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Functional nanocomposite wet gels and aerogels induced by transition/lanthanide metal ions coordination

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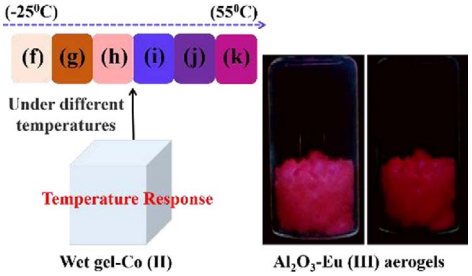
GRAPHICAL ABSTRACT

We design to synthesize a series of functional nanocomposite materials by transition/lanthanide metal ions coordination.



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ABSTRACT

Nanocomposite wet gels and aerogels, combining the novel properties of transition/lanthanide metal ions with unique properties of wet gels and aerogels, show new multifunction originated from the synergic effect or complementary performance of components. The preparation of multifunctional wet gels and aerogels using a simple and effective methods is of great significance because it can not only save the practical applications cost, but also expand the functions of the wet gels and aerogels. Here we present a facile route to fabricate a range of multifunctional wet gels, which can be easily converted into aerogel monoliths of macroscopic dimensions via freeze drying. The resulting samples possess excellent properties including high porosity, good mechanical properties, large surface area, impressive environmental stability, unique colorimetric transformations upon different temperatures, and tunable photoluminescence. These make the multifunctional nanocomposite products have potential applications in controlled drug delivery, indicator, catalysis, biomaterials, and optoelectronics.

1. Introduction

Composite multifunctional wet gels and aerogels have attracted intensive research attention in the last decade owing to their fascinating physical, chemical properties, and high porosity, which made them interesting for a wide range of applications in controlled drug delivery, indicator, catalysis, energy storage and conversion, biomaterials, and optoelectronics [1–4]. A variety of methods have been developed for the synthesis of composite multifunctional wet gels such as sol-gel, mechanical cleavage, liquid exfoliation, chemical vapor deposition, and wet-chemical synthesis [5–9]. Just because the simple and efficient preparation process and low cost requirements of equipment, as well as the quality can be controlled, sol-gel technology is considered to be feasible to fabricate multifunctional materials such as compound glass, nano-powder, functional ceramics, thin film, coating layer, fiber, liquid crystal display (LCD), fiber optic sensor (FOS), and biological parasitic

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detector [10–13]. These materials have been widely used in various fields [11–13]. Aerogels are constructed of three-dimensional solid networks whose pores are filled with air [14–16]. The specific structure of aerogels endows them with characteristics of extremely low density, large open pores, and high surface areas, which popularizes their applications in thermal insulation, catalysis, and energy storage and conversion [17–19]. The traditional method for the preparation of aerogels is based on sol-gel method involving hydrolysis and condensation of the precursors [20]. However, the lack functionality of the wet gels and aerogels represents a great obstacle, which limits their practical applications [19]. In this regard, efficient assembly of sol-gel into wet gels and aerogel monoliths with multifunction is a viable strategy to tackle this issue. However, most reports are about functionalization of graphene aerogels in recent years [21,22], only a few literatures report on the assembly of sol-gel into multifunctional wet gels and aerogels. Hence, there is still much room for developing simple and fast method for the synthesis of a range of multifunctional wet gels and aerogels.

Nowadays, transition metals/lanthanides have attracted great attention due to their coordination ability and luminescence characteristics. For instance, lanthanides coordinated-polymeric materials exhibit mechanical flexibility, good chemistry stability and excellent process ability [23,24]. Ni^{2+}-doped materials usually possess enhanced corrosion resistance and mechanical strength [25–28]. Co^{2+}-doped products often used as an indicator [25–29]. Eu^{3+}-doped materials have been widely used as a red phosphor for fluorescent light, cathode ray tube (CRT) screens, and field emission displays [30–32]. Moreover, Al_2O_3 aerogel is a well-known host material for transition metals. Ni^{2+}-doped Al_2O_3 has been widely used as catalyst for many chemical reactions [33–36]. These applications would greatly benefit from the specific features of aerogels such as large surface area, highly porous structure, low density, good mechanical performance, and excellent thermal stability. In fact, Al_2O_3 aerogel monoliths have already been prepared by the conventional sol-gel chemistry method [37]. However, most of the as-synthesized Al_2O_3 aerogels prepared by this method lack functionality. Therefore, using a cheap and low-cost Al_2O_3 matrix to construct controllably composite materials with special functions according to the actual market demand is valuable and strongly demand.

In this work, we design to synthesize a series of functional composite materials by doping Ni^{2+}, Co^{2+}, and Eu^{3+} in the alumina substrate. The as-synthesized Ni^{2+}-doped gel showed good high temperature stability and outstanding corrosion resistance for reagents such as basic, tetrahydrofuran (THF), salty, and buffer. Upon doping the wet gel with Co^{2+}, we could create wet gels with unique colorimetric transformations upon different temperatures. Moreover, by doping the Al_2O_3 matrix with Eu^{3+}, we managed to prepare photoluminescent aerogel monoliths with tunable color emissions from pink to crimson.

