1. Introduction

In the last years, yolk@shell or “rattle-type” nanomaterials have received considerable attention due to their promising applications in the fields of heterogeneous catalysis,[1–4] electrocatalysis,[2,5,6] gas sensing,[7,8] battery development,[9,10] and drug delivery.[5,11] Yolk@shell materials are composed of single (or multiple) nanoscaled cores of a material A encapsulated inside a hollow nanosphere of a material B (A@void@B, in short A@B). Depending on the envisioned application, the surrounding hollow shell can be dense or porous (permeable) allowing control of the interactions between the core and the outer environment. For many applications, it has been shown that yolk@shell nanocomposites feature enhanced properties as a result of their unique structure on the nanometer scale. In the field of heterogeneous catalysis for example, it has been demonstrated that supported metal nanoparticle (M NP) catalysts with a yolk@shell structure are highly resistant against temperature and/or reaction induced M NP sintering, thus preserving the catalysts activity. As such, a variety of yolk@shell nanostructures have been designed, including M NP@carbon,[12–14] M NP@silica,[2,15] Au NP@TiO 2,[16] and Au NP@ZrO 2,[17,18] all superior in terms of catalytic activity and stability when compared to their non-yolk@shell counterparts. Despite their proven potential, the application of yolk@shell structures remains however limited due to challenging and demanding synthesis protocols. Overcoming these limitations, a simple soft-templated approach for the one-pot synthesis of yolk@shell nanocomposites and in particular of multicore metal nanoparticle@metal oxide nanostructures (M NP@MO x) is introduced. The approach here, as demonstrated for Au NP@ITO TR (ITO TR standing for tin-rich ITO), relies on polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP) inverse micelles as two compartment nanoreactor templates. While the hydrophilic P4VP core incorporates the hydrophilic metal precursor, the hydrophobic PS corona takes up the hydrophobic metal oxide precursor. As a result, interfacial reactions between the precursors can take place, leading to the formation of yolk@shell structures in solution. Once calcined these micelles yield Au NP@ITO TR nanostructures, composed of multiple 6 nm sized Au NPs strongly anchored onto the inner surface of porous 35 nm sized ITO TR hollow spheres. Although of multicore nature, only limited sintering of the metal nanoparticles is observed at high temperatures (700 °C). In addition, the as-synthesized yolk@shell structures exhibit high and stable activity toward CO electrooxidation, thus demonstrating the applicability of our approach for the design of functional yolk@shell nanocatalysts.
fastidious synthesis protocols. Common routes imply multiple synthetic steps, involving colloidal synthesis of size controlled colloids, multicoating procedures with more or less expensive sacrificial template shells, as well as aggressive etching for template removal, all of these seriously impeding up-scaling and large-scale application.\textsuperscript{19,20}

To overcome these limitations, we developed a simple and scalable approach allowing the one-pot synthesis of M NP @MO\textsubscript{x} yolk@shell nanocomposites. As exemplified for gold and tin-rich ITO (ITO TR ),\textsuperscript{21–24} the resulting Au NP @ITO TR yolk@shell nanocomposites are composed of finely dispersed Au NP (≈6 nm in diameter) strongly anchored onto the inner surface of porous ITO TR hollow spheres (≈35 nm in diameter). As depicted in Scheme 1 and demonstrated in the following, M NP @MO\textsubscript{x} synthesis is achieved in four simple steps including: (1) Incorporation of a hydrophilic, acidic, and water containing metal precursor into the hydrophilic P4VP micellar core (e.g., HAuCl\textsubscript{4} ·3H\textsubscript{2}O for Au NP @ITO TR ), (2) incorporation of a hydrophobic alkoxidal metal oxide precursor into the hydrophobic PS micellar shell (e.g., indium(I)tin(II)tri-tert-butoxide (ITBO)\textsuperscript{[21–24]} for @ITO TR ), (3) solution processing including solvent evaporation and micellar aggregation (e.g., dip-coating, spin-coating, or spraying), and (4) calcination at elevated temperature inducing concomitant polymer decomposition, metal oxide formation, and metal precursor reduction/nanoparticle formation.

As such, taking advantage of the compartmented structure of polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP) inverse micelles, our approach allows in a one-pot fashion simultaneous control over the composition and size of the metallic yolk components as well as of the size and composition of the metal oxide shell component (see Scheme 1).

2. Results and Discussion

As depicted in Scheme 1, AuNP @ITO TR yolk@shell structures and in particular AuNP @ITO TR yolk@shell-based thin films are synthesized by simply mixing three components in solution: PS-b-P4VP as template; HAuCl\textsubscript{4} ·3H\textsubscript{2}O as hydrophilic, hydrated, and acidic gold precursor; and [In(OrBu)\textsubscript{3}Sn] as hydrophobic ITO TR precursor.\textsuperscript{21–24} Following, the major processes involved in material synthesis as well as the major correlations between synthesis parameters and material structure are described. To begin micelles formation and selective core/corona incorporation of the gold and ITO TR precursors are described in Sections 2.1 and 2.2, respectively. Following, the structure and nature of the resulting materials after solution processing and calcination are extensively investigated in Section 2.3. The driving force for yolk@shell formation is elucidated in Section 2.4, while influence of the gold precursor loading on the materials structure and composition is examined in Section 2.5. Insights into gold nanoparticle formation as well as particle accessibility are given in Sections 2.6 and 2.7, respectively. In Section 2.8, the applicability of the AuNP @ITO TR yolk@shell structures for electrocatalytic applications is demonstrated by CO electrooxidation in alkaline media. Finally, the versatility of our approach is demonstrated in Section 2.9 with the direct synthesis of worm-like yolk@shell materials.

2.1. Micellar Structure and Metal Precursor Loading in PS-b-P4VP Inverse Micelles

The formation and structure of PS-b-P4VP inverse micelles in toluene as well as their HAuCl\textsubscript{4} loading capacity were studied by small angle X-ray scattering (SAXS) and anomalous small angle X-ray scattering (ASAXS). PS-b-P4VP inverse micelles, with a hydrophilic P4VP core and a hydrophobic PS shell, were formed by supramolecular self-assembly of PS\textsubscript{111}-b-P4VP\textsubscript{96} unimers in toluene (Table 1). To determine the size and shape of the PS-b-P4VP micelles, SAXS measurements, sensitive to electron density variations at the nanometer scale, were performed. The recorded scattering curves depicted in Figure 1 are typical for diluted solutions of noninteracting spherical objects. The curves could be fitted at best using a spherical core–shell scattering model (see Figures S1 and S2, Supporting Information, for details).\textsuperscript{[24]} Accordingly data analysis revealed the formation of spherical inverse micelles (64 nm in diameter), composed of...
a P4VP electron-rich core (40 nm in diameter \(R_{\text{core}} = 20 \text{ nm}\)) surrounded by a swollen PS corona (12 nm in thickness). It is important to mention that the size of the PS shell is likely underestimated in the SAXS analysis, as electron density gradients within the PS shell were not taken into account within the chosen core–shell model (Figure S3, Supporting Information).

Taking advantage of the metal cation affinity of the P4VP core,\(^{24–28}\) the PS-\(b\)-P4VP polymer micelles could easily be loaded with variable amounts of HAuCl\(_4\)·3H\(_2\)O. As evidenced by SAXS, 0.2, 0.3, and even 0.6 equivalents of HAuCl\(_4\)·3H\(_2\)O per pyridine unit could be loaded within the P4VP core affecting neither the micellar shape nor size (Figure 1). Indeed, as seen in Figure 1b, the shape of the scattering profile as well as the position of the curve minima remained unchanged with increasing HAuCl\(_4\)·3H\(_2\)O loading; clear indication that the shape and size of the micelles are largely unaffected by the gold precursor loading (Figures S4 and S5, Supporting Information). In contrast, the intensity of the scattering curve, which is proportional to the square of the scattering contrast, drastically increased with increasing gold loading (Figure 1b). Accordingly the electron density contrast between the micellar core and the surrounding solvent \(\Delta\eta_{\text{core}}\), which was determined by data fitting (see inset in Figure 1b), linearly increases with increasing gold loading; result which corroborates the homogenous and exclusive incorporation of the gold precursor within the hydrophilic P4VP core of the micelles.

The homogeneity of the HAuCl\(_4\)·3H\(_2\)O distribution inside the hydrophilic P4VP compartment was further confirmed by ASAXS (Figure 1c,d and Figures S6 and S7, Supporting Information). The ASAXS curves were recorded at three different energies in close vicinity of the Au L\(_3\) absorption edge (\(^{197}\)Au L\(_3\), \(E_{\text{Au}} = 11\,919\text{ eV}, E_1 = 11\,527\text{ eV}, E_2 = 11\,873\text{ eV}, \) and \(E_3 = 11\,915\text{ eV}\)). While the scattering contribution of the gold atoms within the P4VP core of the micelles is expected to vary

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**Table 1.** Number- and weight average molar masses \((M_n, M_w)\), dispersity indexes \(M_w/M_n\), and compositions (molar ratios S:4VP) of PS\(_{111}\)-\(b\)-P4VP\(_{96}\) and PS\(_{135}\)-\(b\)-P4VP\(_{137}\).

<table>
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<th></th>
<th>(M_n) [kg mol(^{-1})]</th>
<th>(M_w) [kg mol(^{-1})]</th>
<th>(M_w/M_n)</th>
<th>Molar ratio S:4VP</th>
<th>Micelle morphology</th>
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<td>PS(<em>{111})-b-P4VP(</em>{96})</td>
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<td>1.27</td>
<td>1.14:1</td>
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<tr>
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<td>28.4</td>
<td>30.7</td>
<td>1.08</td>
<td>0.97:1</td>
<td>Worm-like</td>
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**Figure 1.** a) SAXS curve and corresponding fit (core–shell model) of PS-\(b\)-P4VP inverse micelles. b) SAXS scattering curves of unloaded (black) and HAuCl\(_4\)(X)@PS-\(b\)-P4VP loaded micelles with \(X = 0.2\) (red), 0.3 (blue), and 0.6 (green) eq. of HAuCl\(_4\)·3H\(_2\)O per pyridine unit. Inset: Linear dependence of \(\Delta\eta_{\text{core}}\) (scattering length density difference between the core and the solvent) with increasing HAuCl\(_4\)·3H\(_2\)O loadings. c) ASAXS curves recorded at \(E_1 = 11\,525\text{ eV}\) (black curve) and \(E_2 = 11\,915\text{ eV}\) (red curve) and resulting curve of their subtraction (orange curve). d) Fit of the subtracted ASAXS curve applying a sphere model (details in the Supporting Information).
close to the gold absorption edge, the scattering contribution of the polymer backbone should remain unchanged at energies far from the carbon absorption edge (\( \text{C} \) K-edge \( \approx 290 \text{ eV} \)). In a good approximation, the subtraction of the scattering curves measured at \( E_2 = 11 \, 527 \text{ eV} \) and \( E_1 = 11 \, 915 \text{ eV} \) yields the scattering contribution majorly related to the gold loaded domains (Figure 1c). As can be seen in Figure 1d, the gold contribution can be fitted with a spherical scattering model revealing a gold loaded spherical domain with a size corresponding appropriately to the size of the micellar core. As such, SAXS confirms the homogeneous distribution of the gold precursor throughout the P4VP micellar core (Figure 1d and Figure S7, Supporting Information).

To summarize, SAXS and ASAXS reveal the formation of spherical PS-b-P4VP inverse micelles with a PS shell and a P4VP core, the latter exhibiting an excellent metal loading capacity, making PS-b-P4VP inverse micelles highly attractive templates for the synthesis of M\text{NP}@support yolk@shell nanostructures.

2.2. Formation of Metal Precursor@Metal Oxide Hybrid Micelles in Solution

For the synthesis of Au\text{NP}@ITO\text{TR} yolk@shell materials selected amounts of ITBO were added to the previously described HAuCl\(_4\)-3H\(_2\)O loaded micellar solutions (HAuCl\(_4\)(X)@PS-b-P4VP with \( X = 0.2, 0.3, \) and 0.6 eq of HAuCl\(_4\)-3H\(_2\)O per pyridine unit, Figure S8, Supporting Information). The yellow solutions turned immediately brown after the ITBO addition and in particular for higher gold loadings, indication for an immediate and stoichiometric reaction between the metal and the metal oxide precursor within the micelles. In line with these observations minor to major structural changes of the micelles were revealed by SAXS. As seen in Figure 2a, ITBO addition induces only minor changes in the SAXS curve in case of low HAuCl\(_4\)-3H\(_2\)O loadings (\( X = 0.2 \) eq.; result which indicates a homogeneous distribution of the ITBO precursor within the PS shell and the solvent toluene.\[24\])

In contrast, for higher loadings (\( X = 0.3 \) and \( X = 0.6 \)) a large increase of the scattering intensity as well as a shift to lower q values of the form factor minima is observed (Figure 2b,c). These drastic changes can be explained either by the formation of larger micelles or—as depicted in Scheme 1—by the formation of core@shell@shell structures exhibiting a newly formed electron density rich shell at the P4VP/PS interface. Considering the respective polarity of the metal and metal oxide precursors (i.e., HAuCl\(_4\), 3H\(_2\)O and ITBO), their initial repartition in the inverse micelle as well as their reactivity (ITBO is highly sensitive toward oxidation, hydrolysis, and condensation), the formation of core@shell@shell structures, as a result of an interfacial inter-precursor reaction at the P4VP/PS interface, seems more than likely.

Neglecting in a first approximation the scattering contribution of the swollen PS shell, the SAXS data could best be fitted employing a core–shell model composed of a \( \approx 40 \text{ nm} \) in diameter electron density rich core surrounded by a \( \approx 1.7 \text{ nm} \) thick electron density rich shell (Figure S9, Supporting Information).

As such, strong indication for the formation of an ITBO derived shell via hydrolysis–condensation at the P4VP/PS core/corona interface is given in the presence of higher HAuCl\(_4\)-3H\(_2\)O loadings. Further spectroscopic corroboration of this hypothesis will be given in Section 2.4.

To summarize, SAXS analysis revealed that depending on the precursor’s stoichiometry different types/structures of metal precursor@metal oxide micelles are formed in solution comprising a more or less developed ITBO derived shell at the PS/P4VP interface.

2.3. Nanostructured Au\text{NP}@ITO\text{TR} Thin Films: Relation between Micellar Structure and Material Structure

For the synthesis of Au\text{NP}@ITO\text{TR} yolk@shell thin films, the previously described HAuCl\(_4@ITBO\) precursor micelles were spin-coated onto selected substrates (among others silicon). The resulting hybrid films were dried and subsequently calcined at 400 °C for 2 h in air to induce ITO\text{TR} formation, polymer decomposition, and gold nanoparticle formation. Investigation of the formed nanostructures was performed with scanning electron microscopy (SEM) (Figure 2). In line with the previously described SAXS results, SEM measurements revealed the formation of different types of Au\text{NP}@ITO\text{TR} nanostructures for different HAuCl\(_4\)-3H\(_2\)O loadings (i.e., different \( n(\text{HAuCl}_4\cdot 3\text{H}_2\text{O})/n(\text{ITBO}) \) molar ratios, Figure S8, Supporting Information). As such, low HAuCl\(_4\)-3H\(_2\)O loadings (i.e., low \( n(\text{HAuCl}_4\cdot 3\text{H}_2\text{O})/n(\text{ITBO}) \) ratios) lead to mesoporous ITO\text{TR} thin films with an open porous structure, homogeneously loaded with one size-controlled Au\text{NP} per pore of \( \approx 6 \text{ nm} \) in diameter (SEM images, Figure 2d). In contrast, higher HAuCl\(_4\)-3H\(_2\)O loadings (i.e., higher \( n(\text{HAuCl}_4\cdot 3\text{H}_2\text{O})/n(\text{ITBO}) \) ratios) resulted in thin films build of closely packed yolk@shell nanostructures (see Figure 2e,f).

As revealed by scanning electron microscopy (SEM, Figure 2), transmission electron microscopy (TEM) (Figure 3), energy dispersive X-ray spectroscopy (EDX) (Figure S11, Supporting Information), X-ray diffraction (XRD) (Figure 3), and X-ray photoelectron spectroscopy (XPS) (Figure S12, Supporting Information), these structures are composed of \( \approx 40 \text{ nm} \) (in diameter) ITO\text{TR} hollow spheres with a shell thickness of \( \approx 2.5 \text{ nm} \) (Figure S13, Supporting Information), all filled with multiple, finely dispersed, and uniformly sized \( \approx 6 \text{ nm} \) Au\text{NP} per sphere (Figures 2e,f and 3).

The formation of Au\text{TR} was thereby evidenced by XRD, high resolution TEM (HRTEM), and XPS. The X-ray diffraction pattern of the samples calcined at 400 °C featured broad Au\text{TR} reflections in line with the JCPDS file No. 04-0784 for Au\text{TR} (space group Fm3m). In addition, HRTEM measurements performed on the nanoparticles anchored on the inner side of the shell, revealed lattice fringes in line with the \( d_{111} \) lattice distance of Au\text{TR}. Finally, XPS also revealed the presence of Au\text{TR} in the nano-composites (Figure S12, Supporting Information). On the other hand, formation of amorphous ITO\text{TR} with an In to Sn ratio close to 1 was revealed by XRD, EDX, and XPS.\[21,23,29\] No contribution of crystalline tin doped indium oxide (ITO, Sn\text{In}_2\text{O}_3), indium oxide (In\text{O}_3), or tin oxide (SnO\(_2\)) could be observed in the XRD pattern, while Sn, In, and O were detected by EDX in a ratio of \( \approx 1:1:2 \) (see Figure S11, Supporting Information) with...
Figure 2. SAXS scattering curves of HAuCl$_4$·3H$_2$O loaded inverse micelles before (orange curves) and after (green curves) the addition of ITBO with $n_{\text{Au}}/n_{\text{ITBO}}$ of a) 0.07,* b) 0.28, and c) 0.55. Top-view and cross-sectional SEM images of thin films after spin-coating the previous micellar solutions on Si wafers followed by calcination in air at 400 °C ($n_{\text{Au}}/n_{\text{ITBO}} = \text{d) } 0.07,* \text{ e) } 0.28, \text{ and f) } 0.55$). *Adapted with permission. [24] Copyright 2014, American Chemical Society.
In and Sn present in the oxidation state +III and +IV, respectively (Figure S12, Supporting Information). \textsuperscript{[24]}

From all these results we could conclude that the structure and composition of the AuNP/ITO\textsubscript{TR} nanocomposites are imprinted by the structure and composition of the HAuCl\textsubscript{4}@ITBO precursor micelles (see previous SAXS results). In case no shell formation occurs within the micelles (i.e., for low HAuCl\textsubscript{4} loadings), mesostructured ITO\textsubscript{TR} thin films with an open porous structure and a gold loading of one Au NP (≈6 nm) per pore are obtained. In contrast, in case shell formation occurs within the micelles (i.e., for high HAuCl\textsubscript{4} loadings), AuNP/ITO\textsubscript{TR} nanocomposites with a yolk@shell nanostructure, composed of multiple AuNP (≈6 nm) encapsulated inside 40 nm ITO\textsubscript{TR} hollow spheres, are obtained. In addition, increasing the gold precursor loading does not only lead to the observed nanostructural transformation but also affects the porosity of the ITO\textsubscript{TR} shells (see SEM data in Figure 3).

Important to note is that independent of the gold precursor loading, the size of the AuNP is always centered around 6 nm (for samples calcined at 400 °C). As such 6 nm seems to be an energetically stable size for AuNP grown on an ITO\textsubscript{TR} interface heated to 400 °C (see Figure 5). This result suggests a strong Au–ITO\textsubscript{TR} metal–support interaction allowing the stabilization of the particle dispersion on the amorphous ITO\textsubscript{TR} support. Considering that the particle formation occurs on a highly amorphous metal oxide surface, a high density of OH surface functionalities can be assumed which might help to stabilize the forming nanoparticles.

