Summary

[0004a] In an aspect of the present disclosure, there is provided a filtration apparatus, comprising:

a support substrate; and

a graphene oxide membrane disposed on the support substrate, the graphene oxide membrane including a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer,

wherein:

the chemical spacer comprises 4-aminophenylacetic acid, 2-(4(aminophenyl) ethanol, acrylamide, propionamide, isobutyramide, pivalamide, or a derivative thereof;

the graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature; and

after the graphene oxide membrane is contacted with a solution that is at least 80 °C for a period of time, the graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature.

[0004b] In another aspect of the present disclosure, there is provided a method for processing black liquor, the method comprising flowing black liquor through the filtration apparatus disclosed herein, wherein the black liquor comprises lignin, sodium sulfate, sodium carbonate, sodium hydrosulfide, sodium thiosulfate, sodium hydroxide, or a combination thereof.

[0004c] In a further aspect of the present disclosure, there is provided a filtration apparatus, comprising:

a support substrate; and

a graphene oxide membrane disposed on the support substrate, the graphene oxide membrane including a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer,

wherein:

the chemical spacer comprises 4-aminophenylacetic acid, 2-(4-aminophenyl) ethanol, acrylamide, propionamide, isobutyramide, pivalamide, or a derivative thereof;

the graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature; and

after the graphene oxide membrane is contacted with a solution having a pH of at least 11 for a period of time at room temperature, the graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature.

[0004d] In another aspect of the present disclosure, there is provided a filtration apparatus, comprising:

a support substrate; and

a graphene oxide membrane disposed on the support substrate, the graphene oxide membrane including a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer,

wherein:

each of the graphene oxide sheets is not covalently crosslinked to the adjacent graphene oxide sheet;

the graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature; and

after the graphene oxide membrane is contacted with a solution that is at least 80 °C for a period of time, the graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature.

[0004e] In a further aspect of the present disclosure, there is provided a filtration apparatus, comprising:

a support substrate; and

a graphene oxide membrane disposed on the support substrate, the graphene oxide membrane including a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer,

wherein:

each of the graphene oxide sheets is not covalently crosslinked to the adjacent graphene oxide sheet;

the graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature; and

after the graphene oxide membrane is contacted with a solution having a pH of at least 11 for a period of time at room temperature, the graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature.

[0004f] In another aspect of the present disclosure, there is provided a filtration apparatus, comprising:

a support substrate, the support substrate has a thickness of at least about 150 μm and a Young's modulus of at least about 0.9 GPa; and

a graphene oxide membrane disposed on the support substrate, the graphene oxide membrane including a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer,

wherein:

each of the graphene oxide sheets is not covalently crosslinked to the adjacent graphene oxide sheet;

the graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature; and

after the graphene oxide membrane is subjected to a pressure of about 1000 psi for a period of time, the graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature.

[0004g] In a further aspect of the present disclosure, there is provided a method for processing black liquor, the method comprising flowing black liquor through the filtration apparatus of disclosed herein, wherein the black liquor comprises lignin, sodium sulfate, sodium carbonate, sodium hydrosulfide, sodium thiosulfate, sodium hydroxide, or a combination thereof.

[0005] Examples described herein relate generally to durable graphene oxide membranes for fluid filtration. For example, the graphene oxide membranes can be used for concentration, removal, and purification of different salts.

[0006] One example of the present disclosure relates to a filtration apparatus comprising: a support substrate, and a graphene oxide membrane disposed on the support substrate. The graphene oxide membrane includes a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer, wherein each of the graphene oxide sheets is not covalently crosslinked to an adjacent graphene oxide sheet. The

graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature. The graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature after the graphene oxide membrane is contacted with a solution that is at least 80 °C for a period of time.

[0007] In some examples, the second lactose rejection rate is substantially the same as the first lactose rejection rate.

[0008] In some examples, the second lactose rejection rate is greater than the first lactose rejection rate.

