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Short Communication

Solvent free nanoscale ionic materials based on Fe_3O_4 nanoparticles modified with mussel inspired ligands

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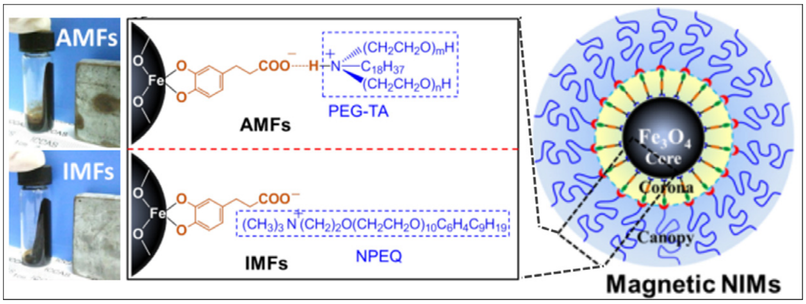
GRAPHICAL ABSTRACT



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ABSTRACT

Mussels exhibit robust adhesion capability with varied materials mainly due to the strong affinity of catechol moieties in their adhesive proteins. Nanoscale ionic materials (NIMs) are special organic-inorganic hybrid materials comprising a charged oligomer corona attached to inorganic nanoparticle cores, which can behave from glassy solids to liquids in the absence of any solvent. Herein, Fe_3O_4 nanoscale ionic materials (NIMs) exhibiting inorganic-organic core-shell structure and liquid-like behavior were obtained by using a mussel-inspired bifunctional ligand of 3,4-dihydroxybenzenepropanoic acid (DHPA), which could link Fe_3O_4 nanoparticles core and cationic organic shell, respectively. A simplified one-step aqueous co-precipitation method to prepare DHPA decorated Fe_3O_4 nanoparticles is developed, which shows advantages in productivity and is more environmental friendly compared with the traditional core preparation first and then surface modification. This research proposes a simple and effective approach to obtain solvent-free NIMs with tailorable core-shell structure using versatile adhesion of mussel mimetic adhesives and various available ion pairs.

1. Introduction

Nanoscale ionic materials (NIMs) are a new class of hybrid materials with nanoparticles (NPs) densely functionalized with organic ionic liquid shell [1–3]. The organic shell is typically

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composed of charged corona and ionized tethered canopy which can serve as a solvent for encapsulated NPs. Thus, NIMs can be considered as one-phase solvent-free molten salts or supramolecular ionic liquids [4,5], and it can behave from glassy solids to free flowing liquids in the absence of any solvent [6,7]. NIMs promise many valuable applications in high performance nanoparticle/polymer composites [8], optical and electronic devices [9], CO_2 absorbents [10] and so on. Plenty of NIMs based on inorganic [11–15] or organic [16–18] cores have been demonstrated. However, most of the NIMs reported involve labor-intensive multistep sequences, including NPs synthesis, surface ionization by covalent grafting, and subsequent canopies attachment. The repeated purification of each step, commonly using organic solvents and under rigorous reaction conditions, will pollute environment and reduce productivity inevitably. Some efforts have incorporated ionic coronas into cores during NPs synthesis, but the used coronas require sophisticated chemical reactions mostly performed in non-aqueous systems [19,20]. To meet the enormous potential of NIMs for advanced materials and techniques, facile and environmental-friendly preparation of NIMs is highly desired.

Mussels exhibit versatile, robust, and long-lasting adhesion in wet environment [21,22]. The adhesive proteins secreted by mussel's byssus contain numerous catechol species [23], which are prone to form covalent and non-covalent interactions with various surfaces and responsible for the noticeable adhesive properties [24,25]. Among these interactions, the strong coordination ability of catechol with transition-metal ion is the main reason for the high affinity to inorganic surface [26–30]. Inspired by mussels, catechol-metal interaction has been widely utilized for the surface functionalization of metal oxide NPs [31–37]. However, the exploitation of mussel-inspired chemistry for the design of NIMs has not been reported to the best of our knowledge.

Herein, we demonstrate a mussel-inspired strategy to prepare Fe_3O_4 based NIMs by using a commercially available ligand 3,4-dihydroxybenzenepropanoic acid (DHPA) as the corona. DHPA can bridge NPs core and organic canopy via catechol-metal coordination and ion interaction, respectively. The synthesis and DHPA modification of Fe_3O_4 NPs are achieved synchronously by a single step of aqueous co-precipitation of iron salts in the presence of DHPA, avoiding the general step-by-step fabrication [38] and precise synthesis of coronas [1,12,15,19,20]. Fe_3O_4 NIMs with tailorable structures and properties are obtained via altering the ion-tethering canopy. The magnetic response behavior of the Fe_3O_4 NIMs afforded by the superparamagnetic core is illustrated. By virtue of the versatile adhesion of mussel mimetic adhesives and various available ion pairs, this method can be applied to the modification of various of NPs, hence we propose a simple and effective approach to obtain tailorable solvent-free NIMs by bridging the cores and shells with suitable catechol ligands. This kind of materials may find many potential applications in the fabrication of functional materials like manufacturing by 3D printing.

