Nanocomposites synthesized using supercritical fluids

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Abstract. Herein, our recent work on synthesis of nanocomposites including carbon nanotube-based, polymer-based and porous material-based composites via chemical reactions in supercritical fluids (SCFs) is introduced. The described examples highlight that SCFs allow facile synthesis of nanocomposites, leading to some new nanomaterials with special structures that are very difficult to achieve by conventional methods. The potential applications of these nanocomposites were also discussed.

1. Introduction
Nanocomposites have attracted great interest due to their unusual properties and promising applications in many fields. Up to date, various methods have been developed for the preparation of this kind of materials. In particular, clean synthesis of functional materials has been paid much attention with development of green chemistry in recent years. Green solvents including supercritical fluids (SCFs) and ionic liquids (ILs) provide new opportunity for the development of advanced functional materials. A supercritical fluid (SCF) can be defined as a substance, the temperature and pressure of which are higher than its critical temperature ($T_c$) and critical pressure ($P_c$), respectively, and which has a density close to or higher than its critical density ($\rho_c$) [1]. SCFs possess some unique properties such as low viscosity, high diffusivity, near zero surface tension, etc, and these properties can be tuned via changing pressure and temperature. SC $\text{CO}_2$ and SC $\text{H}_2\text{O}$ are the widely used SCFs due to their unusual properties as well as green feature, and have been applied in many areas. Especially, they display promising applications in material science. Some new and clean methods involved with SCFs have been developed for the synthesis and processing of functional materials, and many materials with special structures and enhanced performances have been prepared.

In recent years, our group focuses on the synthesis of functional materials using green solvents. Taking advantage of SCFs and ILs, we proposed some novel methods for the synthesis of nanomaterials, especially for nanocomposites [2-6]. Herein the work on the synthesis of nanocomposites using SCFs is summarized, concentrating on the description of the methods and microstructures of the as-prepared nanocomposites.

2. Synthesis of nanocomposites using SCFs
Besides their common features, different SCFs including SC $\text{CO}_2$ solutions, SC $\text{H}_2\text{O}$, SC ethanol, SC diethyl amine have their inherent characteristics. By means of SCFs, several methods to prepare...
nanocomposites have been developed, and a series of nanocomposites such as carbon nanotube-based, polymer-based and porous material-based nanocomposites have been fabricated in our previous work.

2.1 Synthesis of carbon nanotube-based composites

Functionalization of carbon nanotubes (CNTs) has attracted much attention since it can widen their applications in electronic devices, sensing area, catalysis, etc. Synthesis of CNT-based composites is an important way to functionalize CNTs. However, it is a challenging topic because the surface of CNTs is rather inert and it is not easy to be wetted by liquids with surface tension higher than 100-200 mN m⁻¹. SCFs have near zero surface tension, which show intriguing advantages for the synthesis of various CNT-based composites. In this paper, our recent advances in the synthesis of CNT composites using SC CO₂ and SC CO₂-based solutions, SC water, SC methanol will be summarized, focusing on the synthesis of metal/CNT, metal oxide/CNT and polymer/CNT composites [7,8].

2.1.1 Deposition of Ru nanocrystals on CNTs in SC H₂O

Different from normal and heated water, SC H₂O has dielectric constant close to that of some organic solvents (e.g., acetone). Therefore, SC H₂O has been proven a good solvent for many organic reactions, and it also has displayed excellent advantages for synthesis of inorganic materials. Using SC H₂O as reaction medium, we developed a one-pot route to deposit metal nanoparticles (e.g., Ru) on CNTs [5]. In this method, CNTs were first dispersed in RuCl₃ aqueous solution at room temperature and placed in a high-pressure autoclave; then the autoclave was put into an air-bath with temperature of 400 °C or 450 °C; keeping at these conditions for certain time, Ru/CNT nanocomposites were obtained. It was demonstrated that Ru nanoparticles with size less than 5 nm were uniformly distributed on the surface of CNTs, and some particles seemed to be present in the inner channels of CNTs. This special structure may result from the property change of H₂O during the reaction process. At room temperature, the precursor was soluble in water. With increase in temperature, the solvent power of water for the precursor declined, which could render some precursor molecules to precipitate from the aqueous solution and further to be adsorbed on the surface of CNTs. At high temperature, these precursor molecules chemically converted into metallic form, and preferentially nucleated on the surface of CNTs and formed particles, producing metal/CNT composites finally. Since the surface tension of SC H₂O is zero, some precursor molecules could infuse into the inner cavity of CNTs to yield metal particles inside CNTs after chemical conversion. Changing the weight ratio of CNTs to RuCl₃, the loading content and particle size of Ru particles were readily tuned. Reaction temperature also influenced the particle size of Ru particles, and larger particles were obtained at higher temperature (e.g., 450 °C).

