

Techno-Economic Analysis of Recycled Ionic Liquid Solvent Used in a Model Colloidal Platinum Nanoparticle Synthesis

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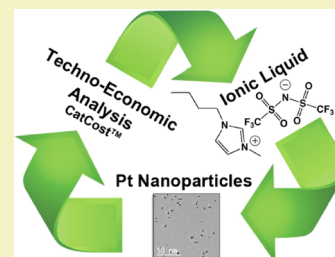
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Supporting Information

ABSTRACT: Ionic liquids have garnered significant attention over the past 20 years as alternatives to conventional volatile organic solvents because they are non-flammable, have negligible vapor pressures, possess high thermal and chemical stabilities, and can potentially be recycled. A more recent use of ionic liquids is their application as a solvent in the synthesis of colloidal inorganic nanoparticles; however, a major challenge in the adoption of ionic liquids is that they are generally more expensive than their traditional organic solvent counterparts. Herein, we provide insight into how recycling an ionic liquid solvent affects the product characteristics in a model colloidal platinum nanoparticle synthesis, the structure of the ionic liquid through each recycle, and the overall cost of nanoparticle fabrication using a techno-economic analysis. Using a standard ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM-NTf₂), as the solvent for a Pt nanoparticle synthesis, we demonstrate that the ionic liquid can be recovered and reused through multiple successive reactions following the initial reaction with virgin, or as-purchased, ionic liquid. The use of recycled ionic liquid does not cause any degradation in the product quality or change in nanoparticle morphology. Techno-economic analysis of this synthesis method revealed that, through ionic liquid recycling, nanoparticle preparation using BMIM-NTf₂ can achieve a cost that is not only competitive but also potentially lower than that of the conventional organic solvent, 1-octadecene.

KEYWORDS: nanoparticle, ionic liquid, solvent, recycling, techno-economic analysis



INTRODUCTION

While volatile organic compound (VOC) solvents, such as traditional organic solvents, are employed in many chemical processes and reactions, they have detrimental effects on the environment because of their emissions contributing to pollution when used for commercial and industrial processes.¹ Specifically, industrial processes that utilize organic solvents comprise the largest source of VOC emissions into the atmosphere, totaling close to 60% of U.S. pollutant emissions in 2014.² These VOC solvents are flammable and possess high vapor pressures, which make them not only environmental toxins but also workplace hazards; they are also challenging to recycle, resulting in large amounts of waste.^{3,4} One alternative class of solvents that has been widely studied as a sustainable replacement to VOC solvents is ionic liquids (ILs). Ionic liquids are molten salts, usually comprised of an organic cation and an inorganic or organic anion, that melt below 100 °C.⁵ There has been interest in utilizing ILs as alternatives to VOC solvents because of their many advantages over traditional organic solvents, namely, being non-flammable, having negligible vapor pressures (~10⁻¹⁰ Pa at 25 °C), possessing high thermal stability, and having the potential to be more easily recovered and recycled.^{6,7} The vast number of combinations of anions and cations that can be generated allows tailoring of IL properties, such as solubility, density, hydrophobicity, and viscosity.^{8,9} Finally, ILs are known to be rather chemically inert and display unique liquid–liquid phase

separation behaviors, which allow for both facile solvent recycling and simple extractive purification.¹⁰

A growing body of work has explored ILs as alternative solvents for the fabrication of colloidal inorganic nanoparticles. When employed in nanoparticle synthesis, the low interfacial tension in ILs tends to facilitate rapid nucleation, while their high dielectric constant and ionic charge help to stabilize nanoparticles and support high colloid concentrations.^{11–13} Recent studies have shown that structured solvation layering of the ions in ILs at the nanoparticle surface prevents agglomeration and ultimately aids in colloidal stabilization of the particles.^{14–19} However, the main issue in adapting and ultimately scaling ILs lies in the high cost of these solvents, which can exceed \$800/kg,²⁰ making many industrial-scale applications untenable. To some extent, the high prices for IL solvents can be attributed to the relatively small scales at which these solvents are currently produced;²¹ however, unless and until larger IL production volumes yield lower prices, IL applications must prove their value in the context of high purchase costs. As long as commercially available ILs are much

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more expensive than traditional organic solvents, the most promising pathway to economically feasible large-scale applications is IL recycling and reuse. Applications that can use and reuse ILs without a decrease in functionality may achieve cost competitiveness with their conventional counterparts while having the potential to greatly reduce the environmental footprint of nanoparticle synthesis compared to traditional organic solvents.^{20,21} While there have been several literature reports on the feasibility of IL solvent recycling for nanoparticle syntheses, many of these examples use organic solvents to extract and wash residual precursors from the IL solvent,^{22–25} potentially reducing the sustainability benefits. In addition, to date, there are no projections of the potential cost outcomes of using recycled ILs for industrially scaled nanoparticle fabrication.

