

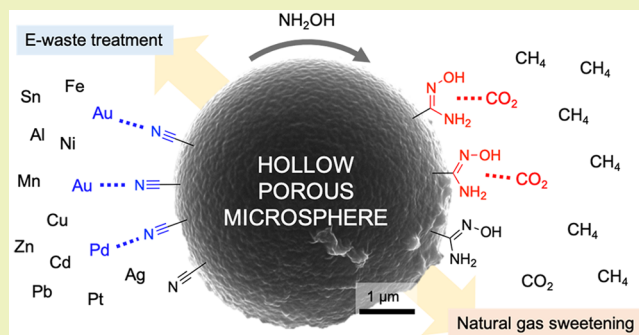
Nanoporous Polymer Microspheres with Nitrile and Amidoxime Functionalities for Gas Capture and Precious Metal Recovery from E-Waste

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Supporting Information

ABSTRACT: Nanoporous materials could offer sustainable solutions to gas capture and precious metal recovery from electronic waste. Despite this potential, few reports combine target functionalities with physical properties such as morphology control. Here, we report a nanoporous polymer with microspherical morphology that could selectively capture gold from a mixture of 15 common transition metals. When its nitriles are converted into amidoxime, the capacity increases more than 20-fold. Amidoximes are also very effective in CO₂ binding and show a record high CO₂/CH₄ selectivity of 24 for potential use in natural gas sweetening. The polymer is successfully synthesized in 1 kg batches starting from sustainable inexpensive building blocks without the need for costly catalysts. Because the morphology is controlled from the beginning, the nanoporous materials studied in lab scale could easily be moved into respective industries.

KEYWORDS: Porous polymers, Electronic waste treatment, Sustainable adsorbents, Hollow microspheres, Methane separation, Gold capture, Large scale synthesis



INTRODUCTION

Porous materials composed of lightweight elements often feature permanent porosity and low mass density, while few offer easy postmodification of functional groups without sacrificing key properties such as surface area. Porous polymers, in particular, found great use in gas storage and separation, especially for mixtures containing CO₂, CH₄, and H₂. Large surface areas and suitable functional groups are known to show high capture capacity and high CO₂/N₂ and CO₂/CH₄ selectivity.^{1–4} Several reports using crystalline or amorphous frameworks with suitable functionalities^{5–10} are examined; however, the quest still remains for an industrially feasible, sustainable adsorbent.¹¹

Amidoximes, amines, and their parent nitriles offer favorable binding to CO₂, and we had previously used them to capture CO₂ under ambient and high-pressure conditions.^{12–17} But morphology control is almost never considered. The porous polymers are usually insoluble and have a tightly knit network structure, the latter being a necessary feature for permanent

porosity. Also, subsequent treatments to make pellets reduce the porosity and structural integrity greatly.

Our recent work provided a versatile platform using industrially feasible microemulsion techniques.¹⁸ The porous polymer (i.e., COP-122) is made in well-defined microspheres that minimized column/bed packing related diffusion limitations. However, the post-modification of the nitrile also led to significant reduction of the contact surface. In this work, we combine the powerful microemulsion technique that yields microspheres of porous polymers with the noninvasive modification of amidoxime formation.¹⁹ Together with morphology control, amidoximes are expected to deliver good capture and separation properties.

In addition to the CO₂ uptake, amidoximes are also known to bind to transition metals very strongly.^{20,21} Morphology