2.1.2 Synthesis of metal oxide/CNT composites using SC CO₂ solutions

SC CO₂ is the most widely used SCF because it is non-toxic, non-flammable, chemically inert and easily available. The SC CO₂-involved process is usually operated at mild conditions because the critical temperature of CO₂ (Tc=31.1°C) is close to room temperature and its critical pressure (Pc=7.38MPa) is not too high. However, the major shortcoming of SC CO₂ is that it cannot dissolve most of polar compounds, especially, ionic compounds (e.g., metal salts). SC CO₂ is miscible with some polar organic solvents to form solutions, which possess the similar properties to SCFs. Therefore, the SC CO₂-based solutions are intensively investigated, and have been applied in many processes. In our recent work, SC CO₂ solutions including SC CO₂-ethanol and SC CO₂-methanol have been successfully applied in the synthesis of CNT composites.

Metal oxide decorated CNTs are a kind of important materials, and have many potential applications. We developed an one-pot route to synthesize this kind of composites via decomposition of metal nitrates in SC CO₂ solutions. In this method, CNTs were first dispersed in the ethanol solution of metal nitrate, and CO₂ was then charged into the ethanol solution at relatively low temperature (e.g. 35°C) up to a desired pressure to form a CO₂-ethanol solution. Subsequently, temperature was increased to a higher value, at which the reaction media reached supercritical state.
and the metal nitrate decomposed into metal oxide as well, resulting in metal oxide/CNT composites. Using different metal nitrates as precursors, a series of metal oxides, such as Eu$_2$O$_3$ [9], Al$_2$O$_3$ [10], Co$_3$O$_4$ [11], Fe$_2$O$_3$ [6], ZrO$_2$ [12], CeO$_2$ [13], Mn$_3$O$_4$ [14], Cr$_2$O$_3$ [15], SnO$_2$ [16], etc, were decorated on CNTs in SC CO$_2$-ethanol solutions in the temperature range of 100-150°C.

Figure 1 TEM images of the metal oxide/CNT composites prepared in SC CO$_2$-ethanol solutions: (a) Mn$_3$O$_4$/CNT, (b) CeO$_2$/CNT, (c) SnO$_2$/CNT, (d) Fe$_2$O$_3$/CNT, (e, f) α-Fe$_2$O$_3$ nanotubes, (g) Eu$_2$O$_3$/CNT, (h) Co$_3$O$_4$/CNT, (i) Al$_2$O$_3$/CNT. Reprinted from references [6, 9-14], and [16b]

The resultant composites displayed different morphology, as illustrated in Figure 1. In general, the metal oxides exist in the form of nanoparticles on CNTs (Figures 1a, b), and some particles could be intercalated into the inner cavity of CNTs under suitable conditions (Figure 1c). Several metal oxides with amorphous structure can be coated outside the CNTs to form core-shell structures (Figures 1d). Calcining the core-shell structures to remove the CNT at high temperature (e.g., 600 °C), metal oxide nanotubes with structure similar to CNTs could be produced (Figures 1e, f) [6,15]. This means that CNTs can act as a template for the preparation of some metal oxide nanotubes. Some special structures of metal oxide/CNT composites were also achieved. For instance, crystalline Eu$_2$O$_3$ nanotubes were coated on CNTs for the first time (Figure 1g) [9]; Co$_3$O$_4$ spheres composing of
nanocrystals were beaded on CNTs to form necklace-like structure (Figure 1h) [11]; discontinuous Al₂O₃ layer was wrapped outside CNTs (Figure 1i) [10]. These unique structures are difficult to prepare by conventional methods. For comparison, some control experiments were performed to prepare metal oxide/CNT composites in ethanol under the similar conditions. It was demonstrated that large particles of metal oxide formed out of CNTs. This suggests that the property of the reaction media plays a key role in the formation of metal oxide/CNT composites. In the process to synthesize metal oxide/CNT composites using SC CO₂-ethanol as reaction media, with the addition of CO₂ to the ethanol solution, the solvent power of the ethanol and CO₂ mixture to dissolve the precursor molecules reduced gradually, which caused some precursor molecules to precipitate out of the mixture and be adsorbed on the surface of CNTs. The dissolved precursor molecules could infuse into the inner cavity of CNTs due to the very low surface tension and high diffusivity of the solvent mixture. At the reaction temperature (e.g., 120 °C), the precursor on the CNT surface decomposed into metal oxide and preferentially nucleated on CNTs to form particles distributing on the CNTs or oxide layer wrapping the CNTs. It should be mentioned that most oxides wrapping outside the CNTs are amorphous, probably because the reaction temperature was too low to form crystalline phases. The differences in the microstructures of the resultant metal oxide-CNT composites may be caused by the differences in the interactions of the precursors and the CNTs used. The above method also indicates that SC CO₂-ethanol is a good medium for the synthesis of metal oxide-CNT composites under mild conditions.