For these reasons, we performed a techno-economic analysis of applying a standard IL, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM-NTf₂), as a replacement solvent in a model colloidal inorganic nanoparticle synthesis. We demonstrate that BMIM-NTf₂ matches the synthetic performance of a conventional high-boiling organic solvent used in nanoparticle syntheses (with respect to product yield, nanoparticle morphology, and crystallinity), but with the improved sustainability of IL solvents. Importantly, we demonstrated a method for recovery and reuse of BMIM-NTf₂ in subsequent nanoparticle syntheses via simple aqueous extractions to wash the IL between each reaction. Nanoparticles produced with the recycled IL exhibit an isolated yield, product quality, and estimated production cost that are similar to or better than those of a conventional synthesis using an organic solvent, 1-octadecene (ODE).

RESULTS AND DISCUSSION

The model colloidal Pt nanoparticle synthesis is based on a polyol reduction of K₂PtCl₄ by ethylene glycol in BMIM-NTf₂ with polyvinylpyrrolidone (PVP) as the stabilizing agent.²⁵ The reaction was heated to 150 °C for 15 min. The resulting Pt nanoparticles were then compared to those from a conventional reaction in which an equivalent volume of ODE was used in place of BMIM-NTf₂ with the reaction conditions being otherwise identical. ODE was selected because it is commonly used as a conventional once-through solvent in nanoparticle syntheses, including for Pt nanoparticle syntheses.²⁶ The reaction conditions are based on standard polyol reduction syntheses of Pt nanoparticles,^{27,28} and were not specifically optimized for either the BMIM-NTf₂ or ODE solvents; rather, the reaction conditions were kept identical, so a direct comparison could be made between the two solvents (vide infra). After quenching the reaction, the black solution was allowed to phase separate into the solvent layer (either BMIM-NTf₂ or ODE) and the Pt nanoparticle suspension dispersed in ethylene glycol. The Pt nanoparticles were isolated by standard workup and the BMIM-NTf₂ layer was separated and set aside for recycling.

Following phase separation, the BMIM-NTf₂ solvent was purified after the synthesis to remove residual ethylene glycol, PVP, precursor salts, and byproducts by washing the IL three times with equal volumes of water. We previously reported washing BMIM-NTf₂ with hexanes to remove the excess reducing agent.²⁵ However, for this procedure, we noted that the reagents (K₂PtCl₄ and PVP) are more soluble in water than hexanes; therefore, water offered both process efficiency and solvent sustainability benefits compared to using hexanes, a

VOC solvent. The purified BMIM-NTf₂ was dried under vacuum at 120 °C to remove residual water. Of the original IL volume, ~94% was recovered. Virgin BMIM-NTf₂ was added to make up the volume of the recovered and washed IL to maintain a constant reaction volume across all reactions; this mixture of 94% purified post-reaction BMIM-NTf₂ and 6% virgin BMIM-NTf₂ comprised the recycled IL solvent for the next reaction.

The Pt nanoparticle synthesis reaction was then performed with BMIM-NTf₂ that had been recycled (used in a reaction and then purified) between one and five additional times, and the results were compared to those using the virgin IL solvent (summarized in Table 1). The naming of samples is based on

Table 1. Summary of the Isolated Yield (%), Average Nanoparticle Size (nm)^a, and Standard Deviation about the Mean Diameter (%) for the Pt Nanoparticles Synthesized in Virgin, 1×, and 5× Recycled IL.

ionic liquid	isolated yield (%)	size (nm)	σ/d (%)
virgin	29	3.1	16
1× recycled	30	2.8	18
5× recycled	54	2.9	17

^aThe average nanoparticle sizes (nm) were determined based on TEM images using ImageJ, a pixel-counting software (*N* = 300).

