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Fabrication of α-MoO_3 nanobelts membrane showing a three-dimensional cross-linked nano-scale network structure for water and oil mixture separation

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α-MoO_3 nanobelts with amphiphilic property have been successfully fabricated via a hydrothermal method. The nanobelts membrane with three-dimensional cross-linked nano-scale network structure was prepared on the filter paper surface by suction filtration process. After being modified by water, the wetted membrane could be applied for nonpolar liquids and water separation, especially in the emulsion forms. The separation process was simple, without employing any extra power, and this nanobelts membrane was easily recyclable. Based on this study, the separation mechanism was proposed. Our results suggest an innovative inorganic material that has excellent oil/water selectivity in the cleanup of oil from water.

1. Introduction

In recent years, with increasing industrial oily wastewater and the frequent oil spill accidents, oil/water separation has become a worldwide challenge.[1] Because oil/water separation is an interfacial puzzle, using special wettability to design novel materials is an effective and facile way to separate oil from water, or water from oil. Materials with both hydrophobic and oleophilic properties have received broad attention due to their wide applications for both fundamental and potential research.[2-5] In real applications, the separation mediums usually need to use a certain kind of polymer or organic matter to make the surface super-hydrophobic or super-hydrophilic. Therefore, various materials had been developed to effectively separate oil/water mixture, such as nanofibrous membranes,[6] carbon-based materials,[7] cellulose aerogel,[8] superhydrophobic/superoleophilic film[9] and so on.[10-14] However, they are easily fouled or even blocked up by oils because of their intrinsic oleophilic property.[15] Oils adhered or absorbed are hard to remove, which results in secondary pollution during the post-treatment process.[16] To some extent, those approaches are always involved in special equipment, multistep procedures and energy-consuming processes. Therefore, it is of great importance to develop novel materials for oil/water separation with high separation efficiency, excellent recyclability and the anti-pollution ability.

One-dimensional (1D) nanostructures have attracted much attention in recent years due to their importance in mesoscopic physics and technological applications in nanoscale device generation. Although significant progress has been made in the area of fabricating 1D nanostructures in the past several years, the development of appropriate methodologies to apply these nanostructures has been lagging behind.[17-19] Here, we report the fabrication of α-MoO_3 nanobelts via a hydrothermal method. The nanobelts membrane was obtained under suction filtration process. It presents three-dimensional porous nanostructures, which can form hydrogen bonds with the water molecules on the surfaces of the nanobelts throughout the membrane and can effectively prevent the transport of nonpolar liquids, for example, cyclohexane, carbon tetrachloride, diesel, and even oil/water emulsion system. During the separation process, the membrane can prevent oil phase passing through the web woven fabricated by water molecules. However, water permeated through the membrane under the drive of gravity without any extra energy. After being used, it can be re-dispersed into nanobelts-suspension in water again by ultrasonic treatment and then re-formed a new membrane by suction filtration for recycled utilization numerous without any damage.

2. Experimental

In a typical procedure, 1.24 g of ammonium molybdate powders (1.00 mmol) was added into a beaker containing 20 mL of deionized water under strong stirring. After stirring for 10 min at room temperature, 10 mL of nitric acid (2.4 mol/L) was dropped slowly into the solution and the clarified solution was obtained. Subsequently, the transparent solution was transferred into a Teflon-lined stain-less steel autoclave (50 mL) and treated at 180 ℃ for 18

h. After cooling to room temperature naturally, white α-MoO_3 powers was collected after washed and centrifuged with distilled water for several times and then dried in a vacuum oven at 60 ℃ for 8 h.

The separation experiment of a water (colored by $Cu(NO_3)_2$ for clarity) and oil (cyclohexane) emulsion system was performed by using a simple instrument fabricated by ourselves. A wet α-MoO_3 membrane（wetted by water just only one second）prepared on the filter paper was mounted in a dead-end cell equipped with a syringe and then a certain amount of fresh water-cyclohexane emulsion was poured into the syringe.