2.4. Interfacial Reactivity as Driving Force for Yolk@Shell Formation

To reveal the driving force responsible for the ITBO derived shell formation, X-ray absorption spectroscopy (XAS) and \textsuperscript{119}Sn-nuclear magnetic resonance (NMR) measurements were performed. For this purpose, three different solutions containing ITBO, ITBO in the presence of unloaded PS-b-P4VP micelles (ITBO/PS-b-P4VP), and ITBO in the presence of HAuCl\textsubscript{4}·3H\textsubscript{2}O loaded PS-b-P4VP micelles (ITBO/HAuCl\textsubscript{4}(X)@PS-b-P4VP) were investigated. Information about the average oxidation states of In and Sn in the different precursor solutions were gained by XAS at the L-edges of the metals, as the shape and position of an element specific absorption edge depends on the element oxidation state and local environment. \textsuperscript{119}Sn L\textsubscript{3} = 3730 eV and \textsuperscript{119}Sn L\textsubscript{2} = 4156 eV. As can be seen for the indium and tin edge in Figure 4 a,1 and Figure S14,1 (Supporting Information), no difference is observed between the XAS spectra of ITBO and ITBO in the presence of PS\textsubscript{111}-b-P4VP\textsubscript{96} micelles. This suggests that Sn and In maintain their initial oxidation states (i.e., Sn(II) and In(I)) and remain in their initial coordination. In contrast, when ITBO is added to HAuCl\textsubscript{4}·3H\textsubscript{2}O loaded PS-b-P4VP micelles, clear evidence for an increasing oxidation state with increasing HAuCl\textsubscript{4}·3H\textsubscript{2}O loading is observed at the indium edge (Figure 4a). For the highest gold loading of 0.6 equivalents, the position of the In edge is even similar to the one recorded for an In(III)(OT\textsubscript{Bu})\textsubscript{3} reference, evidencing the quantitative oxidation of the In(I) to In(III) in the presence of HAuCl\textsubscript{4}·3H\textsubscript{2}O. In contrast, no such change is observed in the position of the Sn edge (Figures S14,2 and 3, Supporting Information), which suggests that Sn remains as Sn(II). However, closer examination of the XAS spectra at the Sn edge reveals a change in the first coordination sphere of tin (see comparison between the XAS spectra of ITBO and Sn(II)(OT\textsubscript{Bu})\textsubscript{3}, marked oscillations in Figure S14,2 and 3, Supporting Information); change which might result from a ligand substitution/addition at the tin center. In line with the XAS results, room-temperature \textsuperscript{119}Sn-NMR confirms that a reaction between the ITBO and the HAuCl\textsubscript{4}·3H\textsubscript{2}O precursors takes place within the micelles. While no change of the \textsuperscript{119}Sn-NMR spectra of ITBO is observed in the presence of unloaded polymer micelles, two new Sn(II) species (δ = −148 ppm and δ = −170 ppm) are formed in case of HAuCl\textsubscript{4}·3H\textsubscript{2}O loaded micelles (HAuCl\textsubscript{4}(X)@PS-b-P4VP). At intermediate loadings (X = 0.3), ITBO is only partially converted, as evidenced by the remaining ITBO signal at δ = −78 ppm (Figure 4b). In contrast, complete ITBO conversion is achieved at higher loadings (X = 0.6) in line with the complete disappearance of the ITBO signal at δ = −78 ppm (Figure 4b). Although it is not possible to determine the exact nature of the Sn(II) species, the formation of a two to three times coordinated Sn(II)–alkoxo–chloro species is very likely, as chemical shifts between −140 and −170 ppm are typical for these kind of Sn(II) compounds. \textsuperscript{[30,31]}

Figure 3. a) HRTEM image of one single Au\textsubscript{0.6}NP@ITO\textsubscript{TR} yolk@shell particle scratched from a thin film calcined at 400 °C. The insets represent the FFTs of the marked areas. A lattice spacing of 2.35 Å could be determined corresponding to the lattice distance d\textsubscript{111} of crystalline gold. b) XRD pattern of Au\textsubscript{0.6}NP@ITO\textsubscript{TR} calcined at 400 °C thin films deposited on ultra thin Si[100] (transmission measurement).
As such XAS, NMR, and SAXS confirm an interfacial reaction between the gold precursor and the ITBO precursor, leading to a gold induced oxidation of In(I) to In(III) as well as to a ligand addition/substitution at the Sn(II) center. Considering the standard electrode potential of the following redox reactions the oxidation of In(I) to In(III) along with the concomitant reduction of the Au(III) atoms is indeed very likely

\[
\text{AuCl}_2 + 2e^- \rightarrow \text{AuCl}_2^2+2\text{Cl}^- \quad (E^\circ = 0.92\text{V})
\]

\[
\text{In}^+ \rightarrow \text{In}^{3+} + 2e^- \quad (E^\circ = -0.43\text{V})
\]

In addition, in view of the hydrate/acidic nature of the HAuCl\textsubscript{4}·3H\textsubscript{2}O precursor, hydrolysis-condensation of the highly reactive ITBO precursor is more than likely to take place at the P4VP/PS interface, thus leading to an ITBO derived shell formation within the micelles.

2.5. AuNP@ITO\textsubscript{TR} Yolk@Shell Thin Films: Processability and Influence of the Gold Precursor Loading

As the structure-directing precursor micelles are formed in solution, our approach should in principle be compatible with all processing methods involving solvent evaporation. This includes, for example, spraying,[32] printing,[33] dip- or spin-coating,[24] as well as impregnation and so on. Despite their a priori hydrophobic nature, the solutions were easily coated on various substrates by either spin- or dip-coating. Interestingly, the viscosity of the ITBO/HAuCl\textsubscript{4}(X)@PS-b-P4VP solutions increased with increasing HAuCl\textsubscript{4}·3H\textsubscript{2}O loading: observation in line with the hydrolysis-condensation hypothesis made earlier. As a result, the film thickness increased from 70 to 200 nm for an increasing gold loading of 0.3 and 0.6, respectively (Figure 2e,f). Further control of the film thickness could also be achieved by varying the concentration of the precursor solution, as illustrated for Au\textsubscript{0.6NP}@ITO\textsubscript{TR} thin films (Figure S15, Supporting Information). Bilayers of 50 nm as well as thick multilayers of 200 nm could thus be synthesized starting from diluted and concentrated precursor solutions, respectively ([PS-b-P4VP] = 10 mg L\textsuperscript{-1} and [PS-b-P4VP] = 30 mg L\textsuperscript{-1}, Figure S15, Supporting Information, and Experimental Section for experimental details). In all cases, the ITO\textsubscript{TR} hollow spheres exhibit a diameter of 40 nm, in line with the size of the P4VP core domain of the precursor micelles (Figure 5).

The limited thickness of the ITO\textsubscript{TR} shell (2.5 nm) most probably results from the limited diffusion of the reacting precursors at the PS/P4VP interface. For all gold loadings, Au NP of 6 nm in diameter are formed after calcination at 400 °C, demonstrating the existence of a stable Au NP size for particles supported/grown on ITO\textsubscript{TR} at 400 °C. This result is surprising considering that the Au\textsubscript{NP} are formed in a very small volume and are separated by only a few nanometers and should thus be prone to sinter, especially at elevated temperatures (Figure 6). As a result, increasing the HAuCl\textsubscript{4}·3H\textsubscript{2}O does not lead to an increase of the particle size, as would be expected in case of particle sintering, but rather increases the number of Au NP encapsulated per hollow sphere. As such, ultrahigh particle loadings of ~6–12 size controlled gold nanoparticles per hollow sphere could be obtained for Au\textsubscript{0.3NP}@ITO\textsubscript{TR} and Au\textsubscript{0.6NP}@ITO\textsubscript{TR}, respectively (Figure 5c,f).