how many cycles the solvent had completed at the start of the synthesis; for example, the 5× recycled IL sample describes the sixth sequential reaction using that solvent batch. Notably, the isolated yields increased from 29% for the first reaction using virgin IL to 30% for 1× recycled IL and reached 54% for 5× recycled IL. We hypothesized that the increase in isolated yield results from Pt being retained in the recycled IL, as it has been previously reported that imidazolium ILs can extract and bind Pt;^{29,30} indeed, there is a slight brown coloration of the recycled IL as compared to the colorless, virgin IL. The conclusion that the increase in yield results from Pt being carried over in the recycled IL is further consistent with data from inductively coupled plasma optical emission spectroscopy (ICP-OES) performed on the 1× and 5× recycled IL, where the Pt content in the recycled IL was found to increase from 519 to 826 ppm, respectively. Continued IL recycling past 5× resulted in isolated yields of 54 ± 1%. A simple consideration of the material balance of Pt with carryover between recycling steps suggests that an initial increase in isolated yield reaching a steady state is a characteristic of this system (see Supporting Information). While it has been proposed by others that process efficiency, and yield, for nanoparticle syntheses should account for size polydispersity, we do not include it in our analysis because the relative significance (or insignificance) of polydispersity is application dependent.³¹

Powder X-ray diffraction (XRD) analysis of the isolated nanoparticles confirmed the synthesis of phase pure face-centered cubic Pt nanoparticles throughout all experiments with recycled IL, which gave identical diffraction patterns (Figure 1). An average lattice parameter of *a* = 3.86 Å was calculated from these XRD patterns, which agrees with the lattice parameter for bulk Pt metal (PDF #00-004-0802). Scherrer analysis indicates an average grain size of ~2.5 nm. Transmission electron microscopy (TEM) analysis of the isolated Pt nanoparticles synthesized with virgin, 1× recycled, and 5× recycled IL reveals that the morphology of the particles remains quasispherical and consistently uniform (Figure 2).

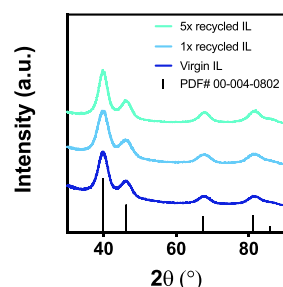


Figure 1. Powder XRD patterns of Pt nanoparticles synthesized in virgin IL, 1X recycled IL, and 5X recycled IL.

For each sample, 300 particles are analyzed, and the average particle diameters of Pt nanoparticles prepared in virgin, 1X recycled, and 5X recycled IL were 3.1 ± 0.5 , 2.8 ± 0.5 , and 2.9 ± 0.5 nm, respectively. The particle sizes and size dispersions are consistent and within experimental error.

The structure of the BMIM-NTf₂ solvent was tracked via solution ¹H and ¹⁹F NMR spectroscopy to assess the chemical stability of the IL during the recycling process. As shown in Figure 3, all of the major ¹H and ¹⁹F NMR resonances remain intact, indicating that there is no significant structural degradation of BMIM-NTf₂ during the recycling process. These observations indicate that the BMIM-NTf₂ solvent remains mostly unchanged during the Pt nanoparticle synthesis, even after being reused in five successive reactions.

For comparison, we also performed the synthesis with virgin, or as-purchased, ODE, which is a conventional high-boiling point organic solvent widely used in nanoparticle syntheses. Using identical reaction and recycling conditions to those employed for the IL, we attempted to purify and reuse ODE. The isolated yield of the Pt nanoparticles was 49% using virgin ODE. Powder XRD and TEM were used to characterize the resulting Pt nanoparticles, and solution ¹H NMR was used to characterize the recovered ODE after synthesis. The XRD pattern confirms the synthesis of phase pure Pt nanoparticles (Figure S1), similar to those synthesized in the IL, but slightly smaller in size. Scherrer analysis indicates an average grain size of ~ 2.0 nm. TEM analysis of the Pt nanoparticles synthesized in ODE returns an average particle size of 1.7 ± 0.3 nm ($N = 300$), and the nanoparticles were more agglomerated than what was observed for IL-synthesized particles (Figure S2). This can be attributed to the fact that ILs can stabilize colloidal nanoparticles (vide supra),^{7,12} reducing agglomeration. Indeed, while the FT-IR spectra of Pt nanoparticles synthesized in ODE and IL both exhibit characteristic bands from PVP, the spectrum of the IL-synthesized particles also exhibits diagnostic bands for both the BMIM cation and the NTf₂

