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Full Length Article

Superhydrophobic and superoleophilic surfaces prepared by spray-coating of facile synthesized Cerium(IV) oxide nanoparticles for efficient oil/water separation

Asif Matin[a], Umair Baig[a], M.A. Gondal[b,*], Sultan Akhtar[c], S.M. Zubair[a,d]

[a] Center for Research Excellence in Desalination and Water Treatment, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia
[b] Laser Research Group, Physics Department & Center for Excellence in Nanotechnology, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia
[c] Electron Microscopy Unit, Institute for Research and Medical Consultations (IRMC), Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam, 31441, Saudi Arabia
[d] Mechanical Engineering Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

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ABSTRACT

In this work, we report the preparation of superhydrophobic and superoleophilic surfaces on stainless steel meshes by spray-coating of Cerium(IV) oxide (CeO_2) nanoparticles obtained by a co-precipitation method. The synthesized particles and the coated meshes were characterized using advanced techniques. Scanning electron microscopy images showed the particles to be present in distinct lumps; merged with each other on calcination to give a homogeneous structure. Transmission electron microscopy analyses showed the agglomeration of individual particles to form the clusters. Contact angle measurements revealed the superhydrophobic and superoleophilic nature of the modified mesh surface in air. Fourier transform infra-red analyses of the synthesized particles showed the characteristics peaks of CeO_2 found in commercial samples. X-ray photoelectron spectroscopy of the glass coated with ceria confirmed the predominant presence of Ce^{4+} that also explained the wetting behavior. Oil-water separation studies using a simple gravity-driven setup showed high separation efficiency of an oil water mixture. An analytical model is discussed in detail to account for the wetting behavior and efficacy of the prepared surfaces in separating the two fluids. To summarize, this work presents a very simple and effective route for oil-water separation with high efficiency.

1. Introduction

Nowadays, large volumes of oily wastewater are produced by different industries, e.g. mining, metal, petrochemicals, textiles, and food. In addition, frequent incidents of oil-leakages/spillages occur during marine transportation or oil production. Both these factors make this type of waste an extremely common pollutant all over the world, a threat to marine environments and ecology, and last but not the least, also represents a great waste of valuable natural resources [1–2]. Furthermore, the rapid growths in population and economy have resulted in greater demand for clean water particularly in water-stressed areas [3]. Therefore, one of the major global challenges right now is the cost-effective and sustainable separation of oil and water.

The last decade or two has witnessed considerable efforts in tackling this issue using different approaches. For example, in the industrial sector, mechanical devices such as oil skimmers or booms [4], have been used to purify these oil/water mixtures. In addition, porous materials e.g. sponges, foams, and textiles, have been commonly used to absorb oils from water in situations involving oil-leakage/spillages. However, both of these strategies suffer from major drawbacks that affect the overall feasibility of their widespread application. While mechanical devices either consume lot of energy or need high pressure to operate, the latter suffer from poor separation selectivity and efficiency as both fluids are absorbed simultaneously. Moreover, the disposal procedures adopted for the porous materials usually result in secondary pollution of the environment [5].

The last couple of decades have witnessed a significant increase in the use of filtration membranes for a wide variety of separation and purification processes. In particular, reverse osmosis membranes have become the first choice for desalination of seawater and brackish water due to their high selectivity and antifouling characteristics [6]. Besides these dense and non-porous membranes, there exists microporous membranes such as metallic meshes that are well suited for high flux applications due their larger average pore size. By appropriate surface

* Corresponding author.
E-mail address: magondal@kfupm.edu.sa (M.A. Gondal).

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modification e.g. deposition of nanoparticles, thin films, etc. to impart desired wetting properties, such filter materials can be tailored for application in oil/water separation.

Cerium oxide (CeO_2) is a rare-earth oxide that has been recently investigated by many researchers for applications as diverse as humidity sensing, solid oxide fuel cells, optical devices and glass polishing materials [7–8]. Due to its inherent hydrophobic nature [9], it also has potential in applications involving fluids with different wettability e.g. oil water separation. The materials currently used in these applications are either very fragile and easily and rapidly deteriorate in harsh environments of pH, chemicals and temperature, or their processing and preparation is extremely tedious and economically non-feasible for large-scale utilization [10].

Several methods have been investigated for the preparation of nanostructured ceria. These include chemical vapor deposition (CVD), biological synthesis, electrochemical methods and photo-induced conversion [11]. However, all of these methods are tedious, difficult to scale-up and require expensive equipment. In contrast, the precipitation method is very simple and facile and has therefore attracted the attention of majority of researchers. The basic idea in this approach is to react a salt of cerium metal (sulfate or nitrate) with a precipitating agent such as ammonia or oxalic acid.

Zhou et al. synthesized ceria particles as small as 4 nm in diameter with cerium nitrate and ammonia as the precursors [12]. Similarly, Chen et al. prepared crystalline CeO_2 by the precipitation method and also investigated the effect of temperature and other reaction conditions on the characteristics of the oxide [13]. In another study, Shih et al. freeze dried cerium oxide powder obtained by co-precipitation from a mixture of $Ce(NO_3)_3$ and NH_4OH at a temperature well below zero Celsius (218 K) [14]. The effect of calcination at different temperatures on the crystal growth and structure was studied using X-ray diffraction (XRD) scanning and transmission electron microscopy (SEM and TEM).

To the best of our knowledge, there exist no report on cerium oxide being used for separation of oil water mixtures. The objective of this study was to prepare nanoparticles of this oxide using a simple and facile precipitation method and then deposit them onto stainless steel meshes using a spray coating technique. It was expected that this surface modification will result in a surface that repels water (due to the intrinsic hydrophobicity) and allows the oil to pass through freely. The coated meshes and the synthesized powders were characterized for surface morphology (SEM and TEM), wettability (contact angle goniometry), molecular bonding (FTIR) and surface elemental analysis (XPS). The oil-water separation efficiency was studied using a simple laboratory-made setup.

2. Materials and methods

2.1. Chemicals and reagents

Cerium(IV) sulphate [$Ce(SO_4)_2$] of very high purity (99.9%) and ammonia (35%) of reagent grade from Sigma Aldrich, Inc. were used without further purification. Similarly, the other chemicals, H_2SO_4 (98%), Tetra hydrofuran (THF), and hexadecane were also of reagent grade from Sigma Aldrich and used as received. The chemicals used for cleaning such as acetone, ethanol and methanol were locally purchased.

2.2. Synthesis of CeO_2 nanoparticles

A facile and simple precipitation method was used to synthesize the oxide nanoparticles. 1 g of cerium sulfate was dissolved in 100 mL deionized water by vigorous stirring for approx. 30 min at room temperature. To obtain a clear solution, a few drops of conc. H_2SO_4 were added to the beaker. The clear solution was slowly added to 1.4 M ammonia water with continuous stirring. Cerium oxide precipitates formed that were separated using filter paper, washed with deionized water and dried. The dried precipitate was calcined for 4 h at two different temperatures, 100 and 200 °C.

2.3. Spray coating of nanoparticles suspension on substrates

To deposit a layer of synthesized nanoparticles on stainless steel meshes and glass slides, spray coating technique was employed. A suspension of ceria nanoparticles in tetrahydrofuran (THF) was prepared by mixing 100 mg of the particles in about 10 mL of the dispersant. To achieve good dispersion, the mixture was stirred overnight using a magnetic stirring rod and then sonicated for 1 h in a water bath. To prevent re-agglomeration of the finely dispersed particles, the suspension was immediately spray coated. Stainless steel meshes with approx. pore size 75 µm and laboratory glass slides were used as the substrates. To ensure good adhesion of the deposited particles, both substrates were sonicated in acetone and DI water sequentially for 1 h. The target materials were placed on a screen and the spray gun kept at a distance of ~ 10 cm. The suspension was sprayed with a nitrogen gas pressure of ~300 psi with the gun moved horizontally over the entire surface.

2.4. Characterization of cerium oxide nanoparticles and its coated substrates

The synthesized ceria nanoparticles and the SS meshes coated with these were characterized for surface morphology using both SEM (FEI, ISPECT S50, Czech Republic) and TEM (FEI, TEM, Czech Republic). The effect of calcination on the surface morphology of the particles was also analyzed. Images at different magnifications were taken from different regions of the powders and the mesh surfaces. Contact angle measurements of both fluids oil and water were performed on coated and uncoated meshes using a goniometer (EasyDrop KRUSS FM40Mk2, Germany). Static contact angles were measured in tangential mode and the droplet images were saved using a built-in camera. To confirm the presence of cerium oxide, Fourier Transform Infra Red analyses of the powder samples was performed. For this purpose, a Nicolet is50 spectrometer (Thermo Scientific, UK) with a ZnSe crystal was used in ATR mode. To investigate the surface elemental composition of substrates coated with ceria, X-ray Photoelectron Spectroscopy was used. For this analyses, glass slides coated with ceria particles and calcined at two different temperatures were used. Initially, survey scans were carried for binding energies in the range 0–1000 eV to identify the different elements present. Later on, high resolution scans of the more relevant elements, Cerium and Oxygen were performed to obtain more intricate details e.g. oxidation states, lattice position, etc.

2.5. Performance evaluation of CeO_2 coated meshes

After completion of the characterizations, the stainless steel meshes deposited with CeO_2 nanoparticles were evