3$ using the microwave-assisted ionic liquid method despite the special benefits this synthetic route may offer for the preparation of high-performance photocatalytically active materials. For that reason, we have investigated the preparation of $SrSnO_3$ by a microwave-assisted ionic liquid method in which the ionic liquid acts as both solvent and template. The effect of the variation of the ionic liquid on the shape, crystallinity, energy band structure, and catalytic activity toward the photohydroxylation of terephthalic acid and photogeneration of H_2 was studied in detail.

EXPERIMENTAL SECTION

Materials. Chemicals were purchased from Iolitec (lithium bis(trifluoromethansulfonyl)amide 99%, butylpyridinium bis(trifluoromethansulfonyl)amide 99%), Sigma-Aldrich (tin(VI) chloride pentahydrate 98%, 1-methylimidazole 99%, ethanol (p.a.), 1-chlorobutane 99%, 1,6-dichlorohexane 98%), Fisher Scientific (sodium hydroxide 98%), J. T. Baker (acetonitrile 99.5%, ethyl acetate 99%), Alfa Aesar (strontium acetate hydrate 98%, terephthalic acid 98%), Cytec Canda Inc. (tetradecyltrihexylphosphonium chloride). All commercial reagents were used directly without further purification. The ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide $[C_4mim][Tf_2N]$, tetradecyltrihexylphosphonium bis(trifluoromethanesulfonyl)amide $[P_{66614}][Tf_2N]$, and 1,6-bis(3-methylimidazolium-1-yl)hexanebis(trifluoromethylsulfonyl)-imide $[C_6(mim)_2][NTf_2]_2$ were prepared according to modified literature procedures.^{17,18}

Synthesis of SrSn(OH)₃, and SrSnO₃. For the synthesis of SrSn(OH)₆ nanoparticles a stoichiometric amount of Sr(CH₃COO)₂. xH₂O (0.138 g) and SnCl₄ × 5 H₂O (0.08 g) and 0.15 g of finely ground NaOH powder were added to a mixture of 1 mL of deionized water and 2 mL of the respective ionic liquids [C₄mim][Tf₂N], [C₆(mim)₂][Tf₂N]₂, [C₄Py][Tf₂N], and [P₆₆₆₁₄][Tf₂N]). The reaction mixture was stirred vigorously for 30 min and then irradiated in a single-mode laboratory microwave operating at 2455 MHz (CEM Discover, Kamp-Lintfort, Germany) in a 10 mL glass vessel equipped with a Teflon septum for 10 min at 80 °C. The product was separated by centrifugation, washed thoroughly with ethanol and distilled water, and dried overnight in air at 80 °C. To obtain SrSnO₃, the dried asprepared SrSn(OH)₆ was calcined at 700 °C in air for 3 h.

Characterization. *Powder Diffraction.* Powder X-ray diffraction (XRD) measurements were carried out on a PANalytical powder diffractometer with a Xcelerator Detector employing Cu K α radiation ($\lambda = 0.15406$ nm). The structure parameters were determined by Rietveld refinement with the program suite Fullprof using a pseudo-Voigt peak shape function.¹⁹

Scanning Electron Microscopy (SEM). Scanning electron microscopy measurements were performed with a high-resolution SEM (Zeiss, LEO 1530 Gemini) with a field emission gun (FEG) at an acceleration voltage of $U_{\rm acc} = 0.2-30$ kV. For the SEM measurements the SrSnO₃ nanopowders were put on a carbon film and dried under vacuum for 20 min.

IR Spectroscopy. Attenuated total reflection (ATR) spectroscopy was carried out on an Alpha ATR spectrometer equipped with a diamond crystal (Bruker, Karslruhe, Germany). Solid samples were pressed on the crystal.

Raman Spectroscopy. Raman spectra were obtained at 150 mW on a Bruker IFS-FRA-106/s instrument at room temperature.

UV-vis Spectroscopy. UV-vis spectra were measured at room temperature on a Cary 5000 spectrometer (Varian, Palo Alto, US) in reflection mode.

Fluorescence Spectroscopy. Photoluminescence (PL) spectra were measured on a Horiba Jobin Yuon FL322 Fluorolog-3 spectrophotometer equipped with a xenon flash lamp. For the measurement, the filtered liquid samples (see below) were filled into a standard 10 mm quartz cuvette and positioned in the incoming beam in the sample chamber.

X-ray Photoelectron Spectroscopy. XPS measurements were done using a Physical Electronic 5500 multitechnique system with an Al K α source. The analysis spot size was 1 × 1 mm. Samples were mounted on double-sided Scotch tape. Charge correction was done by calibration to the carbon peak at 284.8 eV.

Gas Sorption. Nitrogen physisorption experiments were carried out on a modified Autosorb 1C setup (Quantachrome). The sample was thermally pretreated at 200 $^{\circ}$ C for 2 h in He. The physisorption measurement was performed at the boiling point of liquid N₂ (78 K). The surface area was calculated according to the BET (Brunauer–Emmett–Teller) equation. The pore size distribution was obtained applying the BJH (Barrett–Joyner–Halenda) method.

Photocatalytic Activity Test. Hydrogen Generation. Photocatalytic H₂ generation from methanolic solutions was carried out in a closed gas system using a double-walled inner irradiation-type quartz reactor, which contained a suspension of 500 mg of photocatalyst in 540 mL of water and 60 mL of methanol (0.83 g/L). For irradiation a 700 W Hg immersion lamp (set to 57% power = 400 W) was used. By actinometry a photon flux of about 6.4×10^{-5} mol of photons/s was determined. The evolution of hydrogen was detected online using a multichannel analyzer (Emerson) equipped with a detector for the determination of the concentration of hydrogen (paramagnetic detector). Argon was used as the carrier gas. The continuous gas flow (50 N mL/min) was controlled by a Brockhorst mass flow controller. All reactions were performed at 286 K. The whole system was flushed with nitrogen at 100 N mL/min to remove any trace of air prior to irradiation. For some samples, Rh as a cocatalyst (0.5 wt %) was deposited onto the photocatalyst via reductive photodeposition from a Na₃RhCl₆ solution.

Photohydroxylation of Terephthalic Acid (TA). The catalytic test was performed in a reactor which contained a suspension of 100 mg of photocatalyst in 100 mL of 0.01 M aqueous NaOH solution containing 3 mM terephthalic acid ($C_8H_6O_4$). The suspension was continuously stirred in the dark for 30 min to accomplish the adsorption/desorption equilibrium and then illuminated using a 150 W Xe arc lamp (Newport Oriel Instruments). The lamp was switched on 30 min prior to the illumination of the samples in order to stabilize the power of its emission at λ >320 nm (a FSQ-WG320 cutoff filter was used to eliminate spectral intensity below 320 nm). Every 30 min about 3 mL aliquots were sampled and filtered by nylon syringe filters (pore size 0.2 μ m) to remove the photocatalyst before analysis by fluorescence spectrometry (Horiba Jobin Yuon FL322 Fluorolog-3) at 426 nm corresponding to the fluorescence band of 2-hydroxyterephthalic acid (TAOH). Photogenerated holes can react with surfaceadsorbed water molecules, forming *OH radicals. The *OH radicals react with terephthalic acid to give 2-hydroxyterephthalic acid, which exhibits a typical fluorescence band at 426 nm upon excitation at 320 nm. Thus, an increase in intensity of the fluorescence signal with time can be directly linked to an increased amount of photogenerated *OH radicals, which possess a high oxidative power and are involved in the photocatalytic decomposition of organic compounds.²⁴

RESULTS AND DISCUSSION

To check the influence of the structure of ILs on the morphology and the crystallization of the SrSnO₃, four different ILs were investigated (Scheme 1). Bis(trifluorosulfonyl)amide, $[Tf_2N]^-$, was chosen as the IL anion, as it is weakly coordinating and our previous studies have shown that the anion in fact has little direct effect on particle formation and growth of nanooxides in comparison to the cation.²¹ As

Scheme 1. IL Cations Investigated in This Study



 $[Tf_2N]^-$ is well-known to be only a weakly coordinating anion and $[Tf_2N]^-$ -based ILs feature typically low viscosity, this ion appears to be the anion of choice for our investigations.²²

The cations were chosen for the following reasons: $[C_4mim]^+$ was chosen because imidazolium-based ionic liquids are among the most common and well-studied ILs. This is because this cation is well suited to support IL formation in its salts. With respect to its possible interactions that can influence nucleation and particle growth of materials obtained from an IL with this cation, the $[C_4mim]^+$ cation contains an aromatic core, which can participate in π interactions. It possesses a highly electron accepting region, which is likely responsible for the electrostatic attraction with polar moieties on the surface of particles.²³ In addition, the ring protons are fairly acidic, most recognizably the 2-H proton. This acidic hydrogen can act as a bridging species via hydrogen bonding. It is believed that both electrostatic and coordination effects of imidazolium cations contribute to nanoparticle stabilization in the IL.²⁴

The alkyl side chain has a pronounced effect on the size distribution and agglomeration of the nanoparticles. $[C_6(\min)_2]^{2+}$ is a dicationic ionic liquid based on two imidazolium cations connected by a long-linkage alkyl chain. Furthermore, it has two acidic 2-H protons, which increase its H-bonding capability and acidity in comparison with $[C_4\min]^+$. In contrast, $[C_4Py]^+$ is a pyridinium-based cation which does not possess any acidic protons like the imidazolium-based cations. However, the aromatic group is still present, whereas in the $[P_{66614}]^+$, a saturated quaternary phosphonium cation with long aliphatic side chains, neither an acidic proton nor an aromatic ring is present.

ILs based on these cations in combination with the bis(trifluoromethanesulfonyl)amide anion that offered the different interaction mechanisms discussed above were used as synthesis media for the conversion of strontium acetate hydrate with tin tetrachloride under microwave irradiation. XRD patterns for all products were measured to characterize the structure, phase purity, crystallite size, and strain. Figure S1 shows the XRD pattern of the as-prepared $SrSn(OH)_6$ in different ILs. For all samples, all of the diffraction peaks can be indexed to the hexagonal phase of $SrSn(OH)_6$ (PDF 9-86). Calcination of these samples at 700 °C for 3 h led to the formation of SrSnO₃ particles with an orthorhombic perovskite GdFeO₃ type structure in *Pnma* (Figure 1; for cell parameters see Table 1). After calcination no diffraction peaks from $SrSn(OH)_6$ or any intermediate phases can be found (Figure 1a). As shown in Table 1 for SrSnO₃, slight variations of the lattice parameters along with a change in cell volume depending on the IL used can be observed. Figure 1b illustrates the crystal structure of SrSnO3 on the basis of the parameters obtained from a Rietveld refinement of the material obtained from $[C_4 mim]$ [Tf₂N]. The orthorhombic SrSnO₃ adopts a pseudocubic perovskite structure, as the size of the Sr^{2+} ion is smaller than the cavity formed by the SnO_6 octahedra. An adjustment of the cavity size is achieved by a rotation of the SnO₆ octahedra, resulting in a reduction in symmetry of the ideal cubic perovskite structure.²⁵

Average crystallite sizes for each sample were calculated using the Debye–Scherrer formula from the fwhm values of the most intense diffraction peak (200) and are summarized in Table 2. As shown in Table 2, the crystal size of samples varies from 53.7 nm for the sample prepared in $[C_4\text{mim}][Tf_2N]$ to 40.1 nm for the sample prepared in $[C_4\text{Py}][Tf_2N]$.



