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离子液体中无机/高分子杂化材料的制备

Preparation of inorganic/polymer hybrid materials in ionic liquids

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Preparation of inorganic/polymer hybrid materials in ionic liquids

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摘 要

离子液体是指由有机阳离子和无机或有机阴离子构成的，在室温或者室温附近温度下呈液态的盐类。与易挥发的有机溶剂相比，离子液体具有蒸气压小、不可燃、热容大、可设计性强、热稳定性好、离子电导率高、电化学窗口宽等优点，被称为一类新型的绿色溶剂。当前离子液体已广泛应用于分离过程、电化学、催化化学、材料制备等领域，其中在材料制备方面的应用处于起步阶段，研究的范围包括离子液体中聚合物的合成、无机纳米材料的制备、天然高分子的加工等。本论文借助离子液体制备了几种无机/高分子杂化材料，取得了以下成果：

1. 传统制备咪唑离子液体的方法，是用咪唑和卤代烷烃反应，当卤代烷烃沸点低时(如氯甲烷、氯乙烷等)，势必对设备要求高，且制备条件苛刻。我们发现一种新的离子液体制备方法，首先用酸与咪唑反应得到酸性离子液体前驱体，然后酸性离子液体前躯体与碳酸酯反应制得咪唑离子液体，该方法可以克服传统制备方法的缺陷。制得的咪唑氯盐阳离子尺寸小，具有粘度低、电导率高等特点，且对纤维素和壳聚糖有较强的溶解性能。我们以这类阳离子尺寸较小的咪唑氯盐为溶剂制备了壳聚糖/纤维素复合膜和纤维材料。鉴于多壁碳纳米管(MWCNTs)在离子液体中可以实现良好的物理分散，我们将 MWCNTs 分散在溶解纤维素、壳聚糖的离子液体溶液中，经再生过程制备了 MWCNTs/壳聚糖/纤维素杂化膜和纤维材料，MWCNTs 的掺入提升了杂化材料的热稳定性、力学性能和导电性。另外，还制备了 MWCNTs/Fe_3O_4/纤维素杂化纤维。

2. 纤维素的离子液体溶液经再生过程得到了具有微孔结构的凝胶态纤维，这些凝胶态纤维用含Ca^{2+}离子的溶液浸泡后，可以吸附大量的Ca^{2+}离子。在无需模板剂的情况下，吸附了Ca^{2+}离子的凝胶态纤维可以用于$CaCO_3$的可控生长，得到三种特殊的$CaCO_3$晶体：双球状球霰石，大长径比的棒状、带状方解石。并且发现在$CaCO_3$矿化过程中，凝胶态纤维内乙醇的含量对控制$CaCO_3$的形貌和晶型起了重要作用。

3. 研究碳纳米管的分散与回收是项有意义的工作。我们合成了一种聚合物状的功能化离子液体 P(NIPAAm-co-IL)，P(NIPAAm-co-IL)能将 MWCNTs 有效

地分散在水中。该分散 MWCNTs 的方法是一种物理手段，且溶液体系对温度敏感，当温度低于 P(NIPAAm-co-IL)的 LCST 时，MWCNTs 在溶液中稳定存在；当温度高于 LCST 时，P(NIPAAm-co-IL)在水溶液中发生卷曲效应，致使 MWCNTs 在水溶液中的稳定性下降。

4. 目前制备 ZnO 基稀磁半导体(DMSs)纳米结构的传统方法存在设备昂贵、制备工艺复杂等缺点，限制了其在自旋电子器件的研发和应用。我们在含水的离子液体前驱体 $N(C_4H_9)_4OH{\bullet}30H_2O$(TBAH)中制备了一维介孔晶结构的 $Zn_{0.95}Mn_{0.05}O$ 样品，该样品具有室温铁磁性(RTFM)。并发现仅通过控制 $Zn(CH_3COO)_2{\bullet}2H_2O$ 在离子液体中的浓度就可以控制 DMSs 的磁性。该方法是一种简便且绿色的制备 ZnO 基 DMSs 方法。