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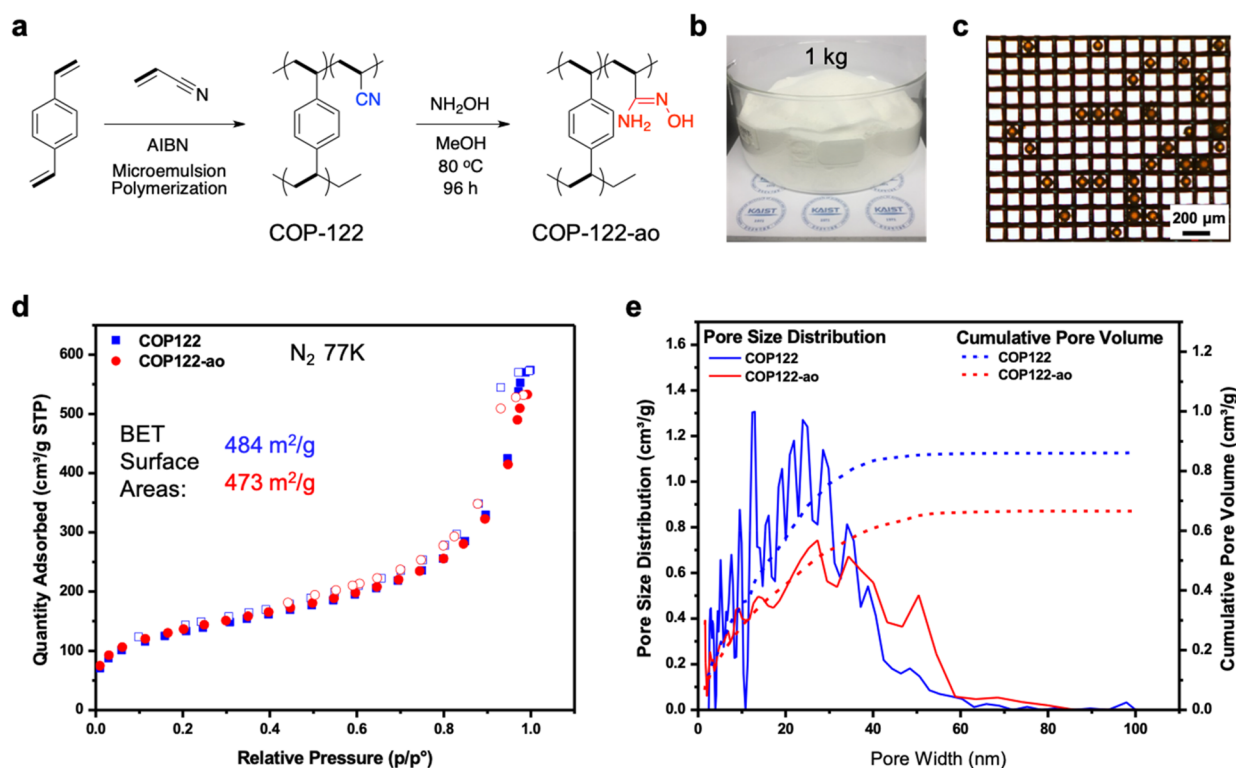


Figure 1. (a) Synthesis of COP-122 and COP-122-amidoxime (COP122-ao). (b) Purified product from a one-pot 1-kg-scale synthesis. (c) Hollow COP-122 microspheres sitting atop a steel mesh filter. Scale bar: 200 μm . (d) BET surface area isotherms of COP-122 (blue) and COP-122-ao (red) using N_2 as a probe gas at 77 K. (e) Pore size distribution and cumulative pore volume of COP-122 (blue) and COP-122-ao (red).

control of the porous polymers is even in greater demand for liquid separations, where pressure buildup is more imminent and unfortunately detrimental. Combining amidoxime metal chelation with microsphere shapes has the potential to provide very selective, sustainable, and industrially feasible water treatment methods. One such field is electronic waste recycling.

Precious metals lost through electronic waste (e-waste) now amount to significant sums since the use of electronics is rapidly increasing. For example, the total amount of e-waste generated in 2014 is 41.8 million metric tons (Mt) whereas the predicted amount for 2018 is 50 Mt.²² And considering that the gold amount is 40 times higher in e-waste compared to the land based ores, 1 t of e-waste could be recycled to yield more gold than could be recovered from 17 tons of a gold ore.^{23,24}

So, herein, we synthesized a highly porous covalent organic polymer (COP) indexed as COP-122 that contains nitrile groups and its amidoxime functionalized variant COP-122-ao. We studied both sorbents for gas uptake and tested for the gold recovery from e-waste. The inexpensive COP-122 microspheres are easily made in high yields, and we show that 1 kg scale in one pot shows the same features as small scale with even slightly higher porosity. Interestingly, the nitrile groups showed high selectivity toward gold ions in e-waste recycling conditions while the gold uptake capacity was significantly enhanced by postmodification to the amidoxime groups.