Figure 1. XRD patterns of the as-prepared $SrSnO_3$ in different ionic liquids in comparison with the database pattern of $SrSnO_3$ (PDF 77-1798) (a) and representation of the $SrSnO_3$ crystal structure (b).

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sample	a (Å)	b (Å) ($b' = b/\sqrt{2}$ (Å))	c (Å)	a/b′	a/c	V (Å ³)
$S1/[C_4mim][Tf_2N]$	5.71561(6)	8.07762(6) (5.71174)	5.71702(6)	1.00068	0.99975	263.947 ± 0.045
$S2/[C_6(mim)_2][Tf_2N]_2$	5.71598(4)	8.07587(5) (5.71050)	5.72846(5)	1.00100	0.99782	264.435 ± 0.036
S3/[P ₆₆₆₁₄][Tf ₂ N]	5.71409(5)	8.07625(5) (5.71079)	5.71634(5)	1.00058	0.99961	263.800 ± 0.039
$S4/[C_4Py][Tf_2N]$	5.71566(6)	8.07808(6) (5.71207)	5.72382(6)	1.00063	0.99857	264.278 ± 0.043

Table 2. Estimated Crystal Size Using the Scherrer Equation, Crystallite Strain Using the W-H Equation, Band Gaps As Determined from UV–Vis Spectroscopic Data, and Band Edge Position

sample	crystallite size (nm)	crystallite strain ($\varepsilon_{ m str}$)	band gap (eV)	$E_{\rm c}({\rm NHE})~({\rm eV})$	$E_{\rm v}~({\rm eV})$
$S1/[C_4mim][Tf_2N]$	53.2 ± 1	0.0015	3.93 ± 0.02	-0.93 ± 0.04	$+3.0 \pm 0.04$
$S2/[C_6(mim)_2][Tf_2N]_2$	51.7 ± 1	0.0013	3.95 ± 0.02	-0.94 ± 0.02	$+3.01 \pm 0.04$
$S3/[P_{66614}][Tf_2N]$	51.6 ± 1	0.0013	3.99 ± 0.02	-0.96 ± 0.02	$+3.03 \pm 0.04$
$S4/[C_4Py][Tf_2N]$	40.1 ± 1	0.0018	3.90 ± 0.02	-0.91 ± 0.02	$+2.99 \pm 0.04$

The crystallite strain values of the SrSnO₃ samples were estimated by the Williamson–Hall (W-H) equation.²⁶ A plot of $B_{hkl} \cos \theta$ against 4 sin θ is shown in Figure 2. The strain ε was



Figure 2. Williamson–Hall plots of SrSnO₃ samples prepared in different ILs.

calculated from the slope of the linear fit as summarized in Table 2. The strain values are remarkably small in the SrSnO₃ samples in comparison to the value reported for the bulk material ($\varepsilon_{str} = 0.039$).²⁷ This phenomenon is well-known for ferroic materials and has been treated theoretically well for perovskite nanomaterials.²⁸⁻³⁰ The strain values for the samples prepared in [C₆(mim)₂][Tf₂N]₂ and [P₆₆₆₁₄][Tf₂N] are the same, while that for the sample prepared in $[C_4Py][Tf_2N]$ is the highest. The sample prepared in $[C_4Py][Tf_2N]$ also exhibits the smallest particle size. The particle strain is most likely caused by lattice defects such as point defects, distorted grain boundaries, dislocation, concentration gradients, and stacking faults. These lattice defects can act as traps for photoexcited electrons and holes, leading to a decrease in the efficiency of the photocatalyst. Therefore, the small values of strains suggest the presence of fewer lattice defects, which might lead to a decrease in the recombination of photogenerated charge carriers and thereby an increase in photocatalytic activity.

To characterize the components and purity of the $SrSnO_3$ prepared by using different ILs, EDS (energy dispersive X-ray spectroscopic) analysis was performed during the SEM measurement (Figure S3 in the Supporting Information). The EDS spectra show peaks related to strontium, tin, and oxygen.



Figure 3. IR (a) and Raman spectra (b) of $SrSnO_3$ prepared from $[C_4Py][Tf_2N]$ as a representative. For other spectra see the Supporting Information.

The observed carbon peak arises from the carbon film of the sample holder. No signals corresponding to elements from the ionic liquids or starting materials such as Na (from NaOH) or Cl (from $SnCl_4$) could be noticed.

The thermogravimetric (TGA) measurement in the range from room temperature to 1050 °C of the as-prepared SrSn(OH)₆ in [C₄mim][Tf₂N] is shown in Figure S4 in the Supporting Information. The major, rapid weight loss (experimental ~20%, calculated 22%) can be attributed to the dehydroxylation process of SrSn(OH)₆ and formation of SrSnO₃. No further notable weight loss could be observed in the TGA curve up to 700 °C, which showed that the precursor SrSn(OH)₆ had been converted completely into SrSnO₃.³¹ For the SrSn(OH)₆ samples obtained from the other ILs a similar thermal behavior was observed.

