

A METHOD OF ACTIVATING AND/OR REVERSIBLY DISSOLVING
CELLULOSE

Cross-Reference To Related Application

5 [0001] This application claims the benefit of priority of Singapore Patent Application No. 10201703735R, filed 5 May 2017, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

10 [0002] The present disclosure relates to a method of reversibly dissolving cellulose in an organic solvent.

Background

15 [0003] With the depletion of fossil resources, the utilization of cellulose, such as processing to fibers and derivatizing to functional materials, is gaining more attention due to cellulose and its application being renewable, sustainable and environmentally friendly.

[0004] Cellulose is one of the main component in plants and is one of the most abundant natural organic polymer on earth. Cellulose may be formed in all kinds of plants, whereas wood pulp tends to be the main source of cellulose used today, for example, in textiles, boards and paper. Currently, cotton appears to remain the main source of cellulose for making textiles in the world. The demand for wood based raw material for textiles, however, seems to be increasing due to environmental drawbacks associated with cotton cultivation and processing, such as high water consumption and land usage.

25 [0005] On the other hand, both wood and cotton based cellulose may be used to produce cellulose derivatives such as cellulose ethers and cellulose esters, which are widely used in pharmaceuticals, food, construction materials and paint. Among the different grades of cellulose available in the market, microcrystalline cellulose (MCC) seems to be of particular interest as MCC can be industrially produced on a large scale.

30 [0006] For producing cellulose derivatives and textiles, MCC has to be dissolved in a solvent to form a homogeneous solution. However, all grades of cellulose, especially

MCC, is a biomacromolecule (polysaccharide) having hundreds to thousands of $\beta(1\rightarrow4)$ linked D-glucose units, with an ordered hydrogen bonding network that makes it insoluble in water and most organic solvents. Therefore, developments of efficient and economical method to dissolve cellulose that helps in producing cellulose fibers and derivatives have been embarked on. Developed conventional methods, however, have their limitations. Such developed methods and their limitations are briefly discussed below.

[0007] In one method, carbon disulfide (CS_2) and NaOH were used to dissolve cellulose. However, this method uses large amount of CS_2 , which is toxic and results in severe pollution.

[0008] In another method, a non-toxic N-methylmorpholine oxide (NMMO)/water system is developed. However, dissolution of cellulose with these reagents has to be conducted at elevated temperatures of 100°C to 120°C and excess water has to be removed under reduced pressure. Moreover, NMMO, as an oxidant, causes severe degradation of cellulose.

[0009] In another method, a urea/NaOH system was used to dissolve cellulose but this method requires the solution to be precooled to -12°C .

[0010] All three methods mentioned above result in aqueous (water-rich) cellulose solutions that cannot be used for water sensitive cellulose derivatizing reactions. A method that circumvents this is the use of a N,N-dimethylacetamide (DMA)/LiCl system, but it suffers from slow dissolution even at elevated temperatures of 130°C to 165°C . Another method that uses a system of 1,1,3,3-tetramethyl guanidine (TMG)/dimethyl sulfoxide (DMSO)/ CO_2 also suffers from slow dissolution, and low concentration of dissolved cellulose. In yet another method that uses a system of TMG/ethylene glycol/DMSO/ CO_2 , it is limited by slow dissolution even when higher temperatures of 80°C to 120°C and higher pressures of 20 atm (2,026,500 Pa) are used.

[0011] Ionic liquids have also been experimented for dissolving cellulose but methods that utilize such ionic liquids tend to be expensive, toxic, difficult with purifying and recycling.

[0012] Details of the developed methods and their limitations as discussed above are provided in the example section of the present disclosure.

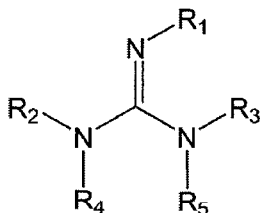
[0013] There is thus a need to provide for a method of dissolving cellulose that ameliorates or resolves one or more of the above issues. The method should at least provide for rapid dissolution of cellulose under mild conditions of room temperature and 1 atm (101,325 Pa) CO₂. The dissolution of such a method should be reversible.

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Summary

[0014] In one aspect, there is provided for a method of reversibly dissolving cellulose in an organic solvent comprising:

mixing a solution comprising dimethyl sulfoxide and cellulose with an organic
base in the presence of carbon dioxide, wherein the organic base is represented by a
formula of:



wherein each of R₁, R₂ and R₃ is C₁-C₂₀ alkyl;

wherein each of R₄ and R₅ is hydrogen or C₁-C₂₀ alkyl; and

maintaining the presence of carbon dioxide to form a transparent solution
comprising dissolved cellulose in the form of cellulose carbonate anions.

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Brief Description of the Drawings

[0015] The drawings are not necessarily to scale, emphasis instead generally being
placed upon illustrating the principles of the invention. In the following description,
various embodiments of the present disclosure are described with reference to the
following drawings, in which:

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[0016] FIG. 1 shows cellulose dissolution and regeneration with CS₂, NaOH and H₂SO₄.

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[0017] FIG. 2 shows the cellulose dissolution mechanism of the present method, using 2-(*tert*-butyl)-1,1,3,3-tetramethyl guanidine (BTMG) and CO₂ to form a switchable ionic system.

[0018] FIG. 3 shows the ¹H-NMR spectrum of pure BTMG (solvent DMSO-*d*₆). NMR refers to nuclear magnetic resonance.

[0019] FIG. 4 shows the ^1H -NMR spectrum of BTMG/cellulose/ CO_2 switchable system (solvent $\text{DMSO-}d_6$).

[0020] FIG. 5 shows the ^{13}C -NMR spectrum of pure BTMG (solvent $\text{DMSO-}d_6$).

5 [0021] FIG. 6 shows the ^{13}C -NMR of BTMG/cellulose/ CO_2 switchable system (solvent $\text{DMSO-}d_6$).

[0022] FIG. 7 shows a comparison of XRD (X-ray diffraction) patterns of regenerated cellulose and microcrystalline cellulose (MCC).