2.6. Particle Formation and Growth

To generate further insight into the gold nanoparticle formation, we monitored their growth during calcination by ex situ TEM analysis (see data for Au\textsubscript{0.6NP}@ITO\textsubscript{TR} (Figure 6)). For that purpose, a monolayer of hybrid core–shell precursor micelles was deposited onto a temperature-resistant silicon nitride membrane TEM grid and calcined to different temperatures. The grid was measured
directly after film deposition (using a special TEM holder providing N₂ atmosphere prior column insertion) and at different stages of the calcination (i.e., between 200 and 700 °C). For the as-deposited micellar monolayer, TEM images revealed the formation of tiny AuNP clusters (smaller than 2 nm in diameter) inside the P4VP core. As no evidence was given for AuNP formation in solution, be it by UV–visible (UV–vis) spectroscopy or by SAXS (Figure S16, Supporting Information), we attribute these cluster formation to electron beam induced gold reduction. After calcination at 200 °C, multiple small AuNP with a mean diameter of 3.6 ± 0.7 nm were formed. Further calcination at 300 °C leads to particle growth (from <2 to 4.8 ± 1.5 nm) along with a decrease of the particle number encapsulated per hollow sphere. The decomposition and reduction of the gold precursor at the origin of the particle formation could further be revealed by EDX (Figure S17, Supporting Information). As can be seen in the EDX spectra in Figure S17

Figure 5. TEM images at low and high magnification of a,b) Au0.3NP@ITO and d,e) Au0.6NP@ITO monolayers deposited on SiN TEM grids after calcination at 400 °C for 2 h. c,f) Corresponding size distribution of AuNP and number of NPs per hollow spheres (HS).

Figure 6. TEM images of Au0.6NP@ITO yolk@shell nanostructures deposited on SiN membrane grids before calcination, i.e., under N₂, and calcined under air at 200 °C for 5 min and 300 °C for 5 min, 500 °C, 600 °C, and 700 °C for 2 h.
(Supporting Information), the Cl signal progressively decreases with increasing temperature until it completely vanishes at 400 °C; results which are in line with the thermal gravimetric analysis (TGA) results of the gold precursor decomposition (Figure S18, Supporting Information). Very interesting is the thermal stability of the gold nanoparticles at temperatures higher than 400 °C (Figure 6).

Indeed, despite a slight increase of the NPs size with increasing temperature (i.e., from 6.4 ± 1.3 nm at 400 °C to 9.4 ± 2.5 nm at 700 °C), the strong anchorage of the Au NP onto the ITO TR support seems to prevent complete sintering of the Au NP into one particle per shell. As such, the particles stay remarkably small and homogeneously sized (<10 nm) up to 700 °C, even though they are separated by only a few nanometers. By inspection of the contact zone between the particles and the ITO TR shell, one can see for some particles a curvature match between the particles and the oxide shell, which results in shallow cavities providing anchor points/surfaces for particle surface stabilization. In this context, the morphological stability of the ITO TR hollow spheres up to 700 °C is certainly helpful for particle stabilization. Indeed, although crystallization of the amorphous matrix into In2O3 and SnO2 occurs at temperature between 600 and 700 °C, the overall shape of the ITO TR shell is fully preserved (Figures S19 and S20, Supporting Information).

2.7. AuNP@ITO TR Yolk@Shell Thin Films: Shell Porosity and Particle Accessibility

In order to gain a better insight into the porosity of the AuNP@ITO TR yolk@shell structures, Krypton physisorption was performed. Considering the film thicknesses of 70 nm for Au0.3NP@ITO TR and 220 nm for Au0.6NP@ITO TR, specific surface areas of 350 and 120 m2 cm−3 were determined for Au0.3NP@ITO TR and Au0.6NP@ITO TR, respectively. The higher value obtained for the Au0.3NP@ITO TR yolk@shell thin film is in good agreement with the higher shell porosity observed for the Au0.3NP@ITO TR yolk@shell particles by HRSEM (Figure 2e). Further elucidation of the particles accessibility was performed by exploiting their plasmonic properties, and in particular the dielectric constant dependent position of the localized surface plasmon resonance absorption band (LSPR). Indeed, according to Mie’s theory,[34] any increase of the dielectric constant of the medium surrounding the AuNP induces an LSPR shift toward lower energies (i.e., to higher wavelengths).[34,35] Thus, probing the LSPR position of the AuNP@ITO TR films when immersed in air or in water allows evaluation of the particles’ accessibility inside the hollow spheres. For both Au0.3NP@ITO TR and Au0.6NP@ITO TR samples, an LSPR absorption is observed by UV–vis spectroscopy (Figure 7a). In agreement with the gold nanoparticle size and the gold nanoparticle spacing, the position of the LSPR is very similar for both samples and comprised between 530 and 540 nm. In both cases, a redshift (with a similar magnitude of Δλ ≈ 20 nm) is observed upon the transfer from air to water. A shift of similar magnitude (Δλ ≈ 20 nm) was calculated for model ITO hollow spheres filled with 6.5 nm sized Au nanoparticles between an air–air or water–air configuration and a water–water configuration (see Figure 7b). As such this shift unambiguously demonstrates the penetration of water inside the hollow spheres and thus the accessibility of the AuNP through the ITO TR shell.

In view of the latter result, we could demonstrate that hydrophobic nanoreactor templating allows the synthesis of yolk@shell nanocomposites with fully accessible core particles, making these yolk@shell structures highly interesting for catalytic or sensing applications.