2.1.3 Synthesis of CNT-based composites using other SCFs

Some organic solvents including ethanol, methanol and diethyl amine, which have critical temperatures around 250 °C, were also used as SCFs for the synthesis of CNT-based composites, and they displayed the similar advantages to the above described SCFs (e.g. SC CO₂ solutions and SC water). The procedures to prepare the CNT-based composites using these solvents are similar to that performed in SC water. Heating the precursor solution to reach supercritical state of the solvent, the CNT-based composites were in-situ obtained. In an example to synthesize TiO₂/CNT composites, the CNTs were dispersed in the ethanol solution of isopropanol titanium, and then heating the solution at 250 °C, a temperature which is higher than the critical temperature of ethanol, TiO₂/CNT composites were successfully obtained. The anatase nanoparticles with size less than 10 nm were homogeneously distributed on CNTs [17]. Similarly, RuO₂ nanocrystals with size around 3 nm were decorated on CNTs uniformly using SC diethyl amine as reaction medium [18].

2.2 Synthesis of polymer-based composites using SCFs

It is well known that SC CO₂ can swell most organic polymers (e.g, polystyrene) while it cannot dissolve them. Based on the particular interactions between SC CO₂ and polymers, several methods involved with SC CO₂ have been proposed to prepare polymer-based composites. A two-step method was developed to prepare silica-polypropylene (PP) nanocomposites [19]. In this method, tetraethyl orthosilicate (TEOS) was first impregnated into PP matrix using SC CO₂ as a swelling agent for PP and carrier for TEOS, and the TEOS intercalated PP was then treated in acidic water, resulting in hydrolysis/condensation reaction of the precursors confined in a polymer network. The resulting composites showed unusual microstructures: fine silica nanoparticles distributed uniformly in the PP matrix without macroscopic phase segregation, and the polymer molecules entangled with the silica network. This unique structure led to a significant increase in Young’s modulus and tensile strength relative to the virgin PP. This impregnation/hydrolysis method represents a straightforward and effective way to prepare silica/polymer hybrid materials. It is particularly advantageous for polymers insoluble in common organic solvents and for synthesis of the composites in which the compatibility between the polymer and silica is poor. Similarly, the mixture of TEOS and titanium isopropoxide (TIP) were simultaneously impregnated into a SC CO₂-swollen PP matrix in SC CO₂, and SiO₂-TiO₂/PP composites were produced via the hydrolysis and condensation reactions of the precursors confined in a polymer network [20]. The resultant composites showed similar structure to the above silica/PP composites, and also displayed enhanced mechanical performances.
Recently, we developed a method to deposit metal or metal oxide in polymer substrate using SC CO2-ethanol solutions [21]. Hollow polymer spheres with size of about 400 nm, which cannot be dissolved and swollen by ethanol, were used as substrate. In a typical procedure to prepare Eu2O3/polymer composites, the polymer spheres were first dispersed in ethanol solution of europium nitrate; CO2 was then charged into the solution up to a designed pressure at low temperature (e.g., 35°C), which mixed with ethanol to form homogeneous solution that can swell the polymer spheres; keeping at this condition for certain time, the temperature was increased to a high value (e.g., 120°C), at which europium nitrate decomposed into Eu2O3 and deposited onto polymer spheres to form Eu2O3/polymer composites. The resultant composites exhibited unique structure: the Eu2O3 nanoparticles were not only decorated on the outer surface, but also intercalated into the polymer shell and further into the inner cavity of the hollow polymer spheres. This special structure is also caused by the unusual properties of SC CO2-ethanol solution. Similarly, Pd nanoparticles were embedded into polymer spheres using SC CO2-ethanol solution as a reaction medium, and the as-prepared Pd/polymer spheres had high activity and stability for alkenen hydrogenations [22]. In another work, zinc acetate was used as Zn2+ precursor and thiourea as S2- resource, and ZnS nanoparticles were decorated on the polymer spheres in SC CO2-ethanol solution at 100 °C. The procedure to prepare this composite was similar to that for preparing Eu2O3/polymer composite. However, the ZnS nanoparticles had much smaller particle size of around 3nm. Since the ZnS/polymer composite was dispersible in water and could form stable suspension, it was used as a photocatalyst to degrade some organic dyes, which was very effective to degrade dyes under the visible light irradiation [23].