RESULTS AND DISCUSSION

Synthesis and Characterization. COP-122 was synthesized using a micro emulsion polymerization technique from widely available monomers, 1,4-divinylbenzene and acryloni-

trile following our previously reported method.¹⁸ In a typical run, acrylonitrile (2 mL, 30.5 mmol) and 1,4-divinylbenzene (8 mL, 56.1 mmol) were dissolved in 10 mL of toluene that contains the initiator, AIBN (50 mg, 0.3 mmol), before mixing into an 50 mL aqueous solution of poly(vinyl alcohol) (1% w/w) and heating up to 75 °C for 24 h (Figure 1). The hollow microspheres (COP-122) were then washed and dried. Amidoxime postfunctionalization is completed at 80 °C in 10 mL methanol with 500 mg of COP-122 reacting with 10 mL NH_2OH (50% in water) for 96 h (COP-122-ao).¹² See Supporting Information for more details on the methods. COP-122 is formed through a well-known mechanism, where radicalic polymerization is initiated by AIBN decomposition and olefins propagate through free radical formation at the most delocalized carbon.^{25,26} Amidoximes, on the other hand, form through a simple nucleophilic attack from hydroxyl amines to the dangling nitriles.¹³

Scale up without losing material properties is an important step for adsorbents to be used in industrial applications, particularly gas capture and water treatment.¹⁶ An ideal goal would be the synthesis of the porous polymer in 1 kg scale at one batch. COP-122 was then synthesized in 1 kg batches following the same procedure without significant modifications from small scale. We believe it is because the procedure does not require any specific treatments such as inert atmosphere or protection from highly sensitive chemicals. The product from scale up featured the same physical (microspherical and porous morphology) and chemical properties (nitriles), even with higher surface area than the small scale (Figure 1). This is highly unusual even for our own set of porous polymers that we studied over the years. Final product is not sensitive to moisture, air or light, and it is not soluble in common solvents,