[0009] In some examples, the first lactose rejection rate is less than or equal to 90%.

[0010] In some examples, the second lactose rejection rate is less than or equal to 90%.

[0011] In some examples, the chemical spacer comprises an amine or a derivative thereof. In some examples, the chemical spacer comprises $–NH-R_1$, wherein R_1 is an aryl, which can be optionally substituted. In some examples, the amine is 4-aminophenylacetic acid or 2-(4-aminophenyl) ethanol.

[0012] In some examples, the chemical spacer comprises an amide or a derivative thereof. In some examples, the chemical spacer comprises $–NH-C(O)-R_2$, wherein R_2 is C_1-C_6 alkyl or C_2-C_6 alkenyl, each of which can be optionally substituted. In some examples, the amide is acrylamide, propionamide, isobutyramide, or pivalamide.

[0013] In some examples, the solution has a pH of about 7.

[0014] In some examples, the solution has a pH of about 11.

[0015] In some examples, the solution has a pH of about 14.

[0016] In some examples, the solution is a phosphate buffer. In some examples, the phosphate buffer comprises Na_2HPO_4.

[0017] In some examples, the room temperature is about 20 °C.

[0018] In some examples, the solution passes through the graphene oxide membrane.

[0019] In some examples, the period of time is about 2-6 hours.

[0020] One example of the present disclosure relates to a filtration apparatus comprising: a support substrate, and a graphene oxide membrane disposed on the support substrate. The graphene oxide membrane includes a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer. The graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature. The graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature after the graphene oxide membrane is contacted with a pH of at least 11 for a period of time.

[0021] In some examples, the solution has a pH of at least about 12. In some examples, the solution has a pH of at least about 14.

[0022] In some examples, the second lactose rejection rate is substantially the same as the first lactose rejection rate.

[0023] In some examples, the second lactose rejection rate is greater than the first lactose rejection rate.

[0024] In some examples, the first lactose rejection rate is less than or equal to 90%.

[0025] In some examples, the second lactose rejection rate is less than or equal to 90%.

[0026] In some examples, the chemical spacer comprises an amine or a derivative thereof. In some examples, the chemical spacer comprises $–NH-R_1$, wherein R_1 is an aryl, which can be optionally substituted. In some examples, the amine is 4-aminophenylacetic acid or 2-(4-aminophenyl) ethanol.

[0027] In some examples, the chemical spacer comprises an amide or a derivative thereof. In some examples, the chemical spacer comprises $–NH-C(O)-R_2$, wherein R_2 is C_1-C_6 alkyl or C_2-C_6 alkenyl, each of which can be optionally substituted. In some examples, the amide is acrylamide, propionamide, isobutyramide, or pivalamide.

[0028] In some examples, the solution comprises Na_2HPO_4.

[0029] In some examples, the room temperature is about 20 °C.

[0030] In some examples, the solution passes through the graphene oxide membrane.

[0031] In some examples, the solution is a buffer solution.

[0032] In some examples, the period of time is about 2-6 hours.

[0033] One example of the present disclosure relates to a filtration apparatus, comprising: a support substrate, the support substrate has a thickness of at least about 150 μm and a Young's modulus of at least about 0.9 GPa; and a graphene oxide membrane disposed on the support

substrate, the graphene oxide membrane including a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer, wherein: the graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature; and after the graphene oxide membrane is subjected to a pressure of about 1000 psi for a period of time, the graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature.

[0034] In some examples, the support substrate has a thickness of no more than about 500 μm.

[0035] In some examples, the support substrate has a Young's modulus of no more than about 2.5 GPa.

[0036] In some examples, the support substrate comprises polypropylene, polyolefin, polyethersulfone (PES), polytetrafluoroethylene (PTFE), polyacrylonitrile (PAN), nylon, or a combination thereof.