The morphology and microstructures of the obtained samples was examined using SEM (Hitachi S-4800) with an accelerating voltage of 10 kV. TEM observation and SAED experiments were carried out with a JEM-2100F. The crystallographic information of the as-prepared samples was established by using powder X-ray diffraction (XRD, D8 DISCOVER with GADDS version of BRUKER Company of Germany) with graphite monochromatized high-intensity Cu Kα. FT-IR spectrometry was performed with a Bruker TENSOR 37 FT-IR analyzer. Microphotographs was taken with Optical microscope BX51 produced by OLYMPUS. The efficiency of oil-water separation was determined by ^1H nuclear magnetic resonance (^1H NMR). Samples prepared in CD_3OD were recorded on a DRX-500 spectrometer operating at 300 MHz (Bruck Co.Ltd.). The wettability of as-prepared nanobelts membrane was measured by dynamic contact angle measurements using the drop shape analysis system (Kruss DSA 100, Germany) at room temperature. The BET surface area was evaluated from the nitrogen adsorption and desorption isotherm (Micromeritics, ASAP 2020).

3. Results and discussion

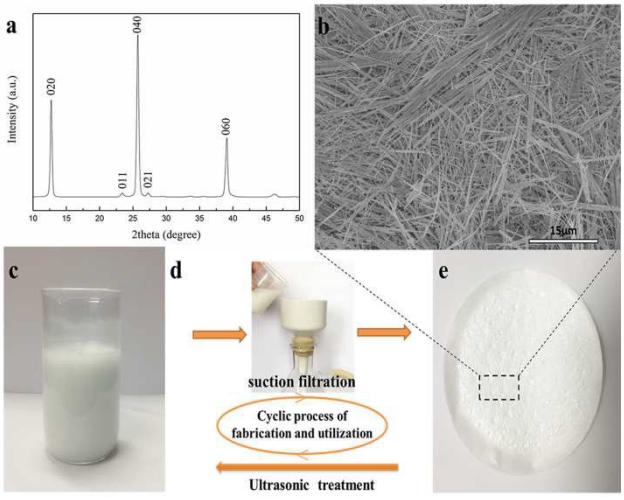

Fig.1. (a) XRD pattern of the MoO_3 nanobelts. (b) SEM characterization of the nanobelts. (c)-(e) Recycling process for fabrication and utilization of the α-MoO_3 membrane.

The structure and morphology of obtained products were investigated by XRD and SEM analyses. As shown in Fig. 1a, all of the diffraction peaks can be perfectly indexed to orthorhombic MoO_3 (JCPDS 05-0508), which is in good agreement with the literature.[20] The strong and sharp diffraction peaks indicate that the as-synthesized products are highly crystalline. No peaks of any other phases are detected, indicating the high purity of the MoO_3. Fig. 1b shows corresponding SEM images of the α-MoO_3, demonstrating that the sample consists entirely of nanobelts. A panoramic view also reveals that the sample shows a three-dimensional cross-linked nano-scale network structure. These nanobelts have an average length of tens of micrometers and its width is around 80–150 nm.

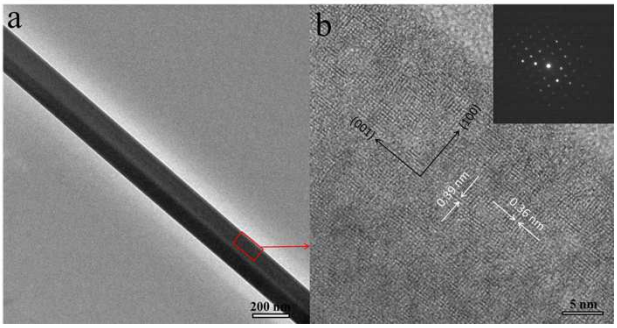

Fig. 2. (a) TEM image of a single α-MoO_3 nanobelt and (b) HRTEM image of enclosed nanobelt area showing interplanar distances along the (001) and (100) directions. The inset of (b) is the corresponding SAED pattern.