2.8. AuNP@ITO TR Yolk@Shell Thin Films: Applicability as Electrodes for Electrocatalytic Applications

Considering the conductive nature of the AuNP@ITO TR yolk@shell nanocomposites (σ = 11.4 S cm−1, see Figure S10, Supporting Information), we evaluated their applicability as electrodes for electrocatalytic applications, in particular for...
electrocatalytic CO oxidation in alkaline media. In this context, CO oxidation was chosen as it represents the model reaction in terms of gold based catalysis\cite{36,37} and electrocatalysis.\cite{24,38,39} For that purpose an Au0.6 NP @ITO TR yolk@shell thin film was coated on a glassy carbon electrode and subjected to cyclic voltammetry (CV) between 0.75 and 1.65 V_RHE in a nitrogen degassed electrolyte to clean the gold surface. Subsequently, the electrolyte was saturated with CO and the CO oxidation activity was determined by CV in the same potential interval (for details see the Experimental Section). In line with other Au NP –ITO electrodes,\cite{24,38,39} the Au0.6 NP @ITO TR hollow spheres show a pronounced CO oxidation activity, as demonstrated by the pronounced CO oxidation current with a current maximum of 1.5 mA cm^2 (geometric surface area) at around 1.1 V_RHE (Figure 8a, red curve, scanning speed = 5 mV s^-1, fifth cycle). As such, we can conclude that the gold nanoparticles inside the ITO TR hollow spheres are accessible to the CO saturated electrolyte and highly active for CO oxidation. The stability during CO oxidation was also probed by CV, though with faster scan rate (100 mV s^-1). The current density maximum of each cycle was plotted against the cycle number as measure of the stability. When compared to non-yolk@shell AuNP–ITO nanocomposites,\cite{24,38,39} the CO oxidation current density is quite stable and decreases only slightly over repeated cycling. Indeed, while for other AuNP–ITO structures a drastic decay of the CO oxidation current density is observed (the current density drops at least by 70%),\cite{24,38,39} the CO oxidation current density of AuNP@ITO TR only decreases by \approx 4% over 60 cycles.

2.9. Au NP @ITO TR Yolk@Shell Thin Films: From Spherical to Worm-Like Structures

Finally, as a final challenge and to demonstrate the versatility of our approach, we synthesized nonspherical yolk@shell materials.\cite{40–42} By simply varying the block length of the PS-b-P4VP template (Table 1),\cite{43,44} block copolymer micelles with worm-like structure could be assembled in solution (see TEM data (Figure 9a)) and SAXS data analysis in Figure S21 (Supporting Figure 8. a) Cyclic voltammogram of Au0.6 NP @ITO TR (black line) measured in a CO saturated 0.1 M NaOH electrolyte (fifth scan, 5 mV s^-1, 1600 rpm). The current is normalized to the geometric area of the electrode. b) CO oxidation current density maxima, determined in each cycle, plotted against the cycle number (time).

Figure 9. a) SAXS measurements of worm-like HAuCl_4·3H_2O (0.6 eq.) loaded PS-b-P4VP micelles in toluene before (orange) and after the addition of ITBO (green). Inset: TEM image of worm-like HAuCl_4 loaded PS-b-P4VP micelles. b) SEM of AuNP@ITO TR yolk–shell based thin film with worm-like structure.Inset: Corresponding TEM image and SEM cross section.
Information. Similar to their spherical counterparts these worm-like micelles, once loaded with HAuCl₄·3H₂O, could easily be used as nanoreactor templates for the synthesis of AuNP@ITO TR yolk@shell thin films. In line with the micellar shape and dimensions, AuNP@ITO TR yolk@shell structures with a worm-like morphology are formed, with a diameter of ~25 nm and a length of several 100 nm (see Figure S21, Supporting Information). As for their spherical counterparts, these worm-like structures are homogeneously loaded with uniformly sized AuNP, which again reveal a diameter of ~6 nm (Figure 9b).

3. Conclusion

In this contribution, a supramolecular approach allowing the one-pot synthesis of AuNP@ITO TR yolk@shell nanostructures is presented. Our approach, entitled hydrophobic nanoreactor templating, relies on PS-b-P4VP inverse micelles as two-compartment nanoreactor templates. While the hydrophilic micellar core serves as reservoir for the hydrophilic and acidic gold precursor (HAuCl₄·3H₂O), the hydrophobic PS shell allows the incorporation of the hydrophobic ITO TR precursor (indium(III)tetrabutoxide). As a result, hybrid core-shell precursor micelles are obtained, which enable the formation of various AuNP@ITO TR nanostructures after solvent evaporation and calcination. The final AuNP@ITO TR nanostructure depends on the precursor’s stoichiometry within the micelles. While for low metal loadings, AuNP@ITO TR nanostructures with an open porous structure and one metal nanoparticle per pore are obtained, higher metal loadings lead to the formation of AuNP@ITO TR yolk@shell nanostructures containing several evenly sized and fully accessible Au nanoparticles. Taking advantage of the conductivity and porosity of the ITO TR shell, the as-synthesized AuNP@ITO TR yolk@shell structures feature high and durable activity for CO electrooxidation. Considering that these highly complex metal@metal oxide yolk@shell structures are simply obtained by mixing three components in solution, i.e., a metal affine amphiphilic block copolymer; a hydrophobic, hydrated, and acidic metal precursor; and a hydrophobic alkoxylic hydrolysis prone oxide precursor—our approach offers an easy and scalable synthetic pathway for metal@metal oxide yolk@shell nanomaterials with potential applications in catalysis and other energy-related applications.

4. Experimental Section

**Materials:** Tetrachloroauric (III) acid (HAuCl₄·3H₂O, Roth) was used as received and stored in a dry glove box (<1 ppm H₂O, <1 ppm O₂). Polystyrene-block-poly(4-vinylpyridine), PS₁₁₁₁-b-P₄V₄P₉₀ and PS₁₃₅₅-b-P₄V₄P₁₇ were synthesized in the group of Prof. Helmut Schlaad as reported in literature by sequential anionic polymerization of styrene and 4-vinylpyridine (initiator: sec-butyllithium/LiCl, solvent: THF, –78 °C).[20,45] The molar ratios S:4VP were determined by ¹H-NMR (CDCl₃) and the number- and weight-average molar masses were determined by size exclusion chromatography (THF, PS calibration) and are listed in Table 1.

**Synthesis of ITO TR:** The heterobimetallic single source precursor ITBO was synthesized as previously reported.[21,22] Briefly, to a suspension of InBr in anhydrous toluene a concentrated solution of Na(OBu)₃Sn in toluene was added under vigorous stirring. The reaction mixture was refluxed at 110 °C for 48 h. After cooling to room temperature, insoluble by-products were removed by filtration. The solvent of the filtrated solution was removed under vacuum and the obtained white product was recrystallized in pentane and stored at –24 °C. The obtained precursor was characterized by ¹H-NMR (CDCl₃ 200.13 MHz, δ = 1.36 ppm [1s, 27 H, OC(CH₃)₃]) and ¹¹Sn-NMR spectroscopy (CDCl₃ 149.21 MHz, δ = –78 ppm).

**Synthesis of Mesoporous ITO TR Thin Films with One AuNP Per Pore:** For the preparation of mesoporous ITO TR thin films loaded with one AuNP per pore, a stock solution of PS-b-P4VP with a concentration of 5 mg mL⁻¹ was prepared by dissolving the corresponding amount of PS-b-P4VP in anhydrous toluene. After 20 min of stirring, 1 mL of this solution was added to 1.6 mg of HAuCl₄·3H₂O (0.2 eq. HAuCl₄·3H₂O per pyridine unit, HAuCl₄·0.2@PS-b-P4VP). The resulting solution was stirred for 12 h to ensure a homogeneous loading. After that, 1 mL of this solution was added to 25 mg of solid ITO SO that n(HAuCl₄)/(n(ITBO) = 0.07. The solution was spin-coated (spinning speed between 3000 and 6000 rpm) on selected substrates (Si wafers, glass, or ITO-coated glass substrates). The obtained films were dried for 1 h inside the glovebox prior to calcination in air at 400 °C for 2 h (heating rate: 5 °C min⁻¹) and in reducing atmosphere (10% H₂, 90% N₂, 300 °C, 90 min).