[0023] FIG. 8 shows a comparison of solid ^{13}C -NMR spectra of regenerated cellulose and MCC.

10 [0024] FIG. 9A(i) shows a comparison of BTMG with TMG and DBU in cellulose dissolution at room temperature (e.g. 20°C to 40°C) and 1 atm (101,325 Pa) CO_2 . Cellulose concentration is 10 wt% relative to DMSO. Specifically, BTMG and a organic base (BTMG) to cellulose molar ratio of 1 is used.

15 [0025] FIG. 9A(ii) shows a comparison of BTMG with TMG and DBU in cellulose dissolution at room temperature (e.g. 20°C to 40°C) and 1 atm (101,325 Pa) CO_2 . Cellulose concentration is 10 wt% relative to DMSO. Specifically, BTMG and a organic base (BTMG) to cellulose molar ratio of 0.57 is used.

20 [0026] FIG. 9B(i) shows a comparison of BTMG with TMG and DBU in cellulose dissolution at room temperature (e.g. 20°C to 40°C) and 1 atm (101,325 Pa) CO_2 . Cellulose concentration is 10 wt% relative to DMSO. Specifically, TMG and a organic base (TMG) to cellulose molar ratio of 1 is used.

25 [0027] FIG. 9B(ii) shows a comparison of BTMG with TMG and DBU in cellulose dissolution at room temperature (e.g. 20°C to 40°C) and 1 atm (101,325 Pa) CO_2 . Cellulose concentration is 10 wt% relative to DMSO. Specifically, TMG and a organic base (TMG) to cellulose molar ratio of 0.57 is used.

[0028] FIG. 9C(i) shows a comparison of BTMG with TMG and DBU in cellulose dissolution at room temperature (e.g. 20°C to 40°C) and 1 atm (101,325 Pa) CO_2 . Cellulose concentration is 10 wt% relative to DMSO. Specifically, DBU and a organic base (DBU) to cellulose molar ratio of 1 is used.

30 [0029] FIG. 9C(ii) shows a comparison of BTMG with TMG and DBU in cellulose dissolution at room temperature (e.g. 20°C to 40°C) and 1 atm (101,325 Pa) CO_2 .

Cellulose concentration is 10 wt% relative to DMSO. Specifically, DBU and a organic base (DBU) to cellulose molar ratio of 0.57 is used.

Detailed Description

5 [0030] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised.

[0031] The embodiments that are described in the present disclosure are in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments
10 may be utilized and structural, and logical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

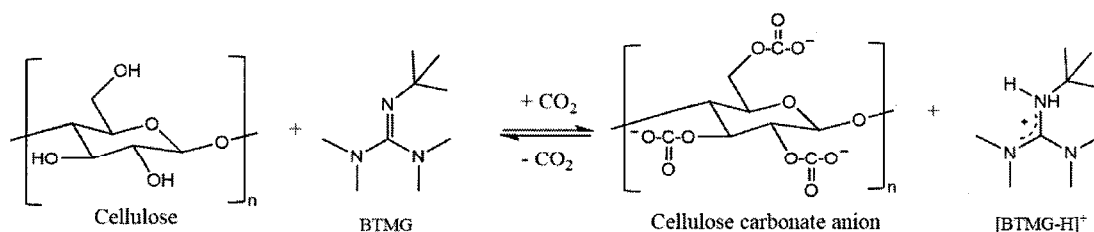
[0032] Features that are described in the context of an embodiment may
15 correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

20 [0033] Cellulose is a substance that does not dissolve or does not easily dissolve in most organic solvents or water at room temperature. To dissolve cellulose, the hydrogen bonding network in cellulose may have to be deconstructed. To deconstruct the hydrogen bonding network of cellulose, several conventional methods that have been reported for dissolving cellulose require elevated temperatures (e.g. up to 130°C)
25 or low temperatures (e.g. down to -12°C), and this renders such methods energy intensive. Moreover, other conventional methods require the use of toxic and/or expensive reagents to dissolve cellulose, or the method may suffer from poor dissolution rate and/or yield. The method of the present disclosure addresses one or more of such limitations.

30 [0034] The present method provides for reversibly dissolving cellulose in an organic solvent using mild reaction conditions, using an organic base in the presence of carbon dioxide. Advantageously, complete dissolution of cellulose based on the

present method can be achieved in less than 13 minutes even at room temperature and 1 atm (101,325 Pa) carbon dioxide. That is to say, heating and cooling are not required by the present method. Even at such conditions, the yield of the dissolved cellulose is not compromised.

- 5 [0035] The present method dissolves cellulose, including microcrystalline cellulose, by forming a switchable ionic system. The switchable ionic system is different from conventional switchable ionic compounds. In the present disclosure, the switchable ionic system refers to one that includes cellulose carbonate anion, which is switchable as shown in the scheme below. “n” in the scheme below may be 1 to 100,000. 2-(*tert*-
- 10 butyl)-1,1,3,3-tetramethylguanidine (BTMG) is used as an example of the organic base in the scheme below. The intermediate cellulose-O⁻ anion is not shown in the scheme below.



- 15 [0036] From the scheme above, the switching can be triggered by CO₂ without any alcohol. CO₂ acts as the switch in this switchable system. Advantageously, no alcohol is used in the dissolution of cellulose for the present method. In this regard, the present solution system may be called a “self-forming switchable system”.

- 20 [0037] Even though the present method is mainly used to dissolve cellulose, the cellulose that has been dissolved in the present method can be regenerated. The cellulose can be regenerated into useful materials, such as fibres and films. The precipitated cellulose can be re-dissolved. Advantageously, the present method may be used for reversible dissolution of cellulose. With the present method, even if alcohol is added, the solution containing the cellulose carbonate anions can easily regenerate cellulose with reduced crystallinity. Nevertheless, the backbone of
- 25 cellulose is still retained.

[0038] Based on the scheme above, in one example, the present method can be used to dissolve microcrystalline cellulose in dimethyl sulfoxide (DMSO) by forming a switchable ionic system with 1 atm CO₂ and BTMG at room temperatures (e.g. 20°C

to 40°C). In such an instance, cellulose (5.1 wt%) can be rapidly dissolved in DMSO in 2 minutes at a room temperature in 1 atm (101,325 Pa) of CO₂.