2. Experimental

2.1. Chemical materials

Unless otherwise specified, all other reagents were of analytical grade and used as received without further purification, and all solutions were prepared with ultrapure water (resistivity 18.2 MΩ cm). Aluminum chloride hexahydrate ($AlCl_3{\cdot}6H_2O$, 97.2%, Aladdin), ethanol (anhydrous, 99.8%, Aladdin), 1, 2-epoxy propane (PO, 99.8%, Aladdin), nickel (II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, 99.8%, Aladdin), cobalt chloride ($CoCl_2{\cdot}6H_2O$, 99.8%, Aladdin), europium (III) chloride (anhydrous, 99.99%, Aldrich).

2.2. Synthesis of wet gel (undoped), wet gel-Ni (II), wet gel-Co (II), and wet gel-Eu (III)

In a typical synthesis, 0.05 mol (12.07 g) of $AlCl_3{\cdot}6H_2O$ was mixed with 12 mL of H_2O, followed by adding 27 mL of absolute ethanol under continuous magnetic stirring. After stirring for 15 min, compared to the Al-, Ni-, Co-based wet gels and aerogels synthesized in room temperature [38-40], the solution was sealed with three layers of cling film and then heated in an oil bath at 80 °C for 1 h to promote hydrolysis. An hour later, when the solution was naturally cooled to room temperature, 1, 2-epoxy propane (PO) (32 mL) was slowly added to the solution (per second drop). After completion, the solution was then carefully transferred to a glass bottle (22 * 52 mL) and stood at room temperature for 35 min (Don't shake the solution), and then a colorless transparent gel-like sample formed at the bottom of the glass bottle. Finally, the product was washed several times with ultrapure water. The wet gel (undoped) was then placed in the glass bottle filled with absolute ethanol and left there overnight to completely fill the pores with ethanol.

For the synthesis of Ni^{2+}, Co^{2+} or Eu^{3+}-doped wet gels, 12.07 g (0.05 mol) of $AlCl_3{\cdot}6H_2O$ and the desired amount of $NiCl_2{\cdot}6H_2O$ (0.015 mol), $CoCl_2{\cdot}6H_2O$ (0.015 mol) or $EuCl_3{\cdot}6H_2O$ (0.3 mol%, 0.4 mol%) were mixed with 12 mL of H_2O and 27 mL of absolute ethanol. All other steps were the same as for undoped wet gel.

2.3. Fabrication of Al_2O_3、Al_2O_3-Ni (II), Al_2O_3-Co (II), and Al_2O_3-Eu (III) aerogels and annealing of these aerogels

The as-prepared wet gel (without doping), wet gel-Ni (II), wet gel-Co (II), and wet gel-Eu (III) were freeze-dried for 8 h to obtained aerogels. The aerogels were then annealed in a Nabertherm P 330 furnace in air at different temperatures (500, 600, and 700 °C) for 2 h with a ramping rate of 3 °C·min^{-1} to obtain Al_2O_3, Al_2O_3-Ni (II), Al_2O_3-Co (II), and Al_2O_3-Eu (III) aerogels.

2.4. Instrumentation and characterization

SEM images were acquired on a Phenom ProX scanning electron microscope (Eindhoven, The Netherlands). EDS analysis was carried out on an analyzer (Superscan SSX-550, Shimazu). X-ray powder diffraction patterns were recorded on an Ultima IV X-ray diffractometer (Rigaku, Tokyo, Japan) and equipped with Cu Kα radiation (45 kV, 40 mA). TEM images were obtained on a JEM-2011 microscope at 200 kV. Nitrogen gas sorption analysis was carried out on an ASA2020 surface area analyzer at 77 K. Prior to the measurements, the samples were outgassed at 100 °C for 24 h. The surface area was determined *via* the BET method, and the pore size distribution and total pore volume were calculated by a DFT analysis using a nonlocal DFT calculation model for nitrogen at 77 K based on cylindrical pores in aluminum oxide. UV–vis DRS spectra were measured on a JASCO-UV2600 spectrophotometer at room temperature. Photoluminescence emission spectra were recorded at room temperature on a JASCO FP-8500 spectrofluorometer.

2.5. Mechanical properties of Al_2O_3, Al_2O_3-Ni (II), and Al_2O_3-Co (II) aerogels

Mechanical properties were measured using a Shimadzu AGS-X Tester with gauge length of 5 mm and loading rate of 1 mm·min^{-1}. All measurements were conducted at room temperature. The samples were selected with the width of 2 cm and the thickness of 10 mm. The stiffness was calculated by the area under the stress-strain curves, and the Young's modulus was determined by the slope of the linear region of the stress-strain curves. The mechanical properties for each sample were based on the average value of 3 specimens.

3. Results and discussion

3.1. Effect of different coordination of metal ions on gelation time (min)

The wet gel-Ni (II), wet gel-Co (II), and wet gel-Eu (III) were synthesized by a simple and green sol-gel route in which $AlCl_3{\cdot}6H_2O$ was