**Synthesis of AuNP@ITO TR Yolk@Shell Based Thin Films:** For the preparation of HAuCl₄(X)@PSₙₙₙₙ-b-P₄V₄Pₙ₉₀, first a stock solution of PSₙₙₙₙ-b-P₄V₄Pₙ₉₀ (30 mg mL⁻¹) was prepared in anhydrous toluene. For a gold precursor loading of X eq. per pyridine unit, 1 mL of the previous PSₙₙₙₙ-b-P₄V₄Pₙ₉₀ stock solution was added to the appropriate amount of HAuCl₄·3H₂O (see Table 2). After addition, the resulting solution (HAuCl₄(X)@PSₙₙₙₙ-b-P₄V₄Pₙ₉₀) was stirred for 12 h to ensure a homogeneous loading of the metal precursor throughout the micellar solution. Note: The HAuCl₄(X)@PSₙₙₙₙ-b-P₄V₄Pₙ₉₀ solutions have to be used in less than 48 h to obtain reproducible results. For the preparation of Au(X)@ITO TR thin films, 1 mL of the respective HAuCl₄(X)@PSₙₙₙₙ-b-P₄V₄Pₙ₉₀ was added to 60 mg of ITO (ITO/Au(X)@PS₁₁₁₁-b-P₄V₄P₉₀). Prior addition, ITO, which is stored at –20 °C, is warmed to room temperature. After addition, the ITO/HAuCl₄(X)@PSₙₙₙₙ-b-P₄V₄Pₙ₉₀ mixture was stirred for 10 min at room temperature. The resulting brown viscous ITO/HAuCl₄(X)@PSₙₙₙₙ-b-P₄V₄Pₙ₉₀ solution was then spin-coated on selected substrates (spinning speed: between 3000 and 6000 rpm, substrates: Si wafers, glass, or ITO-coated glass substrates (Aldrich)). The obtained films, once dried, were then directly calcined under air for 2 h (heating ramp 5 °C min⁻¹). Finally, in order to increase the conductivity, the films were calcined under reducing atmosphere (in 10% H₂, 90% N₂, 300 °C, 90 min).

**Synthesis of Au0.6b@ITO TR Yolk@Shell Based Bilayers:** For the preparation of Au0.6b@ITO TR yolk@shell based bilayers, the same procedure was applied. The concentration of polymer was adjusted to 10 mg mL⁻¹ instead of 30 mg mL⁻¹. The amount of gold was consequently adjusted (see Table 3).

**Characterization Methods:** NMR spectroscopy was performed on an ARX 200 (¹H 200 MHz) and an ARX 400 (¹H 400 MHz, ¹¹Sn)

| Table 2. Mass of HAuCl₄·3H₂O to be added to 1 mL of 30 mg mL⁻¹ PS₁₁₁₁-b-P₄V₄P₉₀ micellar solution. |
|-------------------------------------------------|-------|-------|
| HAuCl₄·3H₂O eq. per pyridine unit               | 0.3   | 0.6   |
| HAuCl₄·3H₂O mass [mg] to be added to 1 mL of    | 14.4  | 28.8  |
| 30 mg mL⁻¹ PS₁₁₁₁-b-P₄V₄P₉₀ solution            |       |       |
| HAuCl₄·3H₂O mass [mg] to be added to 1 mL of    | –     | 36.0  |
| 30 mg mL⁻¹ PS₁₁₁₁-b-P₄V₄P₉₀ solution            |       |       |

| Table 3. Mass of HAuCl₄·3H₂O to be added to 1 mL of PS₁₁₁₁-b-P₄V₄P₉₀ micellar solution with a concentration of 10 mg mL⁻¹. |
|-------------------------------------------------|-------|-------|
| HAuCl₄·3H₂O eq. per pyridine unit               | 0.3   | 0.6   |
| HAuCl₄·3H₂O mass [mg] to be added to 1 mL of    | 4.8   | 9.6   |
| 5 mg mL⁻¹ PS₁₁₁₁-b-P₄V₄P₉₀ solution             |       |       |
149.21 MHz spectrometer from Bruker. UV–vis spectroscopy was performed in transmission on a Perkin-Lambda 20 spectrometer under inert atmosphere using a quartz glass cuvette as sample holder.

Time-dependent Maxwell equations were solved by numerical finite difference time domain (FDTD) simulations. Au/ITO yolk@shell structures were assumed to be illuminated by polarized light in the spectral range between 400 and 800 nm. The 3D geometry consisted of ITO spheres of radius \( r = 20 \) nm containing six Au spheres of radius \( r = 3 \) nm each. The index of refraction of ITO was set to \( n = 1.93 \) in the considered spectral range. Corresponding data for Au were taken from the CRC Handbook of Chemistry and Physics.

XRD was carried out with a Bruker-AXS D8 Advanced diffractometer with a DAVINCI design using CuKα radiation (\( \lambda = 1.5418 \) Å) and a LynxEye detector or at the high energy material science (HEMS) P07 side station beamline of the DORIS III synchrotron source at the DESY facility (Hamburg, Germany). The synchrotron measurements were made with a sample-to-detector distance of 930.8 mm, at a photon energy of 53.7 keV (i.e., \( \lambda = 2.3088 \) Å), and with a single-photon counting pixel detector MAR345 (image plate).

Krypton sorption isotherms were measured at 77 K using a QuantaChrome Instrument ASI-C-11. The film samples were degassed under vacuum at 150 °C for 6 h prior measurement. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method.

SAXS was conducted at the B1 beamline of the DORIS III synchrotron source and at the P03 beamline at PETRA III at synchrotron at DESY (Hamburg, Germany). The data were normalized to absolute intensity scale using a glassy carbon reference. At the B1 beamline of the DORIS III synchrotron source, measurements were made with a sample-to-detector distance of 3.6 m, at a photon energy of 11.5 keV (\( \lambda = 1.08 \) Å), and with a single-photon counting pixel detector Pilatus 1M (Dectris). At the P03 beamline at PETRA III at the synchrotron at DESY (Hamburg, Germany). The synchrotron measurements were made with a sample-to-detector distance of 3.95 m, at a photon energy of 13 keV (\( \lambda = 0.9575 \) Å), and with a Pilatus 300k (Dectris) pixel detector. The collected 2D images were azimuthally integrated to 1D curves, corrected for sample transmission and background scattering. The quartz capillaries used for solution measurements were filled and sealed in a glove box and stored on dry ice prior measurements. The polymer concentration was kept constant (5 mg mL<sup>-1</sup>.