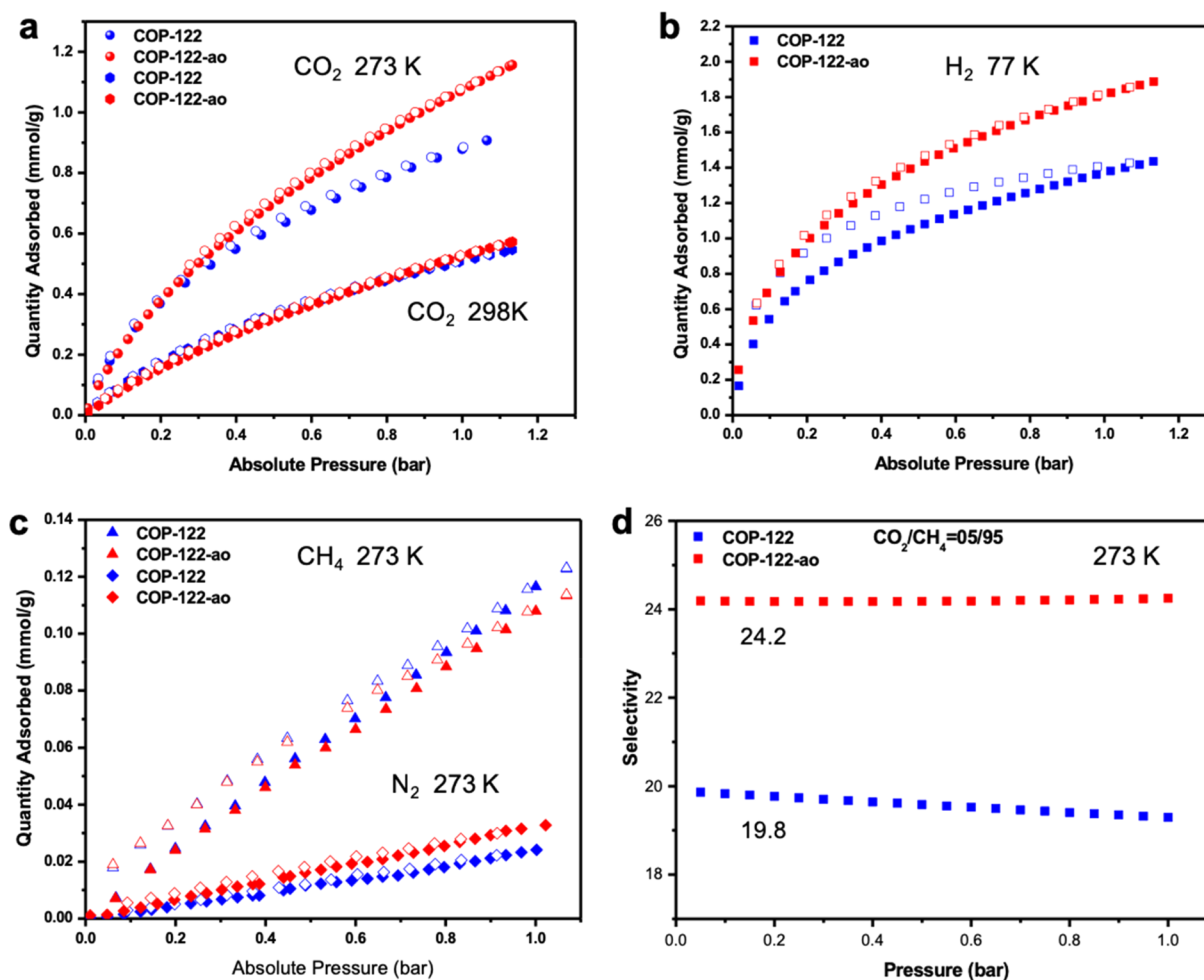


Figure 2. (a) CO₂ uptake isotherms of COP-122 (blue) and COP-122-ao (red) at 273 and 298 K. (b) H₂ uptake isotherms of COP-122 (blue) and COP-122-ao (red) at 77 K. (c) CH₄ and N₂ uptake isotherms of COP-122 (blue) and COP-122-ao (red) at 273 K. (d) IAST based gas selectivity for CO₂ over CH₄ for CO₂/CH₄ = 05/95 mixtures at 273 K for COP-122 (blue) and COP-122-ao (red).

which provides easy handling. Hydrophobic nature of COP-122 also benefits in packing and shipment issues.

The FTIR spectra of COP-122 shows the characteristic nitrile peak at 2215 cm⁻¹ and C–H stretching at 1458 cm⁻¹ and 2921 cm⁻¹ (Figure S1). After modification for amidoxime units, the nitrile stretching almost disappeared. The newly formed imine bond of amidoxime is clearly seen at 1636 cm⁻¹. The region 3200–3400 cm⁻¹ is very broad in COP-122-ao, which represents the combination of NH and OH stretching, and the residual water because of the new, polar functionalities. Modification is further confirmed in elemental analysis that presents 1 to 5 wt % oxygen (Table S3). TGA analysis confirmed thermal stability for both structures up to over 300 °C and showed residual water and solvent evaporations at lower temperatures indicating the polar nature of the pore walls (Figure S2).

