氨基多糖/稀土金属复合光功能材料的制备及应用

王佳琪、李远航、潘江波、王砥、韦双颖、王成毓、李坚

（东北林业大学 材料科学与工程学院 哈尔滨 150040）

摘 要:【目的】在氨基多糖中羧甲基壳聚糖(CMCh)是一种既不含芳香结构也不含共轭结构的非传统发光材料，它可以通过丰富的官能团与稀土离子进行配位，作为一种生物质大分子配体将自身所吸收的能量传递给稀土离子从而使其发出强烈特征荧光。本文探究了以羧甲基壳聚糖作为配体与以铕、铽、铕/铽作为中心离子的配位情况及其发光性能研究，通过表征探究了生物质大分子作配体向镧系中心离子进行能量传递的机理，并拓展多方面的应用。【方法】以绿色的方式制备了 CMCh-Eu^{3+}荧光气凝胶，CMCh-Tb^{3+}荧光探针以及 CMCh-Eu^{3+}/Tb^{3+}多色荧光粉末，分别进行表征并应用于酸性气体的吸附和检测、Cu^{2+}的灵敏响应以及光致发光多色 LED 灯的制备。【结果】CMCh-Eu^{3+}对 HCl 气体和 HAc 气体表现出相反的荧光响应特性，HCl 使其荧光猝灭而 HAc 使其荧光增强。CMCh-Tb^{3+}能够在不受干扰的情况下实现水溶液中 Cu^{2+}的灵敏性检测，探针在 553 nm 处的荧光强度与 Cu^{2+}浓度呈现良好的线性关系，同时具有较短的响应时间以及良好的抗干扰性。CMCh-Eu^{3+}/Tb^{3+}是通过调控两种镧系离子的比例从而实现对荧光粉末的颜色控制，将不同比例的 CMCh-Eu^{3+}/Tb^{3+}粉末在紫外芯片上进行固化后，制备成了不同发光颜色的光致发光 LED 小灯以及近似白光 LED 灯。【结论】HCl 气体的荧光猝灭效果来源于 HCl 对 CMCh-Eu^{3+}配位环境的破坏，切断了配体对中心离子的敏化路径，而 HAc 的荧光增强效果则由于其替代了配位中的水分子。Cu^{2+}对探针的猝灭效果一部分来源于 Cu^{2+}破坏了 CMCh 与 Tb^{3+}之间的协同作用而导致的静态猝灭，另一部分来源于 Cu^{2+}与探针发生碰撞使部分处于激发态的电子发生非辐射跃迁和体系内转换而造成的动态猝灭。CMCh 对 Eu^{3+}、Tb^{3+}的能量传递是基于配体的三重态能级与镧系离子的激发态能级之间发生的荧光共振，同时能量差较小，传递到 Tb^{3+}上的能量一部分回传到配体 CMCh 上去，另一部分还会有一部分转移到 Eu^{3+}上去，从而实现 CMCh-Eu^{3+}/Tb^{3+}的多色发光。

关键词：羧甲基壳聚糖；镧系离子；酸性气体检测；金属离子检测；多色 LED

Preparation and application of amino polysaccharide/rare earth metal composite photofunctional materials

Jiaqi Wang[1], Yuanhang Li, Jiangbo Pan, Di Wang*, Shuangying Wei, Chengyu Wang, Jian Li

College of Materials Science and Engineering, Northeast Forestry University Harbin 150040

Abstract: 【Objective】Among amino polysaccharides, carboxymethyl chitosan (CMCh) is a kind of non-traditional luminous material with neither aromatic nor conjugated structure. It can coordinate with rare earth ions through rich functional groups, and as a kind of biomass macromolecular ligand, it can transfer its absorbed energy to rare earth ions, which makes it emit strong characteristic fluorescence. In this paper, the coordination of CMCh as ligand and Eu^{3+}, Tb^{3+} and Eu^{3+}/Tb^{3+} as central ions and their luminescence properties were studied. The mechanism of energy transfer from biomass macromolecules as ligands to central lanthanide ions was investigated through characterization, and the multifaceted application was expand .【Method】CMCh-Eu^{3+} fluorescent aerogel, CMCh-Tb^{3+} fluorescent probe and CMCh-Eu^{3+}/Tb^{3+} multicolor fluorescent powder were prepared in green mode. It was characterized and applied to the adsorption and detection of acid gas, the sensitive response of Cu^{2+} and the

preparation of photoluminescent multicolor LED lamps.【Result】CMCh-Eu^{3+} exhibits opposite fluorescence response to HCl gas and HAc gas. HCl quenches its fluorescence while HAc enhances it. CMCh-Tb^{3+} can detect the Cu^{2+} sensitively in aqueous solution without interference, and the fluorescence intensity of the probe at 553 nm shows a good linear relationship with the concentration of Cu^{2+}, and has a short response time and good anti-interference. CMCh-Eu^{3+}/Tb^{3+} is to control the color of the fluorescent powder by regulating the ratio of two lanthanide ions. After curing different proportions of CMCh-Eu^{3+}/Tb^{3+} powder on the UV chip, photoluminescent LED lights with different luminous colors and similar WLED lights are prepared.【Conclusion】 The fluorescence quenching effect of HCl gas is due to the destruction of CMCh-Eu^{3+} coordination environment by HCl, which cuts off the sensitization path of the ligand to the central ion, while the fluorescence enhancement effect of HAc is due to the substitution of H_2O molecules in the coordination. The quenching effect of Cu^{2+} on the probe is partly due to the static quenching caused by Cu^{2+} destroying the synergistic effect between CMCh and Tb^{3+}, and partly due to the dynamic quenching caused by the collision between Cu^{2+} and the probe, which causes some excited electrons to undergo non-radiative transition and intra-system conversion. The energy transfer of the CMCh to Eu^{3+} and Tb^{3+} is based on the fluorescence resonance between the triplet level of the ligand and the excited state level of the lanthanide ion. However, due to the small energy difference, part of the energy transferred to Tb^{3+} is transferred back to the ligand CMCh, and part of the energy transferred to Eu^{3+}. Thus, multicolor luminescence of CMCh-Eu^{3+}/Tb^{3+} is realized.

Key words: Carboxymethyl chitosan; Lanthanide ions; Acid gas detection; Metal ion detection; Multicolor LED