[0039] The present method of dissolving cellulose is beneficial to the environment as it uses an abundant greenhouse gas, i.e. carbon dioxide, and non-toxic organic bases.

5 [0040] The obtained transparent solution containing the cellulose carbonate anions may be anhydrous. In other words, various steps of the present method may be anhydrous, i.e. do not require water, and this renders the present method advantageous for subsequent processes where transforming cellulose to its useful derivatives require water to be absent. The present method is also potentially useful for producing
10 regenerated cellulose based films and fibres.

[0041] Having outlined various advantages of the present method, definitions of certain terms are first discussed before going into details of the various embodiments.

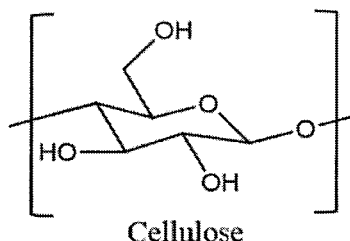
[0042] The term “aprotic” as used herein refers to a substance that does not donate hydrogen or hydrogen ion. For example, an aprotic organic base would refer to an
15 organic base that does not donate hydrogen or hydrogen ion.

[0043] The term “alkyl” as used herein, as a group or part of a group, refers to a straight or branched aliphatic hydrocarbon group, including but not limited to, a C₁–C₂₀ alkyl, C₁–C₁₂ alkyl, a C₁–C₁₀ alkyl, a C₁–C₆ alkyl. Examples of suitable straight and branched C₁–C₆ alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-
20 butyl, sec-butyl, t-butyl, hexyl, and the like. Alkyl groups may be substituted or unsubstituted.

[0044] The expression “cellulose-OCOO⁻” as used herein refers to a cellulose carbonate anion.

[0045] The expression “cellulose-O⁻” as used herein is to specifically refer to a
25 deprotonated cellulose or that the hydroxyl group of the cellulose has been deprotonated.

[0046] The expression “cellulose-OH” as used herein is to specifically refer to the OH group attached to the cellulose (as shown below). For example, when a molar ratio of BTMG to cellulose-OH is 1:1, this means that the molar ratio of BTMG with respect
30 to a hydroxyl group of the cellulose is 1:1, and the molar ratio of BTMG to one repeating unit of cellulose would be 3:1.



[0047] The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

[0048] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

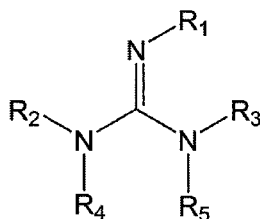
[0049] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance.

[0050] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0051] Unless specified otherwise, the terms “comprising” and “comprise”, and grammatical variants thereof, are intended to represent “open” or “inclusive” language such that they include recited elements but also permit inclusion of additional, unrecited elements.

[0052] Having defined the various terms as mentioned above, details of the various embodiments are now described below.

[0053] In the present disclosure, there is provided for a method of reversibly dissolving cellulose in an organic solvent comprising mixing a solution comprising dimethyl sulfoxide and cellulose with an organic base in the presence of carbon dioxide, wherein the organic base is represented by a formula of:

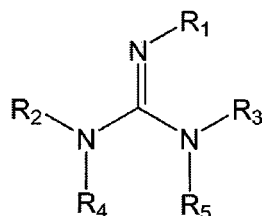


wherein each of R₁, R₂ and R₃ is C₁-C₂₀ alkyl, wherein each of R₄ and R₅ is hydrogen or C₁-C₂₀ alkyl; and maintaining the presence of carbon dioxide to form a transparent solution comprising dissolved cellulose in the form of cellulose carbonate anions.

[0054] As mentioned above, the present method allows for reversible dissolution of cellulose. To reverse the dissolution of cellulose, the present method may further comprise reducing the presence of carbon dioxide to convert the cellulose carbonate anions into cellulose when needed. By reducing the presence of CO₂, the cellulose carbonate anions can be converted back into the intermediate cellulose-O⁻ anions, which is then converted back to cellulose.

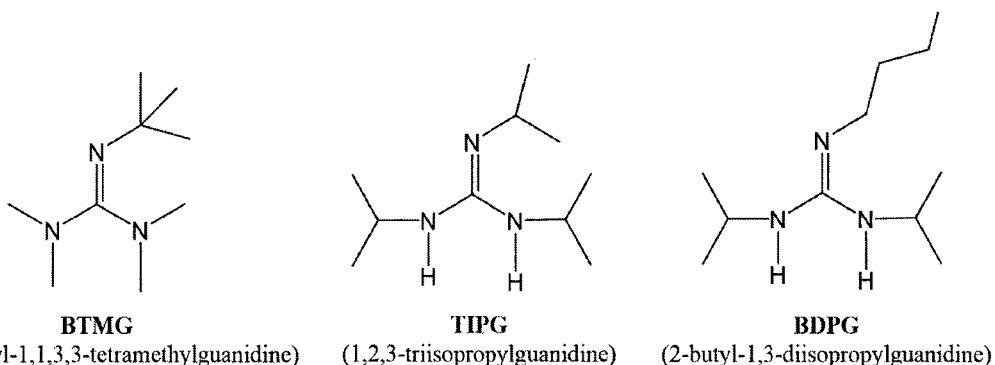
[0055] In the present method, the mixing of the solution comprising dimethyl sulfoxide and cellulose with the organic base in the presence of CO₂, e.g. at room temperature, helps to dissolve the cellulose rapidly to form a cellulose solution comprising intermediate cellulose-O⁻ anions. The cellulose solution is further converted into a transparent solution comprising “self-forming switchable” cellulose carbonate anions. Such solutions may be referred to as a “switchable system” as discussed above. While the mixing is carried out at mild reaction conditions, the cellulose not only dissolves in the dimethyl sulfoxide solvent but also dissolves faster compared to conventional solvents. An example of the mild reaction conditions may be 1 atm (101,325 Pa) CO₂ and 22°C.