[0037] One example of the present disclosure relates to a method of processing black liquor, wherein black liquor is flowed through any one of the aforementioned filtration apparatuses, wherein the black liquor comprises lignin, sodium sulfate, sodium carbonate, sodium hydrosulfide, sodium thiosulfate, and/or sodium hydroxide.

[0038] In some examples, at least a portion of the lignin is rejected by the graphene oxide membrane. In some examples, at least 50% of the lignin is rejected by the graphene oxide membrane. In some examples, at least 90% of the lignin is rejected by the graphene oxide membrane.

[0039] In some examples, at least a portion of the sodium sulfate is rejected by the graphene oxide membrane. In some examples, at least 50% of the sodium sulfate is rejected by the graphene oxide membrane. In some examples, at least 90% of the sodium sulfate is rejected by the graphene oxide membrane.

[0040] In some examples, at least a portion of the sodium carbonate is rejected by the graphene oxide membrane. In some examples, at least 50% of the sodium carbonate is rejected by the graphene oxide membrane. In some examples, at least 90% of the sodium carbonate is rejected by the graphene oxide membrane.

[0041] In some examples, at least a portion of the sodium hydrosulfide is rejected by the graphene oxide membrane. In some examples, at least 50% of the sodium hydrosulfide is rejected by the graphene oxide membrane. In some examples, at least 90% of the sodium hydrosulfide is rejected by the graphene oxide membrane.

[0042] In some examples, at least a portion of the sodium thiosulfate is rejected by the graphene oxide membrane. In some examples, at least 50% of the sodium thiosulfate is rejected by the graphene oxide membrane. In some examples, at least 90% of the sodium thiosulfate is rejected by the graphene oxide membrane.

[0043] In some examples, at least a portion of the sodium hydroxide is rejected by the graphene oxide membrane. In some examples, at least 50% of the sodium hydroxide is rejected by the graphene oxide membrane. In some examples, at least 90% of the sodium hydroxide is rejected by the graphene oxide membrane.

[0044] One example of the present disclosure relates to a method of increasing a flux of the graphene oxide membrane described herein, the method comprising contacting the graphene oxide membrane with a solution that is at least about 50 °C for a period of time, wherein after the contacting step, the flux is increased by at least 50%.

[0045] Another example of the present disclosure relates to a method of increasing a flux of the graphene oxide membrane described herein, the method comprising contacting the graphene oxide membrane with a solution having a pH of at least about 10 for a period of time, wherein after the contacting step, the flux is increased by at least 50%.

Brief Description of the Drawings

[0046] FIG. 1 is a schematic illustration of a graphene oxide membrane in accordance with some embodiments of the present disclosure.

[0047] FIGS. 2A-2F present examples of one-step reactions between graphene oxide sheets and chemical spacers.

[0048] FIG. 3 is a modeling diagram that models an arbitrarily sized membrane system using a simple picture of permeability and rejection from dead end or crossflow. Every constituent species is tracked. Counter ions (e.g., sodium) given same rejection as pair ion (e.g., Na paired with lignin, Na paired with Cl, Na paired with SO_4, etc.). (Total or species flow rate in) * a * t = 2 *(flux through membrane) * dx * t + (flow rate out) * a * t.

[0049] FIG. 4 is a graph showing simulation results for a 1.0 rejection coefficient for divalent salts, a 750-module system size, and 1000 psi operating pressure. Each series of dots represents a different feed concentration. Some mills will have more or less concentrated feed liquor.

[0050] FIGS. 5A-5D, 6A-6D, 7A-7D, 8A-8D, and 9A-9E are graphs showing the recovery percentage of simulated permeate total dissolved solids (perm TDS) for different system sizes (as represented by recovery ratio). Each series of dots represents a different feed concentration.