The fabricating procedure and the cyclic utilization process of the membrane are shown in Fig. 1c–e. As it is presented, the nanobelts that form the membrane structure can be re-suspended in solutions and subsequently re-form the original morphology over many cycles by suction filtration. TEM technique was also carried out to further investigate the inner structure of the nanobelt. A TEM image and corresponding selected area electron diffraction (SAED) pattern of an individual α-MoO_3 nanobelt are shown in Fig. 2a and b. A typical TEM image for a free-standing α-MoO_3 nanobelt is presented in Fig. 2a and a rectanglelike crosssection was clearly visible. The HRTEM image in Fig. 2b indicated interplanar distances of 0.39 and 0.36 nm for the (100) and (001) lattice planes respectively. The SAED pattern of sample (inset of Fig. 2b) indicates a single crystalline of α-MoO_3. The surface area of the α-MoO_3 was determined as 4.11 $m^2 \cdot g^{-1}$ by nitrogen adsorption isotherms using the Brunauer–Emmett–Teller (BET) method.

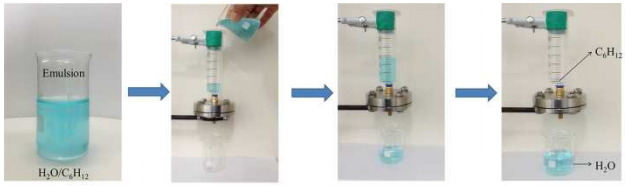

Fig.3. The process of separating oil and water.

The process of separation experiment was realized as graphically shown in Fig. 3. From Fig. 3, we can see the original milky blue solution was gradually separated into two kinds of transparent liquids. Water permeated through the membrane under the drive of gravity while the cyclohexane was rejected by the membrane. Moreover, control experiment was carried out that an ordinary filter paper without α-MoO_3 nanobelts was used in the emulsion separation mentioned above. The emulsion passed through smoothly and neither water nor cyclohexane was obtained. As a result, α-MoO_3 nanobelts membrane plays an indispensable role in this separation process.

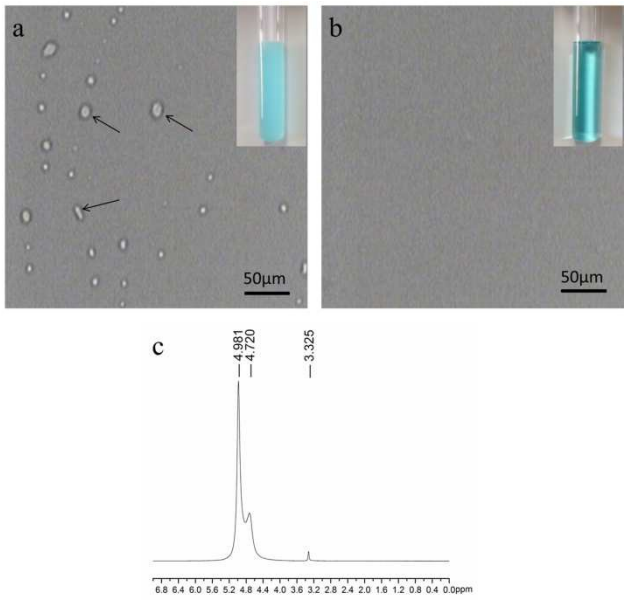

Fig.4. Microphotographs for the emulsion forms with oil/water before (a) and after (b) separation. The inset of Fig. 4 (a, b) are the images of the corresponding solution. (c) ^{1}H NMR spectrum of the permeated solution.

The separation efficiency is so high that nearly no visible oil existed in the permeated water. As shown in Fig. 4a and b, the separation of this mixed system was observed under optical microscope. We can clearly see that the state of separation changed from the oil/water mixed phases (the oil phase was marked by arrows) to water phase only. In order to further investigate the separation efficiency of the cyclohexane in the permeated water, the probably content of the cyclohexane after separation was tested using the ^{1}H nuclear magnetic resonance (^{1}H NMR, Fig. 4c). Sample was prepared in the CD_3OD. The peak associated with permeated products at 3.325 ppm come from the solvent residual peak of MeOD. The singlet peak at 4.981 ppm and the peaks at 4.720 ppm are representative of the HOD and H_2O protons. From the spectrum of ^{1}H NMR, the absence peak of cyclohexane (~1.45 ppm) indicate the high separation efficiency of the membrane.[21]