[0056] In the present method, dimethyl sulfoxide serves as the organic solvent for cellulose to be dissolved in. That is to say, the organic base is not a solvent for dissolving the cellulose. Rather, the organic base is used to deprotonate cellulose. The organic base is represented by the formula below.



[0057] In various embodiments, each of R₁, R₂ and R₃ in the above formula may be C₁-C₂₀ alkyl, C₁-C₁₀ alkyl or C₁-C₆ alkyl. In various embodiments, each of R₄ and R₅ in the above formula may be hydrogen or C₁-C₂₀ alkyl, C₁-C₁₀ alkyl or C₁-C₆ alkyl. Organic bases encompassed by the above formula and usable in the present method may comprise 2-tert-butyl-1,1,3,3-tetramethylguanidine (BTMG), 1,2,3-

triisopropylguanidine (TIPG), 2-butyl-1,3-diisopropylguanidine (BDPG), or their combination thereof. The organic bases used in the present method may be called aprotic organic bases as they do not donate, but accept hydrogen or hydrogen ion(s) when used for deprotonating cellulose. In some embodiments, the organic base may be BTMG. The organic bases mentioned above are shown below.



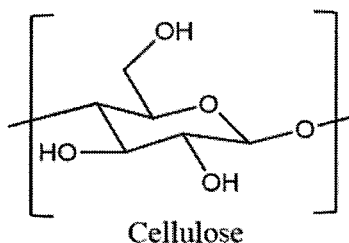
[0058] In various embodiment, the mixing step, and/or the maintaining step, may be carried out at a temperature of 20°C to 40°C, 25°C to 40°C, 30°C to 40°C, 35°C to 40°C, 20°C to 35°C, 25°C to 35°C, 30°C to 35°C, 20°C to 30°C, 25°C to 30°C, 20°C to 25°C, etc. In some embodiments, the mixing step, and/or the maintaining step, may be carried out at a temperature of 22°C. Advantageously, the present method of synthesizing cellulose carbonate does not require temperatures higher than room temperatures, e.g. the temperatures specified above.

[0059] In various embodiments, the carbon dioxide may have a pressure of at least 1 atm (101,325 Pa). The pressure of the carbon dioxide for both the mixing step and the maintaining step may be the same. In some embodiments, the pressure (of the carbon dioxide) may be 1 atm (101,325 Pa) to 20 atm (2,026,500 Pa). In some embodiments, the pressure (of the carbon dioxide) may be 1 atm (101,325 Pa).

[0060] The present method is also advantageous because it is not restricted but applicable to various types of cellulose. In various embodiments, the cellulose used may comprise microcrystalline cellulose, amorphous cellulose or cotton. The cellulose used may also be a combination of such celluloses.

[0061] In various embodiments, the cellulose dissolution in the mixing step may occur at different molar ratios of organic base to cellulose-OH. The molar ratio of organic base to cellulose-OH is used to specifically refer to the molar ratio between the organic base and a hydroxyl (OH) group of the cellulose. This is not to be

confused with a molar ratio of organic base to cellulose, as cellulose is made up of repeating units each having three hydroxyl groups as shown below.



[0062] If the molar ratio of organic base to cellulose is used instead of organic base to cellulose-OH, then the molar ratio should be 3:1 instead of 1:1. Having discussed the definition of “cellulose-OH”, the mixing may be carried out based on a molar ratio of organic base to cellulose-OH ranging from 0.50 to 3.00 according to various embodiments. Advantageously, by employing a ratio as discussed above, a higher concentration of cellulose in the solution may be obtained. In some embodiments, the molar ratio of organic base to cellulose-OH may be 1 to 1. In some instances, where BTMG is used as the organic base, the BTMG may be mixed with the cellulose in a molar ratio of BTMG to cellulose-OH ranging from 0.50 to 3.00, 1:1, etc.

[0063] After mixing the solution, the presence of carbon dioxide may be maintained. The step of maintaining the presence of carbon dioxide helps to form a transparent solution from the solution of the mixing step. The solution of the mixing step may be referred to as a cellulose solution (comprising the intermediate cellulose-O⁻ anions). When carbon dioxide is maintained, the cellulose-O⁻ anion gets converted into cellulose carbonate anions. While the conversion is ongoing, the protonated form of the organic base (e.g. [BTMG-H]⁺) and/or cellulose-O⁻ anions may be present. The presence of these intermediate substances allows for the dissolution of cellulose to be reversed, i.e. conversion of cellulose-O⁻ anions back into cellulose, for example, when the presence of carbon dioxide is not maintained. Accordingly, in some embodiments, the transparent solution may further comprise cellulose-O⁻ anions and/or a protonated form of the organic base. Where BTMG is used as the organic base, the protonated form of the organic base may comprise [BTMG-H]⁺, and the transparent solution may further comprise [BTMG-H]⁺ and/or cellulose-O⁻ anions in such embodiments.

[0064] To regenerate the cellulose that has dissolved, other than or in addition to reducing the presence of carbon dioxide, the method may further comprise adding

water or an alcohol to the transparent solution to precipitate the dissolved cellulose. In various embodiments, the alcohol may comprise methanol or ethanol. In some embodiments, the precipitated cellulose may have a lower crystallinity compared to the crystalline cellulose before dissolving in the organic solvent.

- 5 [0065] While the methods described above are illustrated and described as a series of steps or events, it will be appreciated that some steps, for example, may occur in different orders and/or concurrently with other steps or events apart from those illustrated and/or described herein. In addition, not all illustrated steps may be required to implement one or more aspects or embodiments described herein. Also,
10 one or more of the steps depicted herein may be carried out in one or more separate acts and/or phases.

Examples

- [0066] The present disclosure relates to a method of reversibly dissolving cellulose in
15 an organic solvent using an organic base and carbon dioxide. One example of the present method is briefly described below.