What is claimed is:

1. A filtration apparatus, comprising:

a support substrate; and

a graphene oxide membrane disposed on the support substrate, the graphene oxide membrane including a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer,

wherein:

the chemical spacer comprises 4-aminophenylacetic acid, 2-(4(aminophenyl) ethanol, acrylamide, propionamide, isobutyramide, pivalamide, or a derivative thereof;

the graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature; and

after the graphene oxide membrane is contacted with a solution that is at least 80 °C for a period of time, the graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature.

2. The filtration apparatus of claim 1, wherein the second lactose rejection rate is substantially the same as the first lactose rejection rate.

3. The filtration apparatus of claim 1, wherein the second lactose rejection rate is greater than the first lactose rejection rate.

4. The filtration apparatus of claim 1, wherein the first lactose rejection rate is less than or equal to 90%.

5. The filtration apparatus of claim 1, wherein the second lactose rejection rate is less than or equal to 90%.

6. The filtration apparatus of claim 1, wherein each of the graphene oxide sheets is not covalently crosslinked to the adjacent graphene oxide sheet.

7. The filtration apparatus of claim 1, wherein the solution has a pH of about 7, about 11, or about 14.

8. A method for processing black liquor, the method comprising flowing black liquor through the filtration apparatus of claim 1, wherein the black liquor comprises lignin, sodium sulfate, sodium carbonate, sodium hydrosulfide, sodium thiosulfate, sodium hydroxide, or a combination thereof.

9. A filtration apparatus, comprising:

a support substrate; and

a graphene oxide membrane disposed on the support substrate, the graphene oxide membrane including a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer,

wherein:

the chemical spacer comprises 4-aminophenylacetic acid, 2-(4-aminophenyl) ethanol, acrylamide, propionamide, isobutyramide, pivalamide, or a derivative thereof;

the graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature; and

after the graphene oxide membrane is contacted with a solution having a pH of at least 11 for a period of time at room temperature, the graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature.

10. The filtration apparatus of claim 9, wherein the pH is at least about 12 or at least about 14.

11. The filtration apparatus of claim 9, wherein the second lactose rejection rate is substantially the same as the first lactose rejection rate.

12. The filtration apparatus of claim 9, wherein the second lactose rejection rate is greater than the first lactose rejection rate.

13. The filtration apparatus of claim 9, wherein the first lactose rejection rate is less than or equal to 90%.

14. The filtration apparatus of claim 9, wherein the second lactose rejection rate is less than or equal to 90%.

15. The filtration apparatus of claim 9, wherein each of the graphene oxide sheets is not covalently crosslinked to the adjacent graphene oxide sheet.

16. A filtration apparatus, comprising:

a support substrate; and

a graphene oxide membrane disposed on the support substrate, the graphene oxide membrane including a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer,

wherein:

each of the graphene oxide sheets is not covalently crosslinked to the adjacent graphene oxide sheet;

the graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature; and

after the graphene oxide membrane is contacted with a solution that is at least 80 °C for a period of time, the graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature.

17. The filtration apparatus of claim 16, wherein the second lactose rejection rate is at least substantially the same as the first lactose rejection rate.

18. The filtration apparatus of claim 16, wherein the first lactose rejection rate is less than or equal to 90%.

19. The filtration apparatus of claim 16, wherein the second lactose rejection rate is less than or equal to 90%.

20. The filtration apparatus of claim 16, wherein the chemical spacer comprises an amine or a derivative thereof.

21. The filtration apparatus of claim 20, wherein the chemical spacer comprises –NH-R_1, wherein R_1 is an aryl, which can be optionally substituted.

22. The filtration apparatus of claim 20, wherein the amine is 4-aminophenylacetic acid or 2-(4-aminophenyl) ethanol.

23. The filtration apparatus of claim 16, wherein the chemical spacer comprises an amide or a derivative thereof.

24. The filtration apparatus of claim 23, wherein the chemical spacer comprises –NH-C(O)-R_2, wherein R_2 is C_1-C_6 alkyl or C_2-C_6 alkenyl, each of which can be optionally substituted.