For both gas uptake and precious metal capture, porosity is key to facilitate the adsorptions. The BET specific surface area of the starting material, COP-122, is found to be 484 m²/g with a wide range of micro- and mesopores (Figure 1d–e). As we previously noted in another system¹⁹ COP-122-ao formed without significant surface area loss, unlike most other systems.²⁷ The BET surface area of 473 m²/g is coupled with a pore size distribution range spanning from micropores to large mesopores. Pore volumes for COP-122 and COP-122-

ao are also 0.86 and 0.66 cm³/g, respectively. Rouquerol plots and pressure regimes for calculating BET surface area are included in the Supporting Information (SI), Figures S6–S7. Since it is not possible to obtain an exact pore size distribution for amorphous materials, we have utilized NLDFT Carbon-Slit Pores kernel in the calculations as further explained in the SI.

Gas Uptake and Selectivity. In addition to our work,^{12,13} several others have shown amidoxime–CO₂ interactions. These included polymers of intrinsic microporosity (PIMs),¹⁹ activated carbon,²⁸ porous polymers,¹³ mesoporous organosilica,²⁹ and mixed matrix membranes³⁰ utilizing amidoxime-functionalized PIM-1 and NH₂–UiO-66, microcrystalline cellulose–mesoporous silica composites,³¹ and deep eutectic monomer based poly(ionic liquids).³² These reports, however, never showed bead-like morphologies, a necessary prerequisite for fluidized bed applications. In the tests of COP-122-ao, we dosed CO₂, N₂, CH₄, and H₂ in a volumetric setup at constant temperature (Figure 2).

As expected, the amidoxime functionalized COP-122 showed increased CO₂ uptake reaching up to 1.2 mmol/g at 273 K (Figure 2a). This value is better than the industrial amine solvents but lower than other highly porous materials. However, the morphology control and the fact that the amidoxime loading (1% to 5%) is lesser than other solids²⁸ (10.6%) make up for the differences. (Table S3) It is important