- [0067] For the present method, in the presence of 1 atm (101,325 Pa) CO₂, 2-(*tert*-butyl)-1,1,3,3-tetramethyl guanidine (BTMG), which is an aprotic penta-alkyl guanidine, has the ability to efficiently form a switchable ionic system with cellulose
20 at room temperature. This allows cellulose to be rapidly dissolved in DMSO, affording a high cellulose concentration solution of more than 8.0 wt%. Advantageously, the present method provides for rapid dissolution of cellulose (about 4 to 13 minutes) to afford a high concentration solution at mild reaction conditions of room temperature (e.g. 20°C to 40°C) and atmospheric pressure.

- 25 [0068] Further details of the present method are described, by way of non-limiting examples, as provided below.

[0069] Example 1: Conventional Methods for Cellulose Dissolution

- [0070] *Method-1: CS₂ and aqueous NaOH.* One conventional method to dissolve cellulose is to treat cellulose with CS₂ (33 wt%) and a strong base of aqueous NaOH
30 (18 wt%) to yield a solution called “viscose”, which can be spun into regenerated cellulose fiber in strong acid H₂SO₄ solution (scheme 1). This dissolution method has been industrialized to produce “Rayon fiber”, an “artificial silk”, more than a hundred

years ago. However, this dissolution method uses huge amounts of toxic compound CS₂, resulting in severe environmental pollution.

[0071] **Method-2: *N*-Methylmorpholine oxide (NMMO)/water.** NMMO is considered a non-toxic and a non-derivatizing cellulose solvent. In this method, cellulose is first suspended in NMMO with a large amount of water. The excess water provides a low viscosity mixture for superior mixing. The surplus water is then removed by reduced pressure at an elevated temperature between 100°C and 120°C until the cellulose is completely dissolved. A typical solution usually contains approximately 14wt% cellulose, 10wt% water and 76wt% NMMO. The drawbacks are high energy consumption due to dissolution at an elevated temperature under reduced pressure. Moreover, a stabilizer has to be added as NMMO is an oxidant which causes severe degradation.

[0072] **Method-3: *Urea*/NaOH/water.** In this method, cellulose is dissolved in a urea/NaOH aqueous solution. For example, cellulose was first dispersed in a 7 wt% NaOH/12 wt% urea aqueous solution precooled to -12°C, followed by stirring for 5 minutes to obtain a transparent 4 wt% cellulose solution. The obtained cellulose solution can be used to produce cellulose fibers. However, this dissolution requires considerable amount of energy for the cooling down to -12°C and the method cannot be used for various derivatizing reactions that require anhydrous conditions.

[0073] **Method-4: *N,N*-Dimethylacetamide (DMA)/LiCl.** All the above three dissolution methods result in aqueous or water-rich cellulose solutions that cannot be used for water sensitive cellulose derivatizing reactions, such as cellulose carbonate synthesis with chloroformate. The DMA/LiCl method, on the other hand, can be used to generate an anhydrous cellulose solution: cellulose was first dispersed in DMA and stirred at elevated temperature (above 130°C) for 2 hours or refluxed at 165°C for 30 minutes. Subsequently, the slurry was cooled to 100°C, followed by the addition of LiCl. After which, the slurry was slowly cooled to room temperature and stirred overnight to form a solution. This dissolution method, however, is slow and energy intensive as it takes a long time and high temperatures are used, respectively. The DS (degree of substitution) is also low when this dissolution method was used in the synthesis of cellulose carbonates.

[0074] **Method-5: Ionic liquids and Ionic liquids/co-solvent system.** Ionic liquids are strong polar solvents, and it has been an actively researched area for dissolution of cellulose. Co-solvents such as 1,3-dimethyl-2-imidazolidinone (DMI) can be added to reduce the viscosity and increase the dissolution rate. For example, cellulose (1 g) was dispersed in DMI (5 g) at 100°C. The solid 1-butyl-3-methylimidazolium chloride (BMIMCl, 5 g) was then added into the suspension. This method enables the complete dissolution of cellulose under magnetic stirring at 100°C after only 3 minutes. For comparison, the complete dissolution of cellulose (5 wt%) in neat BMIMCl takes more than 10 hours. However, the applications of ionic liquids are hindered by its high price, toxicity, difficulty when it comes to purifying and recycling systems with ionic liquids.

[0075] **Method-6: 1,1,3,3-Tetramethyl guanidine (TMG)/DMSO/CO₂.** The formation of switchable ionic solvent from DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene), 1-hexanol and CO₂ was first reported. Subsequently, a method to dissolve cellulose by forming a switchable ionic system was through the use of TMG/DMSO at room temperature and 2 bar (200 kPa) CO₂ atmosphere. TMG was proposed to deprotonate cellulose to form cellulose-O⁻ which reacts with CO₂ to form cellulose carbonate anion (cellulose-OCOO⁻). However, as TMG is a protic base, it is less efficient in deprotonating cellulose, resulting in slow dissolution. For example, cellulose solution (8 wt% relative to DMSO) was obtained after 1 hour of stirring at 2 bar CO₂ at room temperature in DMSO containing 9 wt% TMG. Protic TMG can form intermolecular hydrogen bonding, which reduces the opportunity for TMG to form hydrogen bonding with cellulose, resulting in a lower capability to deprotonate cellulose for dissolution. As such, the dissolution is slow and higher concentration of cellulose cannot be achieved.

[0076] **Method-7: TMG/ethylene glycol/DMSO/CO₂.** It was demonstrated that TMG/ethylene glycol/CO₂ was able to form a switchable ionic system in DMSO solvent. The obtained TMG/ethylene glycol/CO₂/DMSO switchable ionic system can dissolve cellulose at elevated temperature (80°C to 120°C) and high pressure CO₂. For example, 5 wt% cellulose solution was obtained in TMG/ethylene glycol/DMSO system with 12 hours stirring at 80°C under 20 atm (2,026,500 Pa) CO₂. However, the dissolution was not done under mild conditions. Also, the high CO₂ pressure and high

temperature consumes a considerable amount of energy, and yet the dissolution rate remains slow.