25. The filtration apparatus of claim 23, wherein the amide is acrylamide, propionamide, isobutyramide, or pivalamide.

26. The filtration apparatus of claim 16, wherein the solution has a pH of about 7, about 11, or about 14.

27. A filtration apparatus, comprising:

a support substrate; and

a graphene oxide membrane disposed on the support substrate, the graphene oxide membrane including a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer,

wherein:

each of the graphene oxide sheets is not covalently crosslinked to the adjacent graphene oxide sheet;

the graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature; and

after the graphene oxide membrane is contacted with a solution having a pH of at least 11 for a period of time at room temperature, the graphene oxide membrane has

a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature.

28. The filtration apparatus of claim 27, wherein the pH is at least about 12 or at least about 14.

29. The filtration apparatus of claim 27, wherein the second lactose rejection rate is at least substantially the same as the first lactose rejection rate.

30. The filtration apparatus of claim 27, wherein the first lactose rejection rate is less than or equal to 90%.

31. The filtration apparatus of claim 27, wherein the second lactose rejection rate is less than or equal to 90%.

32. The filtration apparatus of claim 27, wherein the chemical spacer comprises an amine or a derivative thereof.

33. The filtration apparatus of claim 32, wherein the chemical spacer comprises –NH-R_1, wherein R_1 is an aryl, which can be optionally substituted.

34. The filtration apparatus of claim 32, wherein the amine is 4-aminophenylacetic acid or 2-(4-aminophenyl) ethanol.

35. The filtration apparatus of claim 27, wherein the chemical spacer comprises an amide or a derivative thereof.

36. The filtration apparatus of claim 35, wherein the chemical spacer comprises –NH-C(O)-R_2, wherein R_2 is C_1-C_6 alkyl or C_2-C_6 alkenyl, each of which can be optionally substituted.

37. The filtration apparatus of claim 35, wherein the amide is acrylamide, propionamide, isobutyramide, or pivalamide.

38. A filtration apparatus, comprising:

a support substrate, the support substrate has a thickness of at least about 150 μm and a Young's modulus of at least about 0.9 GPa; and

a graphene oxide membrane disposed on the support substrate, the graphene oxide membrane including a plurality of graphene oxide sheets, each of the graphene oxide sheets covalently coupled to a chemical spacer,

wherein:

each of the graphene oxide sheets is not covalently crosslinked to the adjacent graphene oxide sheet;

the graphene oxide membrane has a first lactose rejection rate of at least 50% with a first 1 wt% lactose solution at room temperature; and

after the graphene oxide membrane is subjected to a pressure of about 1000 psi for a period of time, the graphene oxide membrane has a second lactose rejection rate of at least 50% with a second 1 wt% lactose solution at room temperature.

39. The filtration apparatus of claim 38, wherein the support substrate has a Young's modulus of no more than about 2.5 GPa.

40. The filtration apparatus of claim 38, wherein the support substrate comprises polypropylene, polyolefin, polyethersulfone (PES), polytetrafluoroethylene (PTFE), polyacrylonitrile (PAN), nylon, or a combination thereof.

41. The filtration apparatus of claim 38, wherein the chemical spacer comprises an amine or a derivative thereof.

42. The filtration apparatus of claim 41, wherein the chemical spacer comprises $–NH-R_1$, wherein R_1 is an aryl, which can be optionally substituted.

43. The filtration apparatus of claim 38, wherein the chemical spacer comprises an amide or a derivative thereof.

44. The filtration apparatus of claim 43, wherein the chemical spacer comprises $–NH-C(O)-R_2$, wherein R_2 is C_1-C_6 alkyl or C_2-C_6 alkenyl, each of which can be optionally substituted.

45. A method for processing black liquor, the method comprising flowing black liquor through the filtration apparatus of claim 16, wherein the black liquor comprises lignin, sodium sulfate, sodium carbonate, sodium hydrosulfide, sodium thiosulfate, sodium hydroxide, or a combination thereof.