Figure 3a and Figure S5 in the Supporting Information show IR spectra of the prepared SrSnO3 samples. All samples show similar spectral features, the most characteristic feature being the high-intensity infrared absorption band at 644 cm⁻¹ which corresponds to the vibrations of the stannate group (SnO_3^{2-}) . Moreover, no bands from the precursor $SrSn(OH)_6$ or other impurities can be observed. Figure 3b shows the corresponding room-temperature Raman spectra of the various SrSnO₃ samples. According to factor group analysis 24 Raman-active modes with $\Gamma_{Raman} = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$ can be expected for orthorhombic SrSnO₃.³² They can be classified as follows: two symmetric and four antisymmetric octahedral stretching modes, four bending modes, and six rotational or tilt modes of the octahedra. The other eight modes are related to vibrational motions of strontium cations in the lattice of SrSnO₃. However, due to overlap and very low polarizabilties of some of the expected modes, not all of these modes can be observed. The spectra (Figure S6 in the Supporting Information) show nine bands in the frequency range 100-700 cm⁻¹. Three sharp bands are located at 146, 165, and 223 cm⁻¹; the others are fairly weak in intensity. However, the intensities of these bands for the samples prepared in $[C_4Py][Tf_2N]$, $[C_6(mim)_2]$ - $[Tf_2N]_2$, and $[C_4mim][Tf_2N]$ are relatively higher in comparison with that for the sample prepared using [P₆₆₆₁₄]-[Tf₂N]. The bands in the region 146-254 cm⁻¹ are due to A_g modes attributed to symmetrical vibrations of SnO₆ octahedra. Lee et al. attributed the higher intensity of the Raman bands for nanocrystalline SrSnO₃ prepared by a wet chemical reaction

compared to SrSnO₃ prepared by a solid-state reaction to a higher degree of structural order.³⁸ The bands at 223 cm⁻¹ are attributed to the scissor movement of Sn–O–Sn groups along the *c* axis. The band at 253 cm⁻¹ results from O–Sn–O bending motion within the *ab* plane and Sn–O–Sn scissoring perpendicular to the *c* axis. The band at 554 cm⁻¹ is associated with Sn–O stretching motions.^{33–35}

In addition, X-ray photoelectron spectroscopy (XPS) was used to check the elemental composition and chemical state of the SrSnO₃ samples. The XPS survey spectra of the SrSnO₃ samples are presented in Figure S7 in the Supporting Information, featuring the surface components of Sr, Sn, and O. The binding energies in the XPS spectra are calibrated against the C 1s signal (284.8 eV) from the sample holder. Detailed region scans of Sr 3d, Sn 3d, and O 1s for all samples can be found in Figure 4. The best fit of XPS spectra of Sr 3d in SrSnO₃ samples reveals that the obtained curve is a mixture of two overlapping peaks. These are assigned to Sr $3d_{5/2}$ at 132.6– 132.8 eV and Sr $3d_{3/2}$ at 134.3–134.5 eV with a peak separation of 1.7 eV. The XPS spectra of Sn 3d in SrSnO₃ samples show two peaks at 486-486.2 eV and at 494.5-494.7 eV with a peak separation of 8.5 eV. The peaks can be attributed to Sn $3d_{5/2}$ and Sn 3d_{3/2}, respectively. For the O 1s signal an asymmetric peak is observed that can be fitted into two peaks with binding energies of 529.5-529.7 and 531.2-531.5 eV. The peak at 529.5-529.7 eV can be attributed to O^{2-} lattice oxygen. The peaks at about 531.2-531.5 eV with slightly lower intensities are due to OH⁻ surface groups. These results are in good agreement with reported values for SrSnO3 samples prepared by a high-temperature solid-state reaction, as shown in Table 3_{1}^{36} and a wet-chemical reaction.³⁹ Furthermore, the XPS results verify the EDS and XRD data regarding the purity and composition of the samples, where no peaks for other elements from ionic liquids or impurities can be seen.

The influence of the structure of the ILs on the morphology of the calcined $SrSnO_3$ particles obtained from the as-prepared $SrSn(OH)_6$ in different ILs was investigated. Figure 5 shows representative SEM images of the $SrSnO_3$ samples. Figure 5(1) shows the morphology of the product derived from $[C_4mim]$ - $[Tf_2N]$, indicating that relatively homogeneous rodlike particles with an average diameter of 500 nm and length 5 μ m were obtained. The SEM image (Figure 5(2)) of $SrSnO_3$ grown from $[C_6(mim)_2][Tf_2N]_2$ reveals the formation of rods with a size



Figure 4. Narrow XPS scans of Sr 3d, Sn 3d, and O 1s regions for SrSnO₃.

distribution broader than that observed for those obtained from $[C_4mim][Tf_2N]$. Their length is several micrometers (2–10 μ m), and the width ranges from 500 to 1000 nm. When using $[P_{66614}][Tf_2N]$, these nanorods become more needlelike. In comparison to those obtained from $[C_4mim][Tf_2N]$ the particles are longer with an overage length of 10 μ m and a thickness of 30 nm, respectively. The size distribution is quite narrow. In contrast, when $[C_4Py][Tf_2N]$ is used, the asprepared sample is composed of nanospheres with a diameter

of about 50 nm. These results show that the structure of ILs plays a significant role in shaping the $SrSnO_3$ samples when all other reaction conditions are kept unchanged. Therefore, the formation of different morphologies using different ILs can be attributed to the different interactions between the $SrSn(OH)_6$ seed surfaces and the IL. However, it is not clear yet how exactly the IL interacts with the particle nuclei and what the morphology directing interactions are. Although a good number of reports on the morphology tuning of nanoparticles

