Communication

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Complexation-induced phase separation: preparation of composite membranes with a nanometer-thin dense skin loaded with metal ions

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GRAPHICAL ABSTRACT

ABSTRACT

We present the development of a facile phase-inversion method for forming asymmetric membranes with a precise high metal ion loading capacity in only the dense layer. The approach combines the use of macromolecule-metal intermolecular complexes to form the dense layer of asymmetric membranes with nonsolvent-induced phase separation to form the porous support. This allows the independent optimization of both the dense layer and porous support while

maintaining the simplicity of a phase-inversion process. Moreover, it facilitates control over (i) the thickness of the dense layer throughout several orders of magnitude—from less than 15 nm to more than 6 μm , (ii) the type and amount of metal ions loaded in the dense layer, (iii) the morphology of the membrane surface, and (iv) the porosity and structure of the support. This simple and scalable process provides a new platform for building multifunctional membranes with a high loading of well-dispersed metal ions in the dense layer.

KEYWORDS: phase inversion, asymmetric membrane, macromolecule-metal complex, dense layer, metal ion, chelating polymer

TEXT

Membranes fabricated via phase inversion dominate the current market due to the simplicity and scalability of the process.¹⁻⁴ In some cases, composite membranes with complex fabrication processes, where the porous support and dense layer must be made in different steps, are justified (e.g., when the raw materials are expensive⁵ or when such membranes have superior performance⁶). Nonetheless, most high-performance membranes found in scientific literature have not succeeded commercially because of the complexity of their fabrication processes or the inefficient use of expensive materials. Therefore, simple ways to make complex membranes are highly desirable to close the gap between lab-scale and commercially successful membranes.

Complexation-induced phase separation (CIPS) is a new and simple approach to fabricate complex membranes with a different set of properties. All prior phase-separation techniques used to form membranes have one thing in common: they work by changing the conditions around the

polymer chains, making them insoluble, and provoking a phase separation.^{7, 8} Phase separation is induced by a change in temperature,⁹ a decrease in solvent concentration,¹⁰ or the addition of a nonsolvent to the system.¹¹ Alternatively, complexation-induced phase separation works by crosslinking polymer chains via the intermolecular complexation of polymer chains with metal ions, making them insoluble in the original solvent.

It is well established that phase separation in a polymer solution can occur if sufficient crosslinks are formed.¹² Crosslinks form when metal ions form stable intermolecular complexes with polymer chains. In this case, the coordination of several polymer chains to the same metal ion causes a phase separation.¹³ So far, this technique has been used to produce reversible gels,¹⁴ but not yet to precipitate a desired solid polymer structure out of solution. CIPS uses this approach to precipitate out a dense layer of an asymmetric membrane from a polymer solution. The precipitation is site-specific, fast, smooth, and easy to control, hence there is great flexibility for tailoring the final product. The combination of CIPS with nonsolvent-induced phase separation (NIPS) to form the porous support of a membrane is the first method capable of fabricating thin-film composite membranes by a phase-inversion process.

CIPS produces asymmetric membranes with a well-defined interface between the dense layer and the porous support beneath it (Figure 1). The top dense layer consists of densely packed polymer chains that form coordination complexes with metal ions (polymer-metal complexes); the porous support is formed by only polymer chains (there are no metal ions present). CIPS is advantageous because the thickness of the dense layer can easily be controlled and a high concentration of metal ions can be precisely and homogeneously incorporated in it, preventing them from entering the porous support. The thickness of the dense layer can be controlled over several orders of magnitude, from less than 15 nm to a few micrometers (Figure S2 and S3). The

incorporation of such a large number of well-dispersed metal ions into the dense membrane layer is inspiring for application in areas such as facilitated transport, fouling control, or catalysis.

Figure 1. Cross-sections of a PTU membrane prepared by CIPS. The dense layer contains 27 wt. % of palladium and has a thickness of 186 ± 4 nm.