ASAXS was conducted at the B1 beamline of the DORIS III synchrotron source. The ASAXS curves were recorded at three different energies in close vicinity of the Au L₁ absorption edge (\( \lambda_{\text{Au} L_1}, E_{\text{Au} L_1} = 11 919 \) eV, \( E_1 = 11 527 \) eV, \( E_2 = 11 873 \) eV, and \( E_3 = 11 915 \) eV). The sample-to-detector distance was 3.6 m and the total measurement time was about 120 s for each sample. Briefly, the scattering length density \( \rho \) of an atom depends on the atomic scattering factor \( f(E) \), which at low scattering angles can be expressed by

\[
    f(E) = Z + f' (E) + f'' (E) \quad (3)
\]

where \( E \) is the energy, \( Z \) the atomic number, and \( f' \) and \( f'' \) anomalous scattering coefficients, which change rapidly close to an absorption edge of an element. More details can be found in the Supporting Information.

**Evaluation of the SAXS Data:** Data analysis was done using SASFit.[11] In the case of spherical micelles (PS<sub>111</sub>-b-P4VP<sub>96</sub>) the SAXS curves were analyzed with a spherical core-shell model, assuming a spherical shape of the micelles, a core–shell distribution of the electron density, and a Schultz–Zimm size distribution \((D_2)\). The respective form factor \( F_{CG} \), i.e., spherical shell (iii), was used as defined in the SASFit package[22] (see details in the Supporting Information).

In the case of worm-like micelles (PS<sub>111</sub>-b-P4VP<sub>96</sub>) no data fitting was performed. Instead, a Guinier analysis was performed. The radius of gyration of the transversal cross section, \( R_c \), was determined from the slope of the Guinier plot in which \( lnn(q) vs q^2 \) is plotted versus \( q^2 \).

\[
    lnn(q) = \frac{l(0)}{q} - \exp \left( -\frac{q R_c^2}{2} \right) \quad (4)
\]

\( R_c \) was determined from the slope of the Guinier plot in which \( lnn(q) vs q^2 \) is plotted versus \( q^2 \).

**X-Ray Absorption Near Edge Spectroscopy (XANES):** XAS Sample Preparation: Solid reference \( \text{In(III)}(\text{OBr})_2 \) and \( \text{Sn(II)}(\text{OBr})_2 \) powders were diluted with boron nitride (Sigma Aldrich Chemie GmbH Munich, GERMANY) in a mass ratio of 1:10. A custom-made mount made of a 3 mm thick polyoxometalate (POM) sheet with a 0.5 × 1.5 cm<sup>2</sup> window through which the samples are accessible for the X-rays was specially designed as sample holder. To contain the samples, the window was sealed from both sides with a single layer of Kapton foil (0.013 mm, Goodfellows GmbH, Bad Nauheim, GERMANY) using a one-component adhesive sealant (Sinus Electronic TSE399C, Bad Wimpfen, GERMANY) for fixation. ITBO solutions were prepared in toluene at a concentration of 10 × 10<sup>-3</sup> M. For measurements 200 µL of each solution made of 1 mmol in the volume defined by the two Kapton sealed windows of the sample holder. Once sealed the sample was removed from the glove box and promptly frozen in liquid nitrogen in which it was stored until the measurements.

**XAS Measurements:** The XAS measurements at the indium and tin L-edges were performed at the KMC-1 bending magnet beamline of the Helmholtz-Zentrum Berlin for Materials and Energy (formerly BESSY II, Berlin). The beamline optics and beam characteristics are discussed elsewhere.[49] The specifications of the used setup developed by the group of Prof. H. Dau are already well described.[50,51] The excitation energies (scan range 3623–4530 eV for indium and tin) were selected by a double-crystal monochromator (Si-111). An energy-resolving fluorescence detector with 13 Ge elements (Ultra-LEGE detectors, Canberra GmbH) was employed. Indium and tin edges were recorded simultaneously (LTb and LTb emission of tin, LTc emission of indium).

Details about data extraction are provided in Figure S14 (Supporting Information).

XPS measurements were carried out using an ultrahigh vacuum system from SPECS, Germany. Photoelectrons were excited by an MgKα X-ray source of 1253.6 eV excitation energy.

TEM and EDX measurements were performed on a Tecnai G² 20 S-TWIN electron microscope operated at 200 kV, equipped with an EDAX EDX system (Si(Li) SUTW detector, energy resolution of 136 eV (for MnKα)). For sample preparation, a drop of diluted solution was deposited onto selected TEM grids (i.e., carbon-coated copper grids or thermally stable silicon nitride membrane grids for calcination studies). After solution adsorption on the grid surface, the excess of solution was removed from the grid with a filter paper, leaving behind a micellar monolayer. For TEM investigations of the nanoparticle growth, the silicon nitride grids were calcined at different temperatures. For investigations of the films after calcination, bits of the films were scraped off the substrate and transferred onto a carbon-coated copper grid.

SEM was performed using a FEI 39010 electron microscope equipped with an in-lens secondary electron detector. Image J (Version 1.39x) was employed to determine the lateral conductivity.

Conductivity measurements were performed by four-point probe measurements at room temperature with a resistivity meter Loresta-GP model MCP-T610, PSP 1.5 mm from Mitsubishi Chemical Analytical. The specific resistivity (Ω cm) of the films was calculated by multiplying the sheet resistance (Ω<sup>2</sup> cm<sup>-1</sup>) by the film thickness. Undoped Si wafers (225 µm, (100), 20 000 Ω cm) were chosen as nonconductive substrates. For the conductivity measurements, the yolk–shell based thin films were deposited onto nonconductive Si wafers, previously coated with an ultra thin tin-rich ITO layer (10 nm) to improve the adhesion and ensure lateral conductivity.

Electrochemical measurements were performed with a rotating disk electrode (RDE) setup in a three-compartment electrochemical glass cell equipped with a Luggin capillary and glass frit separating the working and counter electrode compartments. A reversible hydrogen electrode (RHE) (Caskatel), immersed in the same electrolyte, served as reference and a platinum mesh as counter electrode. The 0.1 M NaOH electrolyte was prepared from sodium hydroxide (Sigma-Aldrich, 99.99%) and...
ultrapure water (18 MΩ cm at room temperature). The potential was controlled with an SP-200 potentiostat (BioLogic). For the experiments, the Au(0.6)_{SPIP@TiO_{2} yolk@shell} thin film (a bilayer) was coated on the abutting face of a previously polished and cleaned glassy carbon cylinder (5 mm diameter), which was then mounted into an RDE tip (Teflon) (Pine Research Instrumentation) and connected to the RDE setup described above. The electrode was cycled in the N₂ saturated electrolyte between 0.75 and 1.65 V_RHE (30 cycles). Subsequently, the electrolyte was bubbled with CO (15 min) while the electrode potential was set to 1.2 V_RHE. Thereafter, CV was measured with 5 mV s⁻¹. The initial cycling in N₂ saturated electrolyte was conducted without rotation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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