Table 3. XPS Binding Energies ($\pm 0.1 \text{ eV}$) of Sn, O, and Sr in SrSnO₃ Samples

element	$\begin{array}{c} S1/\\ [C_4mim]\\ [Tf_2N]) \end{array}$	$\begin{array}{c} \text{S2/} \\ [C_6(\text{mim})_2] \\ [\text{Tf}_2\text{N}]_2 \end{array}$	$\begin{array}{c} S3/[P_{66614}] \\ [Tf_2N] \end{array}$	S4/ [C ₄ Py] [Tf ₂ N]	ref 36
Sn (3d _{5/2} ; 3d _{3/2})	486.2; 494.7	486; 494.5	486; 494.5	486; 494.5	485.9; 494,3
O (1s)	529.7; 531,5	529.7; 531.5	529.5;531.2	529.6; 531.5	529.4; 531.4
Sr (3d _{5/2} ; 3d _{3/2})	132.8; 134.5	132.8; 134.5	132.6; 134.3	132.8; 134.5	132.7; 134.4

with ILs exist, little is understood. It is generally accepted that both electrostatic and steric effects govern the particle formation.³⁷ In our case, the growth units of $SrSn(OH)_6$ range from Sr^{2+} cations and $Sn(OH)_6^{2-}$ anions to potentially polynuclear units while the ILs consist of bulky organic cations in combination with the weakly coordinating anion bis-(trifluoromethanesulfonyl)amide. On the basis of our experience the IL cation predominately influences the particle morphology. For that reason we had chosen ILs with cations that can, aside from electrostatic interactions, interact via hydrogen bonds, π interactions, or van der Waals forces. It seems that cation size and hydrogen-bonding ability are important factors that influence the particle morphology. If one compares the rod-shaped materials, from $[C_4 mim][Tf_2N]$ over $[C_6(mim)_2][Tf_2N]_2$ to $[P_{66614}][Tf_2N]$ the rods become thinner and longer. The cation hydrogen-bonding capability is decreasing as well as the cation size is increasing, leading to an overall decreased interaction capability of the IL. It appears that, if the cation is comparatively small but has no hydrogenbonding capabilities and can undergo electrostatic and π interactions, the morphology can be changed from rods to

spheres, as observed for the material obtained from $[C_4Py]-[Tf_2N]$.

Furthermore, the effect of the IL on the morphology and phase of SrSnO₃ has been investigated by preparing SrSnO₃ in demineralized water without IL while the other reaction parameters were kept the same. The SEM images of the product obtained are shown in Figure 6. They illustrate that the sample mostly contains agglomerated rod-shaped particles. Under these nonequilibrium growth conditions with no template or surfactant being added, the growth and shaping of the particles is predominantly controlled by the decrease in surface energy. Seemingly, the rodlike particles tend to selfassemble and to grow radically from the center to form brushlike particles. The associated XRD patterns and Rietveld refinement for this pattern (SI-8 in the Supporting Information) show that the sample crystallizes in the orthorhombic space group Pnma as is also the case for the samples obtained in ILs. This result demonstrates that the presence of IL avoids or minimizes agglomeration and plays an important role in controlling the particle morphology.

The optical absorption properties of SrSnO₃, prepared in different ILs, were measured by diffuse reflectance spectroscopy (DRS) (Figure 7a). The UV–vis spectra of the SrSnO₃ samples show that the absorption edges vary from 342 nm for the sample prepared in $[C_4Py][Tf_2N]$ to 348 nm for the sample prepared in $[P_{66614}][Tf_2N]$. This absorption edge can be attributed to the transition of electrons located in the valence band, which is predominately made up of O 2p states, into Sn Ss states of the conduction band under UV light irradiation.⁴⁵ The absorption edge values are estimated by the linear extrapolation of the steep part of the UV absorption toward the baseline (Figure 7a). The optical band gap (E_g) of the



Figure 5. SEM images of SrSnO₃ prepared in (1) $[C_4 mim][Tf_2N]$, (2) $[C_6(mim)_2][Tf_2N]_2$, (3) $[P_{66614}][Tf_2N]$, and (4) $[C_4 Py][Tf_2N]$.



Figure 6. SEM images of as-prepared SrSnO₃ in demineralized water without ILs.



Figure 7. (a) UV-vis absorption spectra. (b) $(\alpha h \nu)^2 - h \nu$ curves of SrSnO₃ prepared in different ILs.

samples can be calculated on the basis of the optical absorption spectra by using the equation (Tauc plot)

$$(\alpha h\nu)^n = B(h\nu - E_g)$$

where $h\nu$ is the photon energy, *A* is the absorbance, *B* is the related to the effective masses associated with the valence and conduction bands, and *n* is either n = 2 for an indirect allowed transition or n = 1/2 for the direct allowed transition. Plotting $(\alpha h\nu)^2$ versus $h\nu$ on the basis of the spectral response gives the extrapolated corresponding E_g values.^{2,38}

As shown in Figure 7b and Table 2, the band gap of $SrSnO_3$ prepared in different ILs ranges from 3.90 eV for the nanospheres obtained in $[C_4Py][Tf_2N]$ to 3.99 eV for the thin needles obtained in $[P_{66614}][Tf_2N]$. These values are smaller than that of 4.1 eV reported for the bulk sample.³⁹ For SrSnO₃ obtained by a microwave-assisted hydrothermal method,³⁸ solid-state reaction,³⁹ and modified Pechini method⁴⁰ values of 4.1, 4.01, and 4.3 eV have been determined, respectively. Thus, SrSnO₃ nanomaterials prepared by the microwave-assisted ionic liquid methods feature slightly lower band gaps than bulk or SrSnO₃ obtained using other methods, leading to an expected improvement in the photocatalytic performance.