2. Experimental section

2.1. Materials

Ferric trichloride ($FeCl_3$, 97%), ferrous chloride ($FeCl_2$, 98%) were purchased from Aldrich, and 3,4-dihydroxybenzenepropanoic acid (DHPA, 98%) was purchased from Alfa. PEG-substituted tertiary amine (PEG-TA) $(C_{18}H_{37})N[(CH_2CH_2O)_mH][(CH_2CH_2O)_nH]$ ($m + n = 25$) was offered by Jiangyin Huayuan Chemical Co., Ltd. Nonylphenyl poly(ethylene glycol) quaternary ammonium salt (NPEQ) $C_9H_{19}C_6H_4(OCH_2CH_2)_{10}O(CH_2)_2N^+(CH_3)_3Cl^-$ was kindly provided by Henan DaoChun Corp. Other chemicals were analytical reagents from Sinopharm Chemical Reagent Co., Ltd., China. All chemicals were used as received without further purification.

2.2. Synthesis of DHPA modified Fe_3O_4 NPs

Fe_3O_4 NPs were synthesized by a single step aqueous solution co-precipitation method with simultaneous surface modification. 10 mL of $FeCl_3$ solution (1 M) and 11 mL of $FeCl_2$ solution (0.5 M) were mixed, and then poured into 100 mL of deoxygenated NaOH solution (5 M). The solution turned to black immediately. The mixture was stirred for 30 min at room temperature and for another 1 h at 90 °C under N_2 atmosphere. Large excess of DHPA (0.5 M, 100 mL) was added with further 30 min stirring before the reaction was exposure to air and cooled down. The obtained Fe_3O_4 NPs were separated by magnet and washed with deionized water for several times. The final concentration of NPs dispersed in deionized water was 0.35 wt%.

2.3. Acid-base reaction induced magnetic fluids (AMFs)

For the preparation of AMFs, the pH value of Fe_3O_4 NPs aqueous dispersion was adjusted to about 3 and then dialyzed for one day (cutoff molecular weight 12,000–14,000), ensuring the protonation of carboxyl acid. Excess PEG-TA was added to aqueous dispersion of NPs under mechanical stirring. The mixture was reacted overnight at room temperature and dried at 50 °C. The excess PEG-TA and other impurities were removed by several washing/centrifuging recycles with isopropanol and then dialyzed using a cellulose dialysis membrane in deionized water for two days. Finally, the product of AMFs was dried at 50 °C for two days or longer until solvents volatilized completely.

2.4. Ion exchange induced magnetic fluids (IMFs)

Before ion exchange, the pH of Fe_3O_4 NPs dispersion was adjusted to about 10 to ionize the surface coated DHPA. Excess anionic NPs (20 mL) were added dropwise into NPEQ chloroform solution (50 mg/mL, 20 mL) under stirring. After 20 min stirring of the emulsion and 10 min standing, the NPs were almost completely transferred from water to the chloroform layer. The water layer containing NPEQ unreacted and NaCl generated during ion exchange was discarded after the delamination of water/chloroform mixture. The chloroform layer consisting hydrophobic NPs was washed with water for more than five times to remove potential free NPEQ. The resultant materials were dried in a vacuum oven at room temperature.

2.5. Characterization

FT-IR spectra were obtained from a Bruker Equinox 55 FT-IR/FAR 106 spectrophotometer. The samples were mixed and ground with KBr and then pressed to pellets. Zeta potential was characterized using a Zetasizer (Nano-ZS) from Malvern Instruments. The pH values of colloidal suspension were tuned using 0.01 M HCl or NaOH solutions. XRD data were collected on an X-ray diffractometer (Riguku D/max-II) using a Cu Kα target at 40 V and 200 mA. TGA was carried out on a thermogravimetric analyzer (Pyris 1, Pekin-Elmer) at a heating rate of 10 °C/min under N_2 flow. DSC traces were recorded on a TA instrument (Q2000) at a heating or cooling rate of 10 °C/min. Rheological studies were performed on a strain-controlled Advanced Rheometric Expansion System (ARES, Rheometric Scientific) using a 25 mm parallel plate geometry. In the temperature-dependent modulus and viscosity testing, the angular frequency (ω) and strain amplitude (γ) were fixed at 1 rad s^{-1} and 10%, respectively. The temperature range was from 30 to 80 °C with a heating rate of 3 °C/min. The strain-dependent modulus plots were recorded at fixed ω of 1 rad s^{-1} and temperature of 30 °C at shear strain varied from 0.1 to 100%. TEM images were conducted with a JEOL JEM-2011F TEM operating at 200 kV.