CIPS consists of three simple steps: (i) a thin film is cast with the polymer solution (polymer + solvent A); (ii) the polymer solution film is immersed in solvent A, which contains a low concentration of polymer-complexing metal ions; and (iii) the skinned film is transferred to a nonsolvent bath. The second step is the key step, where the polymer chains on the top layer of the viscous polymer solution film form intermolecular complexes with the metal ions (crosslinks) that swiftly phase separate to form a dense layer that floats on top of the remaining viscous polymer solution film. This dense layer acts as a barrier, delaying the diffusion of metal ions to the remaining polymer solution beneath it, resulting in the rapid formation of a dense film (less than one second) that thickens more slowly. By changing the type of metal ion, metal concentration, and contact time, the metal loading and thickness of the dense layer can be controlled. Finally, in the third step the remaining polymer solution below the dense layer is precipitated by solvent/nonsolvent exchange to form a porous support.

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3 Gelation by physical associations has proven to be a key phase in the formation of the thin
4 dense top layer present in asymmetric membranes prepared by phase inversion.^{8, 16-18} During
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8 gelation, several connections between polymeric chains occur, forming a three-dimensional
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10 network that becomes the dense layer later in the process. CIPS is the first technique to use
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12 chemical associations instead of physical associations to form the dense top layer of asymmetric
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14 membranes prepared via phase inversion. Chemical associations are stronger and they offer more
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16 options to tune the morphology and final properties of the membrane (e.g. reaction time, nature
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18 and concentration of reactant). Moreover, the fabrication of the dense layer is completely
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20 separated from the development of the porous support, during which the simplicity of a phase-
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22 inversion process is maintained.
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27 The CIPS process requires (i) a polymer able to form complexes with metal ions and (ii) a
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29 solvent for the first bath (the second step of the process) that does not cause phase separation of
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31 the polymer solution and that can dissolve the desired metal salt. The obvious choice is to use the
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33 same solvent used to prepare the polymer solution if that solvent can dissolve the desired metal
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35 salts.
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39 So far CIPS has been tested successfully with two polymers: poly-thiosemicarbazide (PTSC)
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41 and poly-thiourea (PTU); their structures are depicted in Figure 2 and the synthesis procedure
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43 and characterization is presented in the supporting information. Both of these polymers can form
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45 strong complexes with several transition metal ions through the sulfur-containing groups in their
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47 backbones (thiosemicarbazide and thiourea groups, respectively).¹⁹⁻²¹
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Figure 2. The chemical structures of the two polymers used in this study.

Polymer solutions of 15 wt.% in dimethyl sulfoxide (DMSO) were used to prepare the membranes (unless otherwise specified). All casting solutions were sonicated prior to being used to eliminate gas bubbles. The polymer solutions were cast either on a polyester nonwoven support or on a glass plate using a doctor blade with a 200 μm gap. Next, the films were immersed for certain time in a bath of a metal salt dissolved in DMSO. Finally, the resulting viscous polymer solution film with a solid dense layer floating on top of it was carefully transferred to a nonsolvent bath consisting of water, isopropanol (iPrOH), or a mixture of both. Water was used for this step unless otherwise specified.

PTSC contains two thiosemicarbazide groups in each monomeric unit that can form quite stable chelates with a variety of metal ions²⁰. In the case of PTU the two thiourea groups present in each monomeric unit contain two nitrogen and one sulfur atoms all of which provide potential coordination sites. However coordination through sulfur is favored.²²⁻²⁴ Contrary to PTSC, where chelates are formed upon complexation with metal ions, thiourea groups in PTU act as unidentate ligands. Both of the functional groups, thiourea and thiosemicarbazide, belong to the soft bases category of Pearson's hard soft acids bases (HSAB) principle.²⁵ These functional groups react faster and form more stable complexes with soft acids than with hard acids. For this reason, the use of metal ions classified as soft acids was expected to enhance the formation of the

dense layer during the second step. True to our prediction, soft metal ions like Ag^+ and Pd^{2+} produced thinner dense layers compared with borderline metal ions like Co^{2+} , Ni^{2+} , Cu^{2+} . Meanwhile, the use of metal salts containing hard metal ions that react weakly and slowly with the functional groups of the polymer did not form a dense layer. Figure 3a illustrates that for the same experimental conditions using metal salts with the same counter ion, the HSAB principle helps to predict the trend in dense layer thickness for both polymers. Pd^{2+} , the softer metal ion of these series, generated the thinnest dense layers with a thickness of 186 ± 4 nm and 250 ± 5 nm for PTU and PTSC, respectively. Thicker dense layers were obtained using harder metal ions to the point that no dense layer formed at all using Fe^{2+} , the hardest metal ion investigated, nor did it for many of the hard metal ions tested. Interestingly, Co^{2+} , the hardest of the borderline acids tested, did not form a dense layer with the PTU polymer.