Junploy et al. reported that the concentration of oxygen vacancies of $SrSnO_{3-\delta}$ influence the band gap. The calcination step to convert $SrSn(OH)_6$ to $SrSnO_3$ at high temperature leads to the release of some oxygen atoms from the crystal lattice of $SrSnO_{3-\delta}$ in the form of oxygen gas according to the following equation: $O_0 \leftrightarrow 0.5O_2 + V_0'' + 2e^{-.41}$ The released oxygen leaves vacancies behind which facilitates the electronic

diffusion through the solid and reduces the band gap. In addition a difference in particle size can lead to slightly different band gaps.³⁹

To determine the band edge position of the $SrSnO_3$ samples the equation reported by Butler and Ginley was used:⁴²

$$E_{\rm c} = X - E_0 - 0.5E_{\rm g}$$
$$X = (\chi_{\rm Sr}\chi_{\rm Sn}\chi_{\rm O}^{3})^{1/5}$$

where E_c is the conduction band (CB) edge potential, X is the geometric mean of the Sanderson electronegativity of the constituent atoms, χ is the electronegativity of a neutral atom, which is defined as the arithmetic mean of the atomic electron affinity (A) and the first ionization energy (I_1) , $^1 E_g$ is the band gap energy, and E_0 is the scale factor relating the reference electrode redox level to the absolute vacuum level ($E_0 = 4.5 \text{ eV}$ for a normal hydrogen electrode (NHE)). The value of X was calculated for SrSnO₃ to be 5.537 eV. The bottom CB level and top VB level values of the SrSnO₃ samples are given in Table 2. The conduction band (CB) edge potentials vary from -0.91 eV for the sample obtained in $[\bar{C_4Py}][Tf_2N]$ to -0.96 eV for the sample prepared in $[P_{66614}]$ [Tf₂N]. All values are more negative than the reduction potential of H^+/H_2 (0 V). This means that all samples have a suitable conduction band position for H₂ evolution. Generally, a more negative CB potential leads to higher reduction ability for water by electrons in the CB, thus promoting the photocatalytic H_2 evolution.

Figure 8 shows the photoluminescence (PL) emission spectra of $SrSnO_3$ samples under excitation at 290 nm. All samples feature a broad band centered at around 375 nm. This

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Figure 8. Photoluminescence spectra of $SrSnO_3$ samples prepared from the respective ILs (excitation wavelength 290 nm).

PL behavior can be attributed to the formation states inside the band gap because of the existence of medium-range disorder in the crystalline structure, most likely caused by oxygen vacancies.⁴³ The PL emission originates from a recombination of excited electrons with holes.^{44,45} For that reason, the PL spectra give information about the charge carrier separation efficiency. A high PL emission intensity is associated with a high recombination rate and low activity. As shown in Figure 8, the SrSnO₃ sample obtained in $[C_4Py][Tf_2N]$ shows the PL emission peak with lowest intensity suggesting effective charge carrier separation. Thereby an enhanced photocatalytic activity (as observed, vide infra) can be expected for this sample.

To characterize the textural properties of $SrSnO_3$ samples, the surface area, pore volume, and pore size were measured. The hysteresis loops for the nitrogen adsorption-desorption experiments on the $SrSnO_3$ samples are shown in Figure 9. The BET specific surface areas, pore volumes, and pore diameters of the samples are summarized in Table 4. The isotherms of the synthesized samples are of type IV with a hysteresis loop of H2 type according to the IUPAC classification, characteristic of



Figure 9. N₂ adsorption-desorption of the SrSnO₃ samples.

Table 4. BET Surface Areas, Pore Diameters, and Pore Volume for the Various SrSnO₃ Samples

sample	BET surface area S_{BET} (m ² /g)	pore diameter (nm)	pore volume, V_{pore} (cm ³ /g)
$\begin{array}{c} S1/[C_4mim] \\ [Tf_2N] \end{array}$	10.28	3.23	0.031
$\begin{array}{c} S2/[C_6(mim)_2]\\[Tf_2N]_2\end{array}$	8.98	3.83	0.029
$\begin{array}{c} S3/[P_{66614}] \\ [Tf_2N] \end{array}$	6.58	3.82	0.022
$\begin{array}{c} \text{S4/[C_4Py]} \\ [\text{Tf}_2\text{N}] \end{array}$	11.48	3.92	0.032

mesoporous materials with ink-bottle pores. The pore size distributions of the SrSnO₃ samples were estimated by the BJH method from the adsorption branch. The pore size distribution curves range from 3.2 nm for S1/[C₄mim][Tf₂N] to 3.9 nm for $S4/[C_4Py][Tf_2N]$. The mesoporosity of the samples can be attributed to the spaces between the SrSnO₃ particles. The specific surface area values range from 6.58 m² g⁻¹ in the sample prepared in $[P_{66614}][Tf_2N]$ to 11.48 m² g⁻¹ in the sample prepared in $[C_4Py][Tf_2N]$. Moreover, the surface area values for all samples (Table 4) are larger than those for SrSnO₃ prepared by a solid-state reaction $(2.8 \text{ m}^2 \text{ g}^{-1})$,⁴⁶ by a microwave hydrothermal method at 180 °C for 4 h and subsequent heat treatment process at 800 °C (6.6 m² g⁻¹),⁴ and by calcination at 1100 °C for 6 h of the hydrothermally prepared $SrSn(OH)_6$ at 180 °C for 16 h (0.3–0.5 m² g⁻¹). However, the surface areas of the SrSnO₃ samples are lower than that of SrSnO₃ with peanut-like morphologies synthesized by calcination at 700 °C for 6 h of the prepared $SrSn(OH)_6$ via a wet-chemical reaction $(27 \text{ m}^2 \text{ g}^{-1})$.