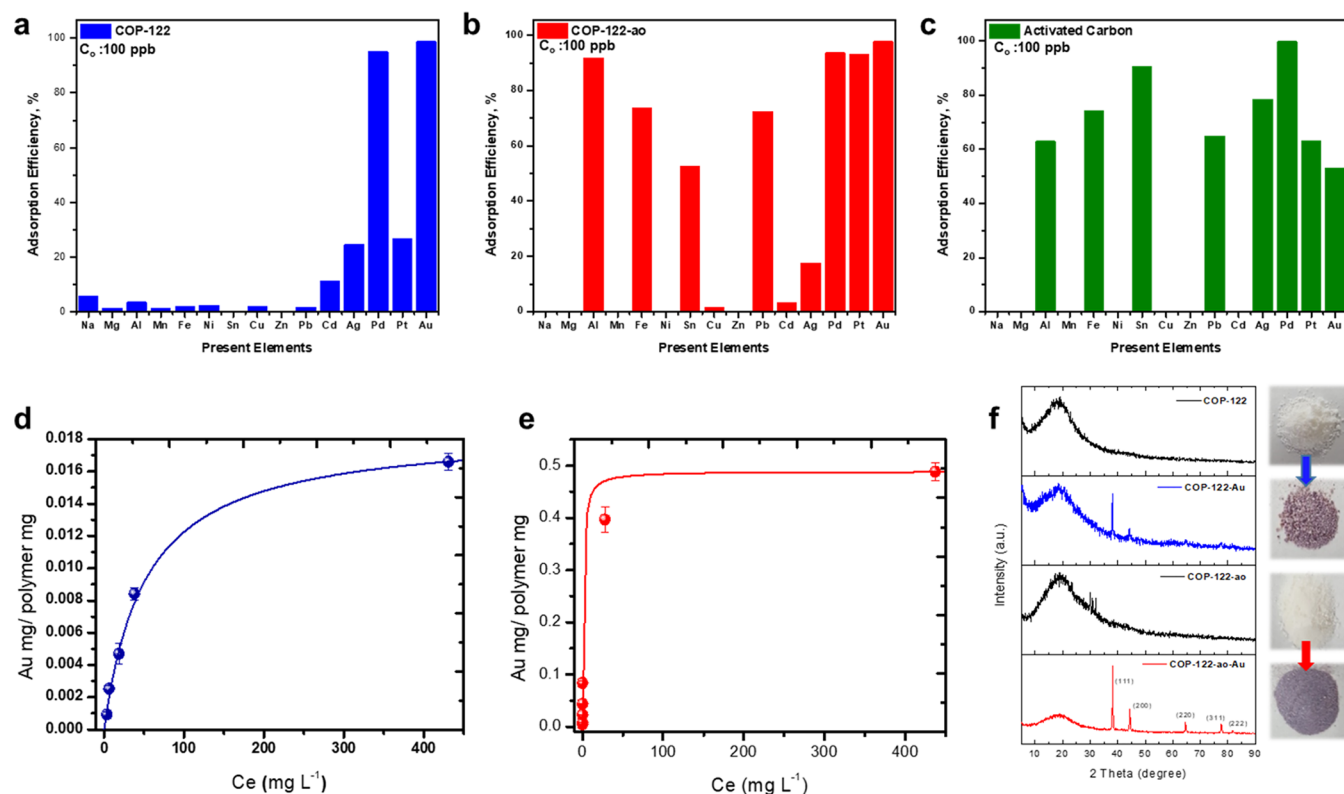


Figure 3. Metal adsorption selectivity of COP-122 (a), COP-122-ao (b), and activated carbon (c). 20 mg of adsorbents were immersed in solutions of 15 metals at each 100-ppb concentration. Gold adsorption isotherms of COP-122 (d) and COP-122-ao (e). (f) The XRD spectra and photographs of COP-122 and COP-122-ao before and after the gold capture.

to note that operational parameters often matter as much as the capacity.¹⁶ Hydrogen uptake at 77 K was also higher in COP-122-ao, reaching up to 2 mmol/g (Figure 2b). But the main difference occurred for the methane uptake. At 273 K, COP-122 took in more CH₄ than the amidoxime counterpart, a reverse order compared to CO₂ (Figure 2c). We suspect that the hydrophobic framework that forms COP-122 has more suitable van der Waals interactions and nonpolar adhesive properties that facilitate methane uptake. Yet, N₂ uptakes are not exemplary, nor unexpected.

We, then, calculated IAST based gas selectivities (see SI for details). Since CO₂ and CH₄ showed inverse trends because of the polarity difference of the adsorbents, we focused on CO₂/CH₄ selectivity. It is of paramount importance for natural gas processing, where “sweetening” is needed to produce commercial natural gas.^{11,33,34} CO₂/CH₄ was found to be at 24 consistently over a 0–1 bar range for CO₂/CH₄ = 05/95 mixtures for natural gas sweetening (Figure 2d) and similar for CO₂/CH₄ = 50/50 mixtures for landfill gas purification (Figure S3). This value is higher than many sorbents reported in the literature.³³ Also for CO₂/N₂, COP-122-ao showed a higher than average selectivity of 88 at flue gas mimicking, a 15:85 ratio (Figure S4). Considering that COP-122-ao is ready to be used in industry without any morphology processing, it provides large incentives for field deployment.

E-Waste Treatment. In order to test the activity of COP-122 and COP-122-ao for precious metal capture, we first identified the metals that we need to study. Fifteen transition metals that are most commonly found in e-waste were selected (Figure 3). A standard mixed solution of metals in an acidic medium was prepared using ICP standards and set for 100 ppb

each for fair comparison (see SI for details). As a comparison, we identified activated carbon as a control since it is the most widely used wide spectrum adsorbent for water treatment. Ionic exchange resins are commonly used for metals, but they are almost always metal specific. The acidic mixed metal solutions are then tumbled with the respective sorbents and determined for the removal capacity by measuring the remaining concentrations.