[0077] The seven methods discussed above are conventionally efficient ones that have been developed. However, all of them have problems, such as environmental pollution caused by CS₂, high energy consumption due to requirements of high temperature (80°C to 130°C), low temperature (-12°C), and/or high pressure CO₂, as well as limitations such as long dissolution time due to low cellulose deprotonation capability, such as that of TMG. A summary of the limitations of these seven conventional methods are provided in table 1 below.

10 [0078] Table 1 - Conventional methods and their limitations

Method	Solvent System	Problems
1	CS ₂ and NaOH aqueous	• Use of large amounts of toxic CS₂.
2	N-Methylmorpholine oxide (NMMO)/water	• Conducted at an elevated temperature between 100 and 120 °C. • The removal of excess water is done under reduced pressure. • NMMO is an oxidant, causing severe degradation.
3	Urea/NaOH/water	• Urea/NaOH aqueous solution needs to be precooled to -12 °C.
4	N,N-Dimethylacetamide (DMA) / LiCl.	• Conducted at elevated temperature up to 130-165 °C. Slow dissolution.
5	Ionic liquids and Ionic liquids/co-solvent system	• Expensive, toxic, difficult purification and difficult recycling.
6	TMG/DMSO/CO ₂	• Slow dissolution and low cellulose concentration.
7	TMG/ethylene glycol/DMSO/CO ₂	• Slow dissolution at elevated temperature (80-120 °C) and high pressure CO₂ (20 atm).

[0079] **Example 2a: Experimental – Materials and Characterizations Used**

[0080] All operations were carried out under an atmosphere of nitrogen or argon by using standard Schlenk line techniques. ¹H and ¹³C-NMR (NMR: nuclear magnetic resonance) spectra were recorded in DMSO-*d*₆ on a BRUKER 400MHz spectrometer. The bases 2-(*tert*-butyl)-1,1,3,3-tetramethylguanidine (BTMG, 97%), 1,1,3,3-tetramethyl guanidine (TMG, 99%) and 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU, 98%) were purchased from Sigma-Aldrich. Microcrystalline cellulose (MCC) was purchased from Alfa Aesar. All chemicals were used as received without purification.

Anhydrous DMSO was purchased from Sigma Aldrich. DMSO- d_6 was purchased from Cambridge Isotope Laboratories, which was bubbled with argon before use. The cotton roll is from Guardian Health and Beauty, and the cotton towel used was from MILTON Home. CO₂ gas was purchased from Air Liquid.

5 **[0081] Example 2b: Experimental – General Procedure for Cellulose Dissolution with Liquid Bases (BTMG, TMG, DBU)**

10 **[0082]** In a 100 mL Schlenk tube charged with required amount of cellulose under CO₂ atmosphere supplied with a latex gas balloon, the required amount of DMSO was added. Under vigorous stirring, the liquid base was added dropwise in less than 0.5 minutes. The resulting mixture was stirred at room temperature (20°C to 40°C) for 2 hours. The dissolution behavior and the stirring time required for complete dissolution were recorded.

15 **[0083] Example 2c: Experimental – General Procedure for NMR Studies**

20 **[0084]** In a 50 mL Schlenk tube charged with cellulose (95 mg, cellulose-OH: 1.76 mmol, 4 wt% relative to DMSO) under CO₂ atmosphere supplied with a latex gas balloon, DMSO- d_6 (2.4 g) was added. This was followed by dropwise addition of BTMG (301mg, 1.76 mmol, 12.5 wt% relative to DMSO) under stirring at room temperatures. A clear solution was obtained after 3 minutes of stirring, which was continued to be stirred constantly for 2 hours at room temperatures. A sample of 0.5 mL was taken for ¹H-NMR and ¹³C-NMR characterizations.

25 **[0085] Example 2d: Experimental - Typical Procedure for Cellulose Dissolution and Regeneration with BTMG**

30 **[0086]** In a 100 mL Schlenk tube charged with cellulose (0.95 g, cellulose-OH: 17.58mmol) under CO₂ atmosphere supplied with a latex gas balloon, DMSO (9.5 g) was added. Under vigorous stirring, a liquid base BTMG (1.71 g, 9.98 mmol) was added dropwise within 0.5 minutes. A transparent cellulose solution was obtained after 13 minutes of stirring. The clear solution was stirred at room temperatures under CO₂ for 2 hours. After which, the solution was vacuumed for 30 minutes, followed by addition of 20 mL methanol. The precipitated cellulose was filtered and washed with methanol (3 times of 20 mL). The regenerated cellulose was dried in vacuum overnight at room temperature (obtained 0.90 g, yield at 95%).

[0087] Example 3a: Discussion - Dissolution Mechanism and Investigations from ^1H and ^{13}C -NMR

[0088] Examples of the present disclosure demonstrated that BTMG, which is an aprotic penta-alkyl guanidine, is extremely efficient in deprotonating cellulose at room temperature (e.g. 22°C) and at only 1 atm (101,325 Pa) CO_2 atmosphere in DMSO solvent. The proposed dissolution mechanism is shown in FIG. 2.

[0089] BTMG first breaks the hydrogen bonding network of cellulose by deprotonating cellulose-OH, forming $[\text{BTMG-H}]^+$ cation and cellulose- O^- anion. The cellulose- O^- anion may be referred to as an intermediate product. Subsequently, CO_2 reacts with cellulose- O^- anion to transform into cellulose carbonate anion (cellulose- OCOO^-), leading to rapid and complete dissolution.

[0090] There are two reasons behind the better efficiency of BTMG.

[0091] (1) BTMG is an aprotic base, hence there is no intermolecular hydrogen bonding among BTMG molecules. This allows the BTMG to form new hydrogen bonding only with the hydroxyl groups of cellulose, which is followed by rapid deprotonation of the hydroxyl groups.

[0092] (2) The 2-alkyl is an electron donating group, which makes the lone pair of electrons on N (=N-alkyl) more electron rich. Thus, it serves as a stronger nucleophile in deprotonating the hydroxyl groups more easily as compared to TMG.