2.3 Synthesis of porous material-based composites

Porous materials including molecular sieves (e.g, zeolite, SBA-15, MCM-41, etc), natural clays usually have high surface areas, which are good supports for catalysts and have promising applications in catalysis. Deposition of chemically active components on the porous materials to prepare the supported catalysts is an interesting topic. SCFs, especially SC CO2 and its solutions, provide new methods for the synthesis of this kind of materials due to their low viscosity, high diffusivity, zero surface tension as well as green features.

SBA-15 possesses a highly ordered mesoporous hexagonal structure with pore diameters varying from 5 to 30 nm. Functionalization of SBA-15 provides it more properties, and can widen its applications. Recently, we presented a monolayer and double-layer coating of TiO2 on the inner surfaces of SBA-15 via surface sol–gel process in SC CO2 [24]. In this work, SBA-15 with high level of silanol groups was adopted as substrate. In a typical experiment, the TIP dissolved in SC CO2 passed through SBA-15, and grafted onto SBA-15 via the reaction of TIP with the surface silanol groups on SBA-15, forming a coating layer onto the inner surface of SBA-15. The unreacted TIP was subsequently extracted by SC CO2. Repeating the impregnating step can result in the multilayer formation of TiO2 on the silica surfaces. Calcining the impregnated SBA-15 at 550°C, TiO2 coated SBA-15 composites were formed. Raman spectroscopy and XPS analyses confirm the formation of Si-O-Si and Ti-O-Ti. N2 sorption analysis indicated that the TiO2 loaded samples retained the similar structure to the SBA-15 used, and the pore diameter was reduced. In this study, the silanol groups on SBA-15 serve as active sites for titanium grafting and were consumed during the reaction process. The high concentration of hydroxyls on the silica surface was required to prepare high surface coverage of molecularly dispersed titanium species. Similarly, coating europium oxide on the walls of SBA-15 was achieved in a SC CO2-ethane solution [25]. Europium nitrate hexahydrate as oxide precursor was first dissolved in ethanol, and mixed with SBA-15. Then ethane was charged into the mixture at 35°C to reach the supercritical state of ethane-ethanol solution, which facilitated the precursor to infuse into the channels of SBA-15. Following in situ thermal decomposition of europium nitrate at 120 °C in the supercritical solution, SBA-15/Eu2O3 composites were fabricated. In another work [26], an effective route was described to prepare TiO2-montmorillonite (MMT) composites via impregnating TTBO into the interlayers of MMT in supercritical ethanol, followed by hydrolysis in water and calcination at 500 °C. The layered structure of MMT in the as-prepared samples was destroyed to some extent based on
the XRD analysis and TEM observation. Anatase particles with size less than 5 nm were deposited in the partially exfoliated MMT layers. These samples showed blue-shifted UV absorption edge compared to TiO₂ particles. The MMT treated with supercritical ethanol has excellent ability to adsorb MB, and the TiO₂–MMT composites can combine the adsorptive ability of MMT and the catalytic degradation ability of TiO₂ to remove MB from its aqueous solution efficiently.

3. Summary

In summary, SCFs have provided new routes and displayed many unique advantages for the synthesis of nanocomposites though the processes have to be operated at high pressure. Remarkable advantages of the SCF techniques lie in their flexibility, simplicity, and large-scale production of the composites. The resultant materials including CNT-based, polymer-based and porous material-based composites usually possess special structures that are difficult to prepare by the conventional methods, and they also have enhanced performances and promising applications in many areas. The utilization of SCFs in material science has opened a new way for the development of advanced materials, and the related technologies may have bright future.

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