Contrary to our expectations, COP-122 has shown significant selectivity toward precious metals, particularly Au and Pd (Figure 3a). The capture efficiencies were 99% and 95%, respectively, noting remarkable selectivity. We believe this unusual activity was due to the weak binding of the pendant nitriles to the chelating heavy metals. It is important to note that common metals such as Fe, Ni, Al, Zn, Cu were only minutely removed. Lead is also not captured, showing great potential for precious metal recycling without the toxic contaminants.

COP-122-ao was far more effective in binding to a variety of metals, as chelating is the suspected mode of action. It made up in capacity for the lack of selectivity (Figure 3b). Despite the lack of precious metal selectivity, we observed some noticeable differences between certain metal pairs. For example, Mn, Cu, or Ni was not captured while Fe was more than 70% recovered. Aluminum was removed as much as Pd and Pt, leading to interesting behavior, one that we have not yet fully understood. Nonetheless, the characteristic uptake of certain metals could very well be used in purifications to form select metal mixtures.

Activated carbon also showed some selectivity for certain metals but fared poorly in precious metal recovery, particularly

for Au and Pt (Figure 3c). Since the economic feasibility relies on the production and resale of the precious metals for e-waste applications, activated carbon seems not to be promising for e-waste treatment.

Apart from precious metals, uranium³⁵ and rare earth metals³⁶ were also tested for recovery. COP-122-ao could remove 86% of uranium from a 200 ppb solution. On the other hand, COP-122 only captures 1.4% of uranium. Detailed results are presented in SI, Figures S8–S9. Both polymers showed a low capacity for rare earth metals (Figures S10–S11). COP-122, therefore, could selectively capture gold from acidic solutions that contain uranium and rare earth metals. The relatively high selectivity of COP-122-ao for uranium is noteworthy, but since vanadium (a common metal in the ocean that always competes with uranium species) was also captured with similar selectivity, it is rather impractical.

From the adsorption isotherms of the mixed metal studies, the maximum gold uptake capacity of COP-122 was found to be 0.1864 g_{Au}/g_{Ads} . The capacity could be significantly increased after postmodification to amidoxime groups, resulting in 0.4567 g_{Au}/g_{Ads} in COP-122-ao (Figure 3d–e). These uptake values are highly competitive when compared with other adsorbents such as MOFs³⁷ even though COPs show much lower surface areas. Additionally, the reduction of gold ions was observed in both COP-122 and COP-122-ao. The sharp peaks in the XRD patterns and color change from white to purple of COP-122 and COP-122-ao after the gold capture demonstrate the formation of gold nanoparticles (Figure 3f). We suspect that the gold reduction during the gold adsorption process by adsorbents is due to the favorable reduction potential of gold ions.³⁸ The nitrile groups in COP-122 could be effective for gold capture at low pH. It is considered that the protonation of nitrile groups at low pH pull the gold ions (the dominant $AuCl_4^-$ species) by electrostatic interaction, which becomes difficult with increasing pH of the solution. On the other hand, the amidoxime groups in COP-122-ao adsorb the gold ions at varying pH and show loss of activity only at pH 7 (Figure S5). Accordingly, the amidoxime groups can provide better gold adsorption characteristics than nitrile groups in terms of capacity and pH resistance, while slightly yielding metal selectivity.

CONCLUSIONS

We have shown that morphology control and chemical functionality could be combined in porous polymers for gas selectivity and precious metal capture from e-waste. The nitrile functionalities were very effective in capturing gold while leaving common metals behind. Amidoxime groups were achieved by direct conversion of nitriles, and they showed very high CO_2/CH_4 separation potential. They also effectively removed precious metals but with less selectivity. Our results indicate nitrile functionalities could be feasibly used in e-waste treatment, whereas amidoximes, once again, are advantageous in interacting with acidic gases as well as transition metals in solutions. The main advantage of the porous polymers reported here was the microsphere morphology and retention of porosity even after postmodification. These features allow easy adaptation in industrial applications where columns or fluidized beds are used.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsschemeng.8b05490.

Materials and methods including synthesis and analysis; Figures S1–S11; Tables S1–S3 (PDF)

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Notes

The authors declare no competing financial interest.

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