Figure 3 illustrates that polymer concentration in the casting solution had a negligible effect on the thickness of the dense layer. However, it is important to use a polymer concentration high enough to favor the formation of intermolecular complexes (crosslinks).²⁶ A concentrated polymer solution with a high density of entanglements will increase the chances of forming intermolecular complexes over intramolecular ones. This is because of the higher probability that functional groups from different chains will be closer together than those from the same macromolecule. Steric effects (i.e., the position of the donor atom) can also strongly influence the formation of intermolecular versus intramolecular complexes.²⁷

Figure 3. The effect of metal salt type, concentration, and immersion time on dense layer thickness. a) PTU and PTSC solution films immersed for 5 seconds in 10 mM solutions of metal acetate salts in DMSO, b) PTU solution films with different polymer concentrations immersed for 5 seconds in a 10 mM solutions of $\text{Pd}(\text{OAc})_2$ in DMSO, c) PTSC solution films immersed for different times in 10 mM solutions of metal salts in DMSO, and d) PTU solution films immersed for 5 seconds in different concentrations of $\text{Pd}(\text{OAc})_2$ and $\text{Cu}(\text{OAc})_2$ in DMSO.

The amount of time the film spent in the solution containing the metal ions had a strong influence on the thickness of the dense layer; shorter contact times resulted in thinner dense layers. Figure 3c gives a summary of the change in layer thickness as a function of immersion time for different metal salts. Curiously, a minimal increase in dense layer thickness was observed between 5 and 20 seconds for all metals. We propose a time lag exists between the formation of the dense layer and its growth, during which the metal ions diffuse through the newly formed barrier and continue crosslinking with more polymer chains beneath it.

Concentration of metal ions also strongly influenced the formation of the dense layer such that lower concentrations produced thinner dense layers: an extremely low concentration of metal ions failed to form any dense layer. Figure 3d shows how PTU solution films immersed in different concentrations of two different metals only formed a dense layer at the lowest $\text{Pd}(\text{OAc})_2$ concentration (2.5 mM); this is the metal salt with the softest metal ion. Copper metal salt did not form a dense layer because the interaction between copper ions and the functional groups of the polymer was not strong or fast enough at such low concentrations. Figure 4 illustrates a comprehensive series of SEM images that show the effect of immersion time and metal salt concentration on dense layer thickness. Any desired thickness within the range presented can easily be obtained by choosing a suitable combination of these two parameters.

The kinetics of the complexation reaction and the stability of the complexes formed also affected the morphology of the membrane's surface. High concentrations of softer metal ions resulted in faster reactions and more stable complexes that ended up producing smoother surfaces (Figures 5c and 5d). On the other hand, harder metal ions or a low concentration of soft metal ions result in slower reactions that produce rough surfaces consisting of a layer of interlinked nodules and an underlying dense layer. A plausible explanation for this is the presence of a transition zone, where competition exists between polymer chains that are trying to escape to the bulk of the bath and metal ions that are forming crosslinks to secure them. The result is the appearance of an interconnected nodular structure that is observed with harder metal ions (Figures 5a and 5b) or a low concentration of soft metal ions (Figure 5e).

Figure 4. SEM cross-sections of membranes prepared via CIPS from a 15 wt.% PTSC in DMSO solution. Solutions of $\text{Cu}(\text{OAc})_2$ in DMSO were used for the first bath for all treatments. The values on the arrows correspond to the metal salt concentration and immersion time used to prepare the imaged membrane.

Figure 5. Surface SEM images of membranes prepared by CIPS from a 15 wt.% PTU in DMSO solution and treated for their first bath by immersed for 5 seconds in a) a 10 mM solution of $\text{Ni}(\text{OAc})_2$ in DMSO, b) a 10 mM solution of $\text{Cu}(\text{OAc})_2$ in DMSO, c) a 10 mM solution of $\text{Pd}(\text{OAc})_2$ in DMSO, d) a 5 mM solution of $\text{Pd}(\text{OAc})_2$ in DMSO; and e) a 2.5 mM solution of $\text{Pd}(\text{OAc})_2$ in DMSO.