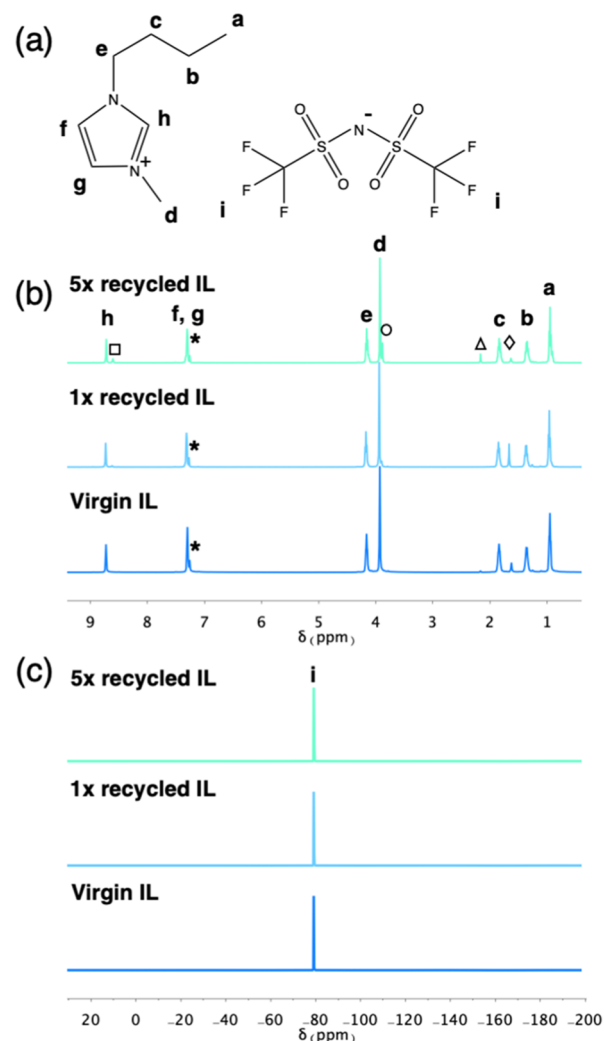


Figure 3. (a) Structure of BMIM-NTf₂ with labels corresponding to (b) ¹H NMR and (c) ¹⁹F NMR spectra of virgin, 1X, and 5X recycled IL solvent used in the Pt nanoparticle synthesis. The impurities in the ¹H spectra are water at 1.56 ppm, open diamond (◇); acetone at 2.17 ppm, open triangle (△); glycolic acid, which is oxidized ethylene glycol, at 3.88 ppm, open circle (○); and an unidentified imidazolium impurity at 8.60 ppm, open square (□). (Asterisks (*)) represent the residual solvent peaks from CDCl₃.

anion (Figure S4). Thermogravimetric analysis also revealed that the larger, IL-synthesized Pt particles possessed a larger surface organic content (94 wt %) than the smaller Pt nanoparticles synthesized in ODE (75 wt %).

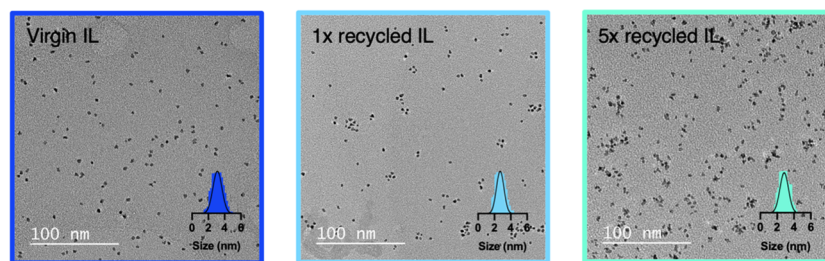


Figure 2. TEM images of Pt particles synthesized in virgin IL, 1X recycled IL, and 5X recycled IL. Size distributions are displayed as an inset for each image ($N = 300$).

Recycling ODE using the same procedure as described above for the IL proved to be infeasible and significant structural degradation of the ODE was observed by ^1H NMR after just one reaction (Figure 4). The vinylic proton