关键词：离子液体，无机，天然高分子，杂化材料

Abstract

Ionic liquids (ILs) are liquid salts at or near room temperature, which are composed entirely of organic cation and organic or inorganic anion. Compared with traditional organic solvents, ILs are regarded as novel and green solvents owing to their advantages such as low vapor pressure, nonflammable, great heat capacity, high designable, fine thermal stability, high ionic conductivity and wide electrochemical window. ILs have been applied in separation process, electrochemistry, catalysis and material preparation. Among these applications, material preparation is in starting stage, and its research scope include synthesis of polymer, preparation of inorganic nano-material, biopolymers process, etc. In this paper we prepared several inorganic/polymer hybrid material in ILs, which focused on the following four aspects:

1. Generally, imidazolium ILs were synthesized by the reaction of imidazole with alkyl halide. However, for the volatile halogenoalkanes, such as chloromethane, chloroethane, the low boiling point often lead to preparations requiring either a sealed tube or an elaborate apparatus, and the preparation process was harsh. We found a novel method to synthesize ILs as follows: firstly acids reacted with imidazole to form acidic ionic liquid precursors, and then acidic ionic liquid precursors reacted with carbonate. This method could conquer defects of the traditional method. The small cation imidazolilum chloride prepared by this novel method presented low viscosity, high conductivity, and high solubility for cellulose and chitosan. We prepared chitosan/cellulose blend membrane and fiber materials. Multi-wall carbon nano-tube (MWCNTs) could be well dispersed in ILs by physical process. We dispersed MWCNTs in chitosan and cellulose ILs solution, then the MWCNTs/chitosan/cellulose hybrid membrane and fiber materials were obtained by a regenerate process. Incorporation of MWCNTs could improve the thermal stability, mechanical properties and electrical conductivity of the composite materials. In addition, we prepared MWCNTs/Fe_3O_4/cellulose hybrid fibers.

2. The gel–forming fibers (GF fibers) were obtained by regeneration of cellulose IL solution. After being marinated in Ca^{2+} solution for some time, plenty Ca^{2+} were adsorbed inside these porous GF fibers. Using these GF fibers, three special $CaCO_3$ crystals, i.e. twin–sphere based vaterite, zonary and rodlike calcite with large aspect ratio, could mineralize on GF fibers without any template. In mineralization of $CaCO_3$, the ethanol content inside GF fibers played an important role in controlling the morphologies and polymorphs of $CaCO_3$.

3. It is significant to study the dispersion and recovery of carbon nanotubes (CNTs). We synthesized a polymeric functional IL, i.e. poly[(N-isopropylacrylamide)-co-(ionic liquid)] (P(NIPAAm-co-IL)), which could make MWCNTs well dispersed in water. This disperse method was a physical process, and the resulting solution was sensitive to temperature. When the temperature lower than the lower critical solution temperature (LCST) of P(NIPAAm-co-IL), MWCNTs could be dispersed in solution steadily, otherwise, MWCNTs would not be dispersed in solution steadily due to the shrinkage of P(NIPAAm-co-IL).

4. So far, the traditional methods to prepare diluted magnetic semiconductors (DMSs) have some disadvantages, such as costly equipment, complicated technology, etc., which limit its research and application in spintronic devices field. We prepared one-dimensional (1D) mesocrystal $Zn_{0.95}Mn_{0.05}O$ sample in a hydrated IL precursor $N(C_4H_9)_4OH{\bullet}30H_2O$ (TBAH). The resulting sample presented room temperature ferromagnetic (RTFM). And the magnetism could be controlled simply by changing the concentration of zinc acetate in IL precursor. It wase a facile and green method to prepare ZnO-based DMSs.

Keywords: ionic liquids, inorganic, polymer, hybrid materials

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