The dense layer of membranes prepared using CIPS is solvent-stable due to the abundance of crosslinks. Submerging the membranes in a good solvent for the polymer (DMSO) caused the porous support to dissolve readily and the solvent-stable dense layer to float alone in the solution. In fact, even after one month of immersion in DMSO, the dense layer failed to dissolve. A significant amount of palladium-rich dense layer was collected by dissolving the support of several PTU membranes containing 23 wt.% loading of palladium (by XPS) in its dense layer. The dense layer was washed with ethanol to remove the remaining solvent and dried before being studied. DSC analysis on a portion of the isolated dense layer evidenced the presence of crosslinks by showing the disappearance of thermodynamic transitions that are present in the unmodified polymer before its degradation temperature at around 200 °C (Figure S7). Another portion of the isolated palladium-rich dense layer was digested in aqua regia with a microwave digestion system, diluted to 20 ml, and analyzed with an ICP-OES. The palladium loading measured was 20 wt.%, corroborating the information obtained by XPS.

Membranes produced by CIPS had a homogenous distribution of metal ions only in their dense layer. To verify this, the dense layer was carefully peeled off and the exposed porous support was analyzed by XPS, revealing absolutely no metal ions (Figure S8). Additionally, XPS analyses in ten different locations of the membrane's dense layer confirmed the homogeneous distribution of metal ions throughout.

The loading of metal ions in the dense layer varied depending on the metal salt used and its concentration in the DMSO solution. As expected, the use of softer metal ions, which interact strongly with the functional groups of the polymer, gave higher metal ion loadings. PTU membranes prepared using Pd^{2+} , Cu^{2+} , and Ni^{2+} under the same experimental conditions (10 mM metal acetate in DMSO and an immersion time of 5 seconds) yielded metal loadings of 27 wt.%,

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3 10 wt.%, and 4 wt.%, respectively. Moreover, when the concentration of Pd(OAc)₂ was reduced
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5 from 10 mM to 5mM and then to 2.5 mM the loading of metal ions in the dense layer decreased
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7 accordingly from 27 wt.% to 23 wt.% and 14 wt.%, respectively. Control over the amount of
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9 metal loaded in the dense layer is possible by choosing the appropriate concentration of metal
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11 salt in the first bath.
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15 This work demonstrates that by choosing suitable conditions for the first bath of the CIPS
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17 process, control over the loading of metal ions and the roughness and thickness of the dense
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19 layer of asymmetric membranes can be achieved. Additionally, by adjusting the conditions in the
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21 second bath, the nonsolvent bath, it is possible to have control over the structure of the support.
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23 When water was used as the nonsolvent, a very porous support with finger-like macrovoids was
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25 produced that covered the entire structure. By changing the nonsolvent to iPrOH, for which
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27 DMSO has less affinity, a support with a close-pore structure and an additional dense layer
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29 below the metal-rich one was produced. Moreover, intermediate structures were obtained from
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31 different ratios of these two nonsolvents. For example, increasing iPrOH concentration caused
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33 the macrovoids to decrease in size until a sponge-like macrovoid-free porous support was
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35 achieved at 95 wt.% iPrOH. SEM images of PTU membranes with a palladium-rich dense layer
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37 and different support morphologies are depicted in Figure 6. Previous works report on techniques
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39 for controlling the structure of polymers precipitated via NIPS.^{7, 8} However, because the dense
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41 layer and the porous support are made in different steps using CIPS, each can be independently
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43 optimized. These tools allow the structure of the support to be constructed with characteristics
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45 that are optimal for a desired application.
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Figure 6. Cross-section SEM images of palladium-rich PTU membranes prepared by CIPS with different porous support morphologies. The conditions of the first bath were the same for all treatments: 5 seconds in a 10 mM solution of Pd(OAc)₂ in DMSO. The second bath consisted of a mixture of water and isopropanol with the following weight ratios (H₂O:IPrOH): a) 100:0, b) 30:70, c) 20:80, d) 10:90, e) 5:95, and f) 0:100. Insets show high-magnification images of each corresponding palladium-rich dense layer. The scale bars represent 1 μm in the main images and 200 nm in the insets.