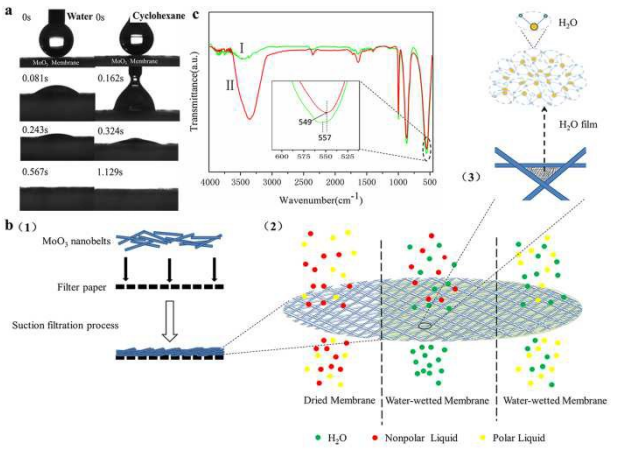

Fig.5. (a) Spreading and permeating behaviors of a droplet on the nanobelts membrane. (b) Schematic of the separation mechanism. (c) FTIR spectras of α-MoO_3 nanobelts before (Ⅰ) and after (Ⅱ) wetting.

The wettability of as-prepared nanobelts membrane was carried out as shown in Fig. 5a. Water droplet about 0.5μL was allowed to contact the surface of the dried membrane, and the water contact angle reached 0° after only 0.567s. The same phenomenon had occurred to cyclohexane/dried membrane system. This amphiphilic feature is quite different from the traditional hydrophobic and oleophilic membranes, which usually have specific hydrophilic or hydrophobic surface properties. A novel filter membrane was fabricated from α-MoO_3 nanobelts by a facile suction filtration process (Fig. 5b (1)). The nanobelts membrane in dry state remained as permeable for both polar and nonpolar liquids. Interestingly, it was found that the transport properties of this membrane could be easily turned by a facile wetting process with H_2O. However, when the water-wetted membrane was treated with polar liquids, the polar liquids would immediately mix with the water cluster system forming a new cluster system and let the polar liquid pass through smoothly (Fig. 5b (2)).[22] A higher magnification of the randomly arranged coated-nanobelts is shown in Fig. 5b (3). Water films formed in the pores reflecting a mutual interaction between H_2O and α-MoO_3. The results of FTIR spectras of the dried nanobelts compared with the wetted one provide insight concerning about the nature of the interaction between the H_2O and the α-MoO_3 framework. In Fig. 5c, the FTIR spectrum of pristine α-MoO_3 nanobelts exhibits three typical peaks at 998, 864, and 557 cm^{-1}, which agree well with those in the literature.[23, 24] By contrast, in the spectrum of α-MoO_3/H_2O system, an obvious peak at 3370 cm^{-1} reveals the existence of water in the α-MoO_3 nanobelts. The aforesaid peak at 557 cm^{-1} in the pristine α-MoO_3 shifts down to 549 cm^{-1}, and displays attenuation in its intensity. Most likely, it is a hydrogen bond formed between oxygen atom of Mo-O-Mo and hydrogen atom of H-O-H in H_2O.[25, 26] The extensive H-bonding network film in the pores throughout the membrane and the whole structure is stabilized by these hydrogen bonds.

4. Conclusions

In summary, we have demonstrated a novel and efficient approach to separate oil/water emulsion using α-MoO_3 nanobelts membrane by a facial wetting process. The existing water molecules distribute evenly throughout the α-MoO_3 nano-scale membrane and form the hydrogen bond network film in the pores. Furthermore, the FTIR results show that the hydrogen atoms in water are H-bonded with the oxygen atoms in the Mo-O-Mo bonds of α-MoO_3 nanobelts. The coated membrane shows perfect water permeation with high separation efficiency, with resistance to nonpolar liquids and energy-saving filtration. This study may prove particularly useful in the design of recyclable separation materials. It is a new attempt to design next-generation materials for oil/water separation.

Notes and references

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