Evaluation of Photocatalytic Activity. *Hydrogen Generation.* The photoreduction activity of the SrSnO₃ samples was evaluated by detecting the hydrogen production from solutions containing 10 vol % methanol in water. To estimate the photocatalytical role of SrSnO₃, a measurement in the absence of the photocatalyst under UV irradiation was carried out, in which no H₂ was detected. Furthermore, no H₂ was generated under dark conditions in the presence of photocatalyst. Figure 10 gives a schematic illustration of the basic processes of water splitting on SrSnO₃. The photocatalytic activities of as-prepared SrSnO₃ samples for hydrogen evolution are shown in Figure 11.

It can be seen that without cocatalyst the order of hydrogen generation rates for bare SrSnO₃ samples is as follows: S2/ $[C_6(mim)_2][Tf_2N]_2$ (66 μ mol h⁻¹) > S4/ $[C_4py][TF_2N]$ (61 μ mol h⁻¹) > S3/[P₆₆₆₁₄][Tf₂N] (44 μ mol h⁻¹) > S1/ $[C_4 mim][Tf_2N]$ (41 μ mol h⁻¹). After loading 0.025 wt % of Rh, the photocatalytic activities of all samples were increased. The sample prepared in $[C_4Py][Tf_2N]$ shows the highest activity (110 μ mol h⁻¹) among SrSnO₃ samples. The order of band gaps of SrSnO_3 samples was S4/[C_4Py][Tf_2N] > S1/ $[C_4 mim][Tf_2N] > S2/[C_6(mim)_2][Tf_2N]_2 > S3/[P_{66614}]$ -[Tf₂N]. The improved H_2 photocatalytic activity of S4/ $[C_4Py][Tf_2N]$ can be attributed to the more negative potential of the conduction band in S4, in comparison to that for the other samples. Therefore, the transfer of photogenerated electrons to Rh more easily leads to increased H₂ generation efficiency in comparison with other samples. The sample prepared in $[C_4Py][Tf_2N]$ shows the highest specific surface area $(11.5 \text{ m}^2/\text{g})$ and smallest crystal size (40.1 nm); both factors are favorable for the generation of photogenerated



Figure 10. Schematic illustration of how SrSnO₃ can act as a photocatalyst for water splitting and the hydroxylation of TA.



Figure 11. (a) Hydrogen production rate from solutions containing 10 vol % methanol in water over SrSnO₃ before and after photodeposition of cocatalyst Rh. (b) Maximum intensities of fluorescence spectra at 426 nm of TAOH as a function of irradiation time during the TA hydroxylation over SrSnO₃ samples prepared using different ILs.

charge carriers and adsorption of more water molecules and sacrificial agent on the surface of the photocatalyst. As reported in the literature,48 the decreased crystal sizes reduces the recombination of photogenerated charge carriers via a decrease in the migration distance of charge carriers to the reactive sites on the surface for redox reactions. In addition, a larger surface area provides more reactive sites and improved adsorption of reactants.⁴⁹ Moreover, when 0.05 wt % of Rh cocatalysts were loaded, the photocatalytic activities of all samples were decreased. It can be speculated that all active sites on the surface of the SrSnO₃ sample were already covered with Rh particles on loading with 0.025 wt %. The loading of more Rh leads to an aggregation of the Rh particles and formation of larger sized Rh clusters, which can scatter the incident light, leading to a decrease in the number of electrons and holes formed and consequently decreasing the photocatalytic activities.50,51

Photohydroxylation of Terephthalic Acid. The photooxidation activity of $SrSnO_3$, prepared in different ILs, was evaluated by the hydroxylation of terephthalic acid (TA) under UV irradiation. Both electrons and holes either migrate to the surface of the particles or undergo an undesired recombination. The charge-separated holes react with absorbed water molecules to generate OH radicals, which can react with TA to form 2-hydroxyterephthalic acid (TAOH) (Figure 10). The latter shows a characteristic fluorescence band at 426 nm.^{52,53} Figure 11b shows the change in the maximum fluorescence intensity of TAOH as a function of the irradiation time during the TA hydroxylation over $SrSnO_3$ samples. The linear dependence of the maximum fluorescence intensity of TAOH with irradiation time approves the stability of the catalyst under operating conditions. The photocatalytic activities of $SrSnO_3$ samples are diverse and follow the order $S4/[C_4py][TF_2N] >$ $S3/[P_{66614}][Tf_2N] > S2/[C_6(mim)_2][Tf_2N]_2 > S1/[C_4mim] [Tf_2N]. As shown in Figure 9, the <math>SrSnO_3$ sample prepared in $[C_4Py][Tf_2N]$ with an average crystal size of 40 nm and specific surface area of 11.5 cm³/g displays higher photocatalytic activity in comparison to the sample with an average crystal size of 53 nm and specific surface area of 10.28 cm³/g obtained in $[C_4mim][Tf_2N]$. As indicated in Table 5, sample S4 reveals 2.2

Table 5. Hydrogen Evolution Rate from Water Splitting and Fluorescence Signal Intensity of 2-Hydroxyterephthalic Acid (TAOH) at 426 nm

sample	$\begin{array}{c} H_2 \; (\mu \text{mol } h^{-1}) \\ (0.025 \; \text{wt } \% \; \text{Rh}) \end{array}$	TAOH (au) (after a reaction time of 120 min)
$S1/[C_4mim]$ [Tf ₂ N]	99	213446.5
$\begin{array}{c} \text{S2/}[\text{C}_6(\text{mim})_2]\\[\text{Tf}_2\text{N}]_2 \end{array}$	90	294036.5
S3/[P ₆₆₆₁₄] [Tf ₂ N]	100	329095.7
$[C_4Py]$ $[Tf_2N]$	110	469139.7

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Figure 12. (top) Reusability of the SrSnO₃ sample obtained in $[C_4Py]$ [Tf₂N] after three successive runs. (bottom) XRD patterns before and after photohydroxylation.

times higher photo-oxidation potential than S1. PL spectra show that the intensity of S4 is lower than that of S1, indicating a lower recombination rate of electron-holes. Therefore, the enhanced activity of S4 can be attributed to the better charge carrier separation. On the other hand, this enhanced capacity to generate OH radicals for the sample prepared in $[C_4py][TF_2N]$ can be ascribed to the synergistic effects of the increased surface area to volume ratio coupled with the nanosized crystals along with the more negative level of the conduction band minimum (CBM) in comparison to that of $O_2/O_2^{\bullet-}$ (-0.33 V).⁵⁴ The crystal strain evaluation (Table 2) shows that all samples possess high degrees of crystallinity and slight variations can be observed, which would not be able to cause this large variation in photocatalytic efficiency. Thus, in this case the crystallinity is not the main reason for the different photocatalytic activities of the samples other than the aforementioned reasons (surface area, crystal size, and energy band structure).

In order to test the stability of the photocatalyst, three photohydroxylation experiments of TA over a $SrSnO_3$ sample obtained in $[C_4Py][Tf_2N]$ were performed (Figure 12 (top)). After each cycle, the photocatalyst was collected by centrifugation, washed two times with deionized water, and then dried. Furthermore, fresh TA solution was used for every cycle test and the loss of photocatalyst during the sampling

procedure was considered. As shown in Figure 12 (top), after three cycles the $SrSnO_3$ sample did not show a significant decrease in the photohydroxylation of terephthalic acid. From the XRD patterns of the $SrSnO_3$ sample obtained in $[C_4Py][Tf_2N]$ before and after photohydroxylation (Figure 12 (bottom)), no significant change can be noticed. Hence, it can be concluded that $SrSnO_3$ could be used as a good stable photocatalyst.

CONCLUSIONS

In summary, we have successfully synthesized SrSnO₃ with an orthorhombic perovskite GdFeO₃ structure by microwave synthesis in different ILs and a subsequent heat-treatment process. This method is fast, mild, effective, and reproducible and omits the need to use a template or surfactant, since the ionic liquids themselves acted as solvent, heat-transfer medium, and template. Varying the cation of the ionic liquid resulted in a change in the morphology of SrSnO₃. While in [C₄mim]-[Tf₂N], [C₆(mim)₂][Tf₂N]₂, and [P₆₆₆₁₄][Tf₂N] nanorods were observed, nanospheres could be obtained in [C₄Py]-[Tf₂N]. The nanorods largely differ in their size, most distinctly in the diameter. In [P₆₆₆₁₄][Tf₂N] quite thin needles were observed and in [C₆(mim)₂][Tf₂N]₂ larger rods with also much

wider size distribution were found; the nanorods obtained in $[C_4mim][Tf_2N]$ have an intermediate size. This points to the H-bonding capability of the IL cation being an important factor that influences the nanomaterial morphology. The higher the H-bonding capability of the IL, the more pronounced the rod shape of the particles is. In the IL that only exhibits electrostatic and π -bonding capabilities, nanospheres were obtained.

All SrSnO₃ samples generate H₂ from 10 vol % methanol in water without any cocatalyst. The sample prepared in $[C_4Py][Tf_2N]$ shows the highest activity for H₂ evolution (110 μ mol h⁻¹) using 0.025 wt % photodeposited Rh as cocatalyst and for photohydroxylation of terephthalic acid among all samples. The improved photocatalytic activity of the sample prepared in $[C_4Py][Tf_2N]$ can be attributed to the synergistic effects of the relatively large surface area associated with the nanosized crystals and a very suitable energy band structure.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00279.

XRD patterns of the as-prepared $SrSn(OH)_6$ in different ILs in comparison with the database pattern of $SrSn(OH)_6$ (PDF 9-86), Rietveld refinement results for $SrSnO_3$ samples, atomic positions as well as *R* factors and χ^2 values for the fit for each sample, EDX spectra of $SrSnO_3$ samples, TG curve of as-prepared $SrSn(OH)_6$ in $[C_4mim][Tf_2N]$, IR and Raman spectra of $SrSnO_3$ samples, and X-ray photoelectron spectrum survey scan of the $SrSnO_3$ samples (PDF)

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Notes

The authors declare no competing financial interest.

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