The selectivity and flux of membranes prepared via CIPS were evaluated to verify that a large and continuous area of metal-rich layer could be achieved. Using a dead-end pressurized stirred cell, the water flux, toluene flux, and dyes rejection was determined for several membranes. PTU membranes with a nickel-rich dense layer of 482 ± 12 nm and a copper-rich dense layer of 436 ± 10 nm had water permeances of 0.005 ± 0.001 and 0.010 ± 0.002 Lm⁻² h⁻¹ bar⁻¹, respectively, with rejections greater than 99% for safranin (MW=350.84, positive charge) and brilliant blue R250 (MW=825.99, negative charge). Expected results were obtained when the copper-rich membrane was further tested with toluene and protoporphyrin IX dimethyl ester (MW=590.71, neutral charge); toluene permeance was higher than that of protoporphyrin IX dimethyl ester

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3 because the hydrophobic nature of the material, reached a value of $0.033 \pm 0.004 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$
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5 with a rejection of $88 \pm 3\%$. Membranes with thinner dense layers achieved higher fluxes but
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7 small molecule rejection was compromised. A PTU membrane with a $186 \pm 4 \text{ nm}$ palladium-rich
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9 dense layer yielded a water permeance of $0.09 \pm 0.01 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and rejections of $87 \pm 3\%$
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11 and $98 \pm 1\%$ for safranin and brilliant blue R250, respectively. The dense layer of this type of
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13 handmade membrane created using CIPS has variable behavior because it has an insufficient
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15 number of defects (pores) to achieve high fluxes in liquid applications yet it has enough defects
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17 to limit gas applications, unless an additional treatment is performed to plug the defects. Fine-
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19 tuning the preparation conditions can optimize the performance of such membranes. For
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21 example, the addition of 10 wt.% polyethylene glycol 400, a water-soluble (pore former)
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23 molecule,^{28, 29} to the casting solution caused a 90-fold increase in the water permeance of PTU
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25 membranes with a copper-rich dense layer—from 0.010 ± 0.002 to $0.9 \pm 0.2 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$.
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27 Aforesaid membranes retained a high brilliant blue R250 rejection (99%) of the unmodified
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29 membranes but lost some of the rejection for safranin ($80 \pm 1\%$). Further investigations in this
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31 direction, those to increase the number of defects (pores) or to completely eliminate them, are
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33 necessary to develop the ideal membrane for a particular application.
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41 Here we have validated the CIPS process for two polymers, one with thiourea units and
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43 another with thiosemicarbazide units as the active functional groups for coordinating to metal
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45 ions. However, in principle the process shown here should be general and could be extended to
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47 other polymers containing functional groups able to form stable complexes with metal ions.
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49 Extension of the process to other materials should be done by carefully selecting the process
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51 conditions to promote a strong and fast complexation reaction. Initial screening from our part
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53 identified as promising candidates for the CIPS process polymers containing azole functional
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units either in the polymer's backbone or in its branches. We envision the use of this process for the fabrication of highly active catalytic membranes and efficient antifouling membranes due to the capability of loading a large amount of metal ions homogeneously in the top layer of the membranes.

In summary, this work illustrates a new method to prepare composite membranes using CIPS, which uses macromolecule-metal intermolecular complexes to form the dense layer of asymmetric membranes and nonsolvent-induced phase separation to form the porous support. Because the dense layer and the porous support are formed independently, while maintaining the simplicity of a phase-inversion process, the result is unprecedented control over the final structure of the membrane. Furthermore, CIPS allows for metal ions to be concentrated in only the dense layer and with the desired loading. The thickness and morphology of the dense layer as well as the porosity of the support can be closely controlled by manipulating simple parameters of the process. This facile method opens up fascinating possibilities for the fabrication of metal-rich polymeric membranes with different properties.

ASSOCIATED CONTENT

Supporting information

Experimental details; PTU and PTSC synthesis procedure and characterization; DSC analysis of an isolated PTU palladium-rich dense layer; additional SEM images of membranes made by the CIPS process; XPS results of the surface and porous support; and a video clip showing the CIPS processes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have approved the final version of the manuscript.

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