[0093] The mechanism was proven by running dissolution in $\text{DMSO}-d_6$, followed by immediate ^1H and ^{13}C -NMR analysis. When BTMG was transformed to $[\text{BTMG-H}]^+$, the signal of $\text{N}-\text{C}(\text{CH}_3)_3$ was shifted from 1.12 ppm to 1.24 ppm in ^1H -NMR spectrum (FIG. 3 and FIG. 4). The signal of $\text{N}(\text{CH}_3)_2$ was also shifted from 2.54 ppm to 2.80 ppm. The H signal of $[\text{BTMG-H}]^+$ was observed at 9.05 ppm. In ^{13}C -NMR spectrum of BTMG (FIG. 5), the signals of $\text{N}-\text{C}(\text{CH}_3)_3$ and $\text{N}(\text{CH}_3)_2$ were overlapped at 32.33 ppm. When BTMG was transformed to $[\text{BTMG-H}]^+$ (FIG. 6), with exception of the signal of $\text{N}-\text{C}(\text{CH}_3)_3$ that shifted to high field from 32.33 to 30.80 ppm, all the other three signals of $\text{N}(\text{CH}_3)_2$ and $\text{N}-\text{C}(\text{CH}_3)_3$ and $\text{C}=\text{N}$ shifted to low field, from 32.33, 52.93, 155.76 to 40.71, 55.16, 159.64 ppm, respectively. This shows that the electron cloud of the π -bond and the cation charge delocalized into the three N atoms and the central carbon, resulting in enhanced stability. These results clearly demonstrated the fast transformation from BTMG to $[\text{BTMG-H}]^+$ cation. The signals of cellulose

carbonate anions (cellulose-OCOO⁻) were observed in the ¹³C-NMR spectrum as a broad multi-peak between 156.26 ppm and 157.38 ppm. Also, the cellulose backbone was observed at 75.16 ppm as a broad peak due to the polymeric nature of cellulose and the equilibrium between cellulose-O⁻ and cellulose-OCOO⁻ induced by CO₂.

5 Hence, CO₂ plays a critical role in the present method of reversible dissolution.

[0094] Example 3b: Discussion - Role of CO₂

[0095] To demonstrate the critical role of CO₂, we dispersed only 1 wt% cellulose in DMSO containing 9 wt% BTMG. The BTMG/cellulose-OH molar ratio is 2.84. No dissolution was observed after the suspension was stirred in N₂ atmosphere for 2
10 hours. Thereafter, N₂ gas was removed using a vacuum pump and back filled with CO₂ gas using a CO₂ latex balloon, which showed an immediate dissolution, producing a clear solution in less than a minute. This experiment showed that CO₂ plays a critical role in cellulose dissolution, and cellulose is unable to dissolve in the absence of CO₂.

15 **[0096] Example 3c: Discussion - The Effect of BTMG/cellulose-OH Molar Ratio**

[0097] In the dissolution process, BTMG breaks the hydrogen bonding network of cellulose by forming new hydrogen bonds between BTMG and the hydroxyl groups of cellulose. Therefore, the BTMG/cellulose-OH molar ratio is a factor that should at least be considered (see table 2 below).

20 **[0098] Table 2 - Cellulose dissolution with different BTMG/cellulose-OH molar ratio^a**

Entry	DMSO (g)	BTMG (g)	MCC (g)	Cellulose concentration relative to DMSO (wt%)	Cellulose concentration relative to DMSO+BTMG (wt%)	BTMG/Cellu-OH (molar ratio)	Stirring time (min) ^b
1	5.39	1.71	0.54	10.0	7.6	1.0	10
2	5.39	1.14	0.54	10.0	8.3	0.67	5
3	9.50	1.71	0.95	10.0	8.5	0.57	13
4	6.74	1.71	0.54	8.0	6.4	1.0	4
5	4.49	0.855	0.27	6.0	5.1	1.0	2
6	5.39	1.41	0.54 ^c	10.0	8.5	0.67	NA ^e
7	3.37	0.855	0.27 ^d	8.0	6.4	1.0	NA ^e

^aDissolution was carried out in a 100 mL Schlenk tube at room temperature and 1 atm (101,325 Pa) CO₂ atmosphere.

^bStirring time to achieve complete dissolution.

^cCotton roll was used.

^dA piece of cotton towel was used.

^eA clear viscose solution was obtained after 4 hours.

- 5 **[0099]** From table 2 above, when the cellulose concentration relative to DMSO is 10 wt%, the fastest dissolution was achieved when BTMG/cellulose-OH molar ratio is 0.67 (entry 2). An overall cellulose concentration of 8.3 wt% was obtained in 5 minutes. At this condition, only 2 out of the 3 hydroxyl groups in each anhydroglucose unit (AGU) were deprotonated. When BTMG/cellulose-OH molar ratio was increased from 0.67 to 1.0 (entry 1), all the 3 hydroxyl groups in every AGU were deprotonated. However, the dissolution rate slows down, requiring 10 minutes of stirring to achieve complete dissolution. This is due to more BTMG forming more [BTMG-H]⁺ cations, which also have to be dissolved into DMSO. When BTMG/cellulose-OH molar ratio was decreased from 0.67 to 0.57 (entry 3), although only 57% of the hydroxyl groups were deprotonated, the cellulose can still be completely dissolved in 13 minutes of stirring. At the condition that BTMG/cellulose-OH molar ratio was 1.0, when the cellulose wt% was decreased from 10% to 8% and 6%, complete dissolution was observed in only 4 and 2 minutes, respectively. The viscosity is lower at lower cellulose concentration, leading to faster dissolution.
- 10 **[00100]** When MCC was replaced with cotton roll and cotton towel (entries 6 & 7), they can also be dissolved to produce a very viscous solution, indicating their higher molecular weights.