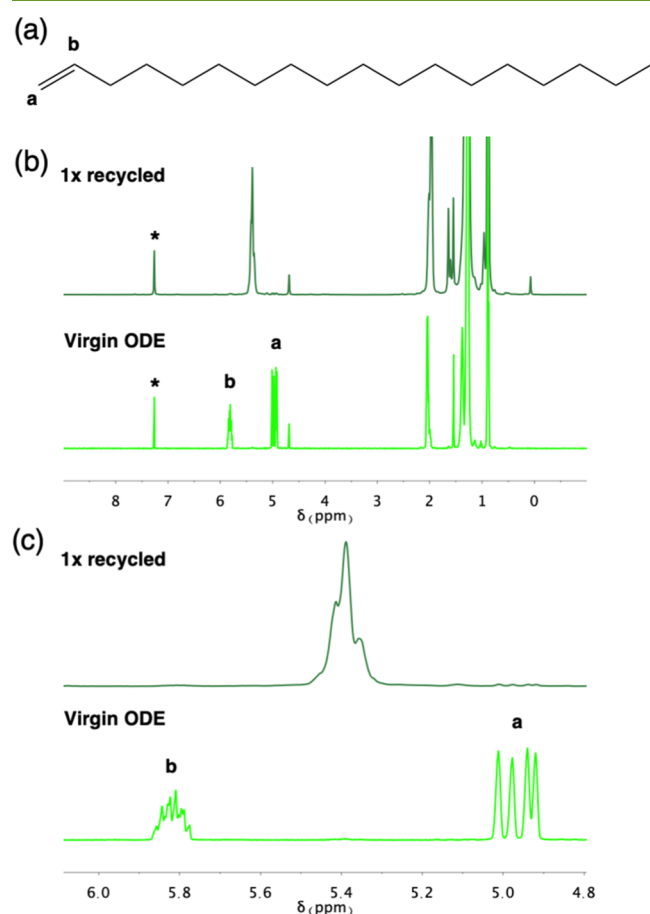


Figure 4. (a) Structure of ODE and (b) full ^1H NMR spectra of virgin and 1 $\times$ recycled ODE used in a Pt nanoparticle synthesis. (Asterisks (*) represent the residual solvent peaks from CDCl_3). (c) Vinylic region of ODE ^1H NMR spectra, highlighting a structural change occurring during the synthesis.

resonances of ODE (at 5.82 and 4.95 ppm) disappeared and a new set of resonances appeared at 5.39 ppm, corresponding to internal alkenyl protons. Furthermore, it was impossible to continue reusing and recycling the ODE following the procedure described above; when a Pt nanoparticle synthesis reaction was performed using the 1 $\times$ recycled ODE, the recycled ODE phase no longer separated from the ethylene glycol layer, complicating reaction workup and ODE recycling.

The observation that ODE is not chemically inert during high temperature nanoparticle synthesis and/or the purification conditions aligns with previous studies.³² It has also been shown that Pt(II) complexes can catalyze the isomerization of terminal alkenes to internal alkenes.³³

To assess the economic outcomes of using recycled ionic liquid in nanoparticle synthesis, we performed a techno-economic analysis using CatCost, a free cost estimation tool.³⁴ To approximate a likely application of the Pt nanoparticles, the estimates were made for the purchase cost of a catalyst material consisting of Pt nanoparticles supported on porous carbon at 0.5 wt % (0.5% NP-Pt/C). All of the cost estimates are performed in USD with 2016 as the pricing basis year. The results are summarized in Table 2. Note that the processing costs (capital, labor, and other operating costs) are very high in general for all of the materials (>\$7000/kg). These high costs are driven by intrinsically high labor (~\$3900/kg for the ODE-based synthesis), operating (\$4200/kg), and capital (\$32/kg) costs resulting from the low throughput of batch nanoparticle syntheses, factors that we have addressed through our development of scalable millifluidic flow syntheses of nanoparticle materials.^{25,35–37} We will quantify the cost savings of flow synthesis compared to batch procedures in a forthcoming manuscript.

The starting point for the analysis was the conventional once-through synthesis using ODE, assuming that ILs will not be implemented in commercial nanoparticle applications unless they can achieve costs that are similar to or lower than those of conventional solvents. This synthesis procedure appears in the first row of Table 2. For the ODE-based synthesis, the reaction solvent alone contributes \$169/kg to the cost of the 0.5% NP-Pt/C, revealing that solvents contribute substantially to both cost and environmental impacts for nanoparticle syntheses. From this starting point, we then evaluated the use of virgin BMIM-NTf₂ ionic liquid as a replacement for ODE. This change results in a dramatic increase in reaction solvent cost up to \$4204/kg, which is nearly 10 times the cost of the K₂PtCl₄ platinum precursor. Coupled with larger processing costs resulting from the lower isolated yield, this increase in solvent cost more than doubles the cost of 0.5% NP-Pt/C produced with virgin IL compared to ODE. This estimate illustrates the barriers to commercial application of ILs without recycling; environmental benefits would in this case have to justify a doubling of cost.