[00101] Example 3d: Discussion - The Effect of BTMG/Cellulose-OH Molar Ratio

- 25 **[00102]** The dissolved cellulose can be easily precipitated by the addition of methanol. It is then filtered, washed with methanol and ether, followed by drying in vacuum at room temperature overnight. Compared to MCC, the regenerated cellulose has much lower crystallinity (FIG. 7). In the solid ¹³C-NMR spectrum (FIG. 8), the peaks at 62.26, 69.35 and 86.01 ppm, which are likely attributed to crystalline cellulose, have disappeared in the solid ¹³C-NMR spectrum of regenerated cellulose, which is mostly amorphous cellulose with very low crystallinity. The solid ¹³C-NMR spectrum also showed that the backbone of the cellulose was retained after the dissolution and regeneration procedure, therefore cellulose remains stable in the presence of BTMG.
- 30

[00103] Example 3e: Discussion - Comparison of BTMG with TMG and 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU)

[00104] To demonstrate the high efficiency of BTMG in cellulose dissolution, BTMG was compared with TMG and DBU using an organic base to cellulose-OH molar ratio of 1.0 and 0.57 (FIG. 9 Figure 7) and the cellulose concentration is 10 wt% relative to DMSO. At both ratios of 1.0 and 0.57, BTMG is able to rapidly dissolve cellulose, affording a clear transparent solution in 5 and 13 minutes, respectively [FIG. 9A(i) and FIG. 9A(ii)]. While TMG can only partially dissolve cellulose, affording a cloudy suspension [FIG. 9B(i) and FIG. 9B(ii)], DBU dissolved the least amount of cellulose, with significant amount of cellulose not dissolved, giving a white slurry suspension [FIG. 9C(i) and FIG. 9C(ii)].

[00105] Example 4: Summary and Applications of Present Method

[00106] The present disclosure provides a method to dissolve microcrystalline cellulose rapidly by forming a switchable ionic system with 1 atm (101,325 Pa) CO₂ and BTMG in DMSO at room temperature. So far, the present method advantageously provides for improved dissolution of cellulose, e.g. microcrystalline cellulose, more rapidly at room temperatures and atmospheric pressures (e.g. 101,325 Pa) to afford a cellulose solution with better concentrations of up to 8.5 wt%. The BTMG/cellulose-OH molar ratio is a factor that affects the dissolution rate. Among the ratios of 1.0, 0.67, 0.57, and at the condition that cellulose concentration is 10 wt% relative to DMSO, the ratio of 1.0 has the fastest dissolution rate with the cellulose completely dissolved in only 5 minutes. The dissolved cellulose can be easily regenerated by the addition of methanol. The XRD patterns in the above examples indicated that the regenerated cellulose has much lower crystallinity compared to their original microcrystalline cellulose. The solid ¹³C-NMR spectra showed that the cellulose backbone was retained after the dissolution and regeneration procedures.

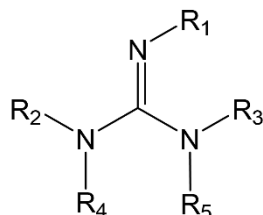
[00107] The dissolution mechanism was investigated with ¹H and ¹³C-NMR. The results showed that BTMG is extremely efficient in deprotonating cellulose at room temperature (e.g. 22°C) in 1 atm (101,325 Pa) CO₂ atmosphere in DMSO solvent. BTMG first breaks the hydrogen bonding network of cellulose by deprotonating cellulose-OH, forming [BTMG-H]⁺ cation and cellulose-O⁻ anion. Subsequently, the cellulose-O⁻ anion reacts with CO₂ to transform to carbonate anion (cellulose-OCOO⁻),

leading to rapid and complete dissolution. The obtained cellulose solution is anhydrous, and it can be used to prepare functional cellulose derivatives, and potentially to prepare regenerated cellulose fibers. The present method is therefore industrially applicable.

- 5 [00108] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within
10 the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A method of reversibly dissolving cellulose in an organic solvent comprising:
 mixing a solution comprising dimethyl sulfoxide and cellulose with an organic
 5 base in the presence of carbon dioxide, wherein the organic base is represented by a
 formula of:



- wherein each of R₁, R₂ and R₃ is C₁-C₂₀ alkyl;
 wherein each of R₄ and R₅ is hydrogen or C₁-C₂₀ alkyl; and
 10 maintaining the presence of carbon dioxide to form a transparent solution
 comprising dissolved cellulose in the form of cellulose carbonate anions,
 wherein the mixing and the maintaining steps are carried out at a temperature
 of 20°C to 40°C.
- 15 2. The method according to claim 1, further comprising reducing the presence of
 carbon dioxide to convert the cellulose carbonate anions into cellulose when needed.
3. The method according to claim 1 or 2, wherein the organic base comprises 2-
 tert-butyl-1,1,3,3-tetramethylguanidine (BTMG), 1,2,3-triisopropylguanidine (TIPG),
 20 2-butyl-1,3-diisopropylguanidine (BDPG), or their combination thereof.
4. The method according to any one of claims 1 to 3, wherein the organic base is
 BTMG.
- 25 5. The method according to any one of claims 1 to 4, wherein the cellulose
 comprises microcrystalline cellulose, amorphous cellulose or cotton.

6. The method according to claim 1, wherein the mixing is carried out at a temperature of 22°C.
7. The method according to any one of claims 1 to 6, wherein the carbon dioxide
5 has a pressure of at least 1 atm (101,325 Pa).
8. The method according to claim 7, wherein the pressure is 1 atm (101,325 Pa) to 20 atm (2,026,500 Pa).
- 10 9. The method according to claim 7 or 8, wherein the pressure is 1 atm (101,325 Pa).
10. The method according to any one of claims 1 to 9, wherein the mixing is carried out based on a molar ratio of organic base to cellulose-OH ranging from 0.50
15 to 3.00.
11. The method according to any one of claims 1 to 10, wherein the transparent solution further comprises cellulose-O⁻ anions and/or a protonated form of the organic base.
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12. The method according to claim 11, wherein the protonated form of the organic base comprises [BTMG-H]⁺.
13. The method according to claim 1, further comprising adding water or an
25 alcohol to the transparent solution to precipitate the dissolved cellulose.
14. The method according to claim 13, wherein the alcohol comprises methanol or ethanol.
- 30 15. The method according to claim 13 or 14, wherein the precipitated cellulose has a lower crystallinity compared to the crystalline cellulose before dissolving in the organic solvent.