Adding IL recycling to the estimate produces large cost savings and shows that BMIM-NTf₂ can be cost-competitive with ODE. Cost analysis for recycled IL assumed that the synthesis and recycling procedure could be repeated until the “startup” cost of purchasing the initial batch of IL is effectively negligible. Under this steady-state assumption, the cost of the

Table 2. Estimated Purchase Costs for 0.5% NP-Pt/C Prepared with Various Solvents Including ODE, Virgin IL, and Steady-State Recycled IL at Two Different Recycling Recovery Values^a

inputs			costs (2016 \$/kg NP-Pt/C)					
reaction solvent	reaction yield	IL recovery	reaction solvent	K ₂ PtCl ₄	other materials	processing	margin	total
ODE	49%		169	261	156	8202	80	8869
virgin IL	29%		4215	441	250	14,458	136	19,501
recycled IL	54%	80%	529	237	143	7497	73	8479
recycled IL	54%	94%	212	237	143	7450	73	8115

^aThe processing column includes all non-materials costs including utilities, operating expenditures, and capital expenditures. The majority (74–92%) of the processing cost for these syntheses is contributed by labor and related operating costs.

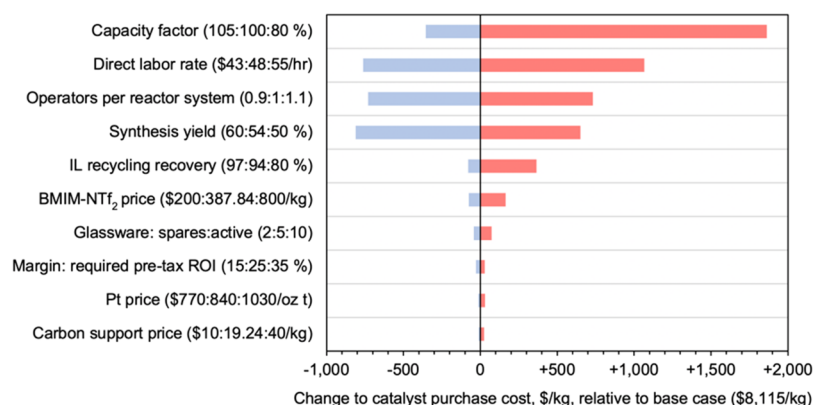


Figure 5. Tornado plot showing the results of sensitivity analysis on the cost of the 0.5% NP-Pt/C material.

IL for each synthesis batch is contributed by the cost of recycling the IL used in that synthesis along with the replacement of the IL lost in the recycling procedure. The nanoparticle yield of the steady-state reaction was based on the observed isolated yield (54%) with IL recycled 5 $\times$ and beyond. The losses during reaction workup and recycling were replaced with virgin IL (vide supra). In the third row of Table 2, a scenario assuming 80% recovery of BMIM-NTf₂ during the recycling procedure achieves a total cost that is lower than that of the ODE procedure. This recovery value is based on earlier, unoptimized recycling procedures. Noting that the reaction solvent cost was still contributing more to the cost than the K₂PtCl₄ precursor at the 80% IL recovery level, we sought to experimentally optimize the recycling procedure further, which ultimately resulted in the 94% recovery procedure described above. In the optimized procedure using recovered IL (fourth row in Table 2), the total cost of the 0.5% NP-Pt/C material is >5% lower than that of the ODE synthesis. The largest material cost for the NP-Pt/C material produced in this way is the K₂PtCl₄ precursor, which is what would normally be expected for a platinum group metal. To return to the assumption that the “startup” costs of purchasing an initial IL batch are negligible, we also calculated the breakeven point, in number of recycles, for the recycling procedure. Dividing the cost of a fresh BMIM-NTf₂ batch (\$4210/kg NP-Pt/C) by the savings in cost (\$754/kg NP-Pt/C) for nanoparticles synthesized using steady-state recycled IL at 94% recovery compared to ODE, the predicted breakeven point is at approximately the sixth reaction (fifth recycle). This analysis reveals that a nanoparticle synthesis using an IL as a reaction solvent can be made cost-competitive with or even cheaper than an equivalent procedure with conventional organic solvents.

To investigate the relative significance of various input parameters in determining the purchase cost of the 0.5% NP-Pt/C material, a sensitivity analysis was performed (Figure 5). This analysis used the steady-state recycled IL solvent, with 94% recovery, as the baseline scenario. The four largest contributors to uncertainty in the cost of 0.5% NP-Pt/C are directly linked to per kg changes in labor and operating costs. These contributors include the capacity factor, which accounts for differences between expected and actual synthesis plant productivity, the labor rate for plant operators, the ratio of operators to each reactor system, and the isolated yield. These factors result in estimated costs spanning a range from –10 to +23% relative to the base case. The fifth and sixth factors, IL recycling recovery and BMIM-NTf₂ purchase price, pertain to

the use of the IL solvent and result in smaller changes to purchase cost on the order of –1 to +5%. The small impact of BMIM-NTf₂ price on the overall synthesis economics highlights the effectiveness of IL recycling in reducing the IL price from a major barrier to a minor factor. Finally, four other factors, covering spare glassware, Pt price, carbon support price, and selling margin, resulted in variations in purchase price of less than $\pm 1\%$. The sensitivity analysis confirms the relative priority of various steps that can be taken to improve the commercial potential of 0.5% NP-Pt/C and similar materials: (1) reduce the labor, operating, and capital requirements associated with batch synthesis; (2) recycle IL solvents and study cheaper IL solvent alternatives; and (3) pursue efficiency in smaller materials and operations cost contributors.

It is important to note that a variety of IL alternatives to BMIM-NTf₂ are commercially available. Replacing the BMIM cation with ammonium or phosphonium cations could lower cost and avoid potential issues with the previously reported lability of the proton at 2-position of imidazolium.³⁸ Furthermore, the perfluorinated NTf₂ anion, which requires a multistep synthesis, is relatively high in cost. Among ILs we surveyed on commercial supplier websites, BMIM-NTf₂ was one of the highest priced (the range of input prices used for BMIM-NTf₂ in Figure 5 reflects this survey). While the TEA can easily be updated to consider any of these alternatives with an accurate bulk-scale price quote, it is important to note that adapting and optimizing the synthesis to use another solvent that can be successfully recycled while also preserving yield, purity, and particle morphology is far from trivial.

CONCLUSIONS

We have demonstrated that BMIM-NTf₂, as a sustainable and cost-competitive solvent for the colloidal synthesis of Pt nanoparticles, can be repeatedly recovered, purified, and reused in subsequent nanoparticle syntheses. The recycling procedure uses water to remove impurities followed by drying *in vacuo*, resulting in a per-cycle recovery of 94% of the IL. The synthetic yield using 5 $\times$ recycled IL (54%) is superior to those obtained with virgin IL (29%) and with ODE (49%). Nanoparticles synthesized using the recycled IL exhibit no detrimental effects of recycling on Pt nanoparticle morphology, and the IL solvent remains mostly unchanged throughout the recycling process. This stands in contrast to an analogous reaction performed in ODE, which showed significant solvent

degradation after just one recovery and purification cycle and could not be recycled further.

Techno-economic analysis of this process indicates that IL recycling can indeed make nanoparticle syntheses using IL solvents cost-competitive, establishing a path to commercialization for this important innovation in sustainable synthesis of nanoparticles. The estimated cost of nanoparticles prepared using steady-state recycled IL is lower than the cost using the conventional solvent, ODE. Furthermore, the IL, unlike ODE, is completely nonvolatile and can be recycled as demonstrated herein. The recycling process described here could potentially be applied to other IL alternatives, many of which are lower in cost than BMIM-NTf₂. Crucially, our analysis shows that even one of the more expensive ionic liquids can be made not only cost-competitive with a conventional solvent but also a relatively minor cost contributor to the overall synthesis through IL recycling. In sum, these results indicate that IL recycling is an effective and valuable technique for lowering IL costs, thereby unlocking the technical and environmental benefits of these solvents for commercial applications of colloidal nanoparticle synthesis.

■ EXPERIMENTAL PROCEDURES

Pt Nanoparticle Syntheses. K₂PtCl₄ (99.9%; Strem), polyvinylpyrrolidone (PVP, Mw = 55,000; Aldrich), ethylene glycol (99.8%; Sigma-Aldrich), 1-octadecene (90%, Sigma-Aldrich), and BMIM-NTf₂ (99%; IoLiTec, Lot #P00164.1) were used as received. In a standard procedure, 39.0 mg (0.094 mmol) of K₂PtCl₄ was dissolved in 2.5 mL of ethylene glycol with mixing. Additionally, 213.1 mg of PVP was dissolved in 7.5 mL of BMIM-NTf₂ (or ODE) by stirring at 130 °C for 10 min, to give a clear, colorless solution. The solutions were rapidly combined in a round bottom flask and placed in an oil bath heated to 150 °C for 15 min, with stirring. The reaction was quenched in an ice bath. In the workup procedure used to determine the reaction yields, the IL layer was isolated and separated from the black ethylene glycol layer (product layer) via centrifugation. Upon separation, the black ethylene glycol solution (2.5 mL) was equally split between two 50 mL centrifuge tubes, with ~1.5 mL of ethanol added to each. The centrifuge tubes were then bath sonicated and vortex mixed for 5 min. The product was precipitated by the addition of 15 mL of acetone to each centrifuge tube and centrifugation (3820 × g, 5 min). The clear supernatant was decanted and the solid in each centrifuge tube was redispersed in 10 mL of ethanol and precipitated again with 30 mL of hexanes and centrifugation (3820 × g, 5 min). The dispersion in ethanol and precipitation with hexanes was repeated two more times. The final nanoparticle product was redispersed in ethanol or dried for further characterization. In an optimized workup procedure that provided better IL recycling yield at a 5× reaction scale (i.e., 12.5 mL of ethylene glycol and 37.5 mL of BMIM-NTf₂), the entire reaction mixture was transferred to a 125 mL separatory funnel and allowed to rest for 12 h. The slightly brown IL layer (bottom) phase separated from the Pt nanoparticles dispersed in ethylene glycol (top). The lower IL layer was collected and saved for later recycling, while the upper ethylene glycol layer was worked up as described above, beginning with the addition of ethanol.

IL Recycling. The IL (~37.5 mL) to be recycled was added to a 125 mL separatory funnel with an equal volume of DI water. The mixture was shaken and allowed to separate. Upon phase separation, the IL (bottom layer) was collected and the water (top layer) was discarded. This procedure was repeated twice more. After the final wash with water, the IL was dried under vacuum at 120 °C for 1 h to remove the residual water. The same procedure was used for recycling ODE.

Supported Nanoparticle Cost Estimation. Cost estimates were compiled in Microsoft Excel v16 using the spreadsheet version of CatCost v1.0.4.³⁴ A full description of all assumptions, including input

costs, cost factors, and other variables, is provided in the [Supporting Information](#). All prices were adjusted to 2016 USD by use of the U.S. Bureau of Labor Statistics Chemical Producer Price Index (ChemPPI) or, for equipment costs, the Chemical Engineering Plant Cost Index. Raw materials prices at 1000 kg order size or greater were estimated through a combination of vendor quotations, freely available and proprietary price databases, and estimates from industry experts. Generally, several sources were consulted to develop an average and/or verify each assumed price. A factor of 3% was added to the raw materials costs to account for waste and spoilage. Processing costs were estimated using the CapEx & OpEx Factors method. For the CapEx & OpEx Factors method, the equipment list is detailed in the [Supporting Information](#). The remainder of the capital costs including direct capital costs like installation, piping, instrumentation, and buildings; indirect costs like engineering, legal, and contingencies; and working capital were estimated as fixed factors (multipliers) of the total purchased equipment cost using the modified Lang factors^{39,40} of Peters and Timmerhaus.³⁹ A similar calculation approach and factors were taken from the same source⁴¹ to determine operating costs such as supervisory labor and maintenance supplies, fixed/indirect costs such as insurance and overhead, and general expenses such as distribution and marketing. Direct labor was calculated by summing the labor factors of all the equipment items after scaling to the specified production rate, then rounding up to the nearest whole number to determine number of operators. Year-round operation (8760 h) with full staffing during maintenance downtime was assumed. A labor rate including benefits of \$48/h for U.S. Gulf Coast production was used. The value of the spent catalyst, which was estimated at \$111.34/kg for all of the catalysts, was not included in the analysis; all cost estimates reflect the purchase cost.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c06993>.

Additional experimental details, XRD patterns, TEM images, ¹H NMR and FT-IR spectra, and techno-economic analysis details ([PDF](#))

CatCost estimates for IL recycling costs at 80% and 94% recovery, Pt nanoparticle costs with once-through IL and with IL recycling at 80% and 94% recovery, and Pt nanoparticle costs with ODE ([XLSX](#), [XLSX](#), [XLSX](#), [XLSX](#), [XLSX](#))

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Notes

The authors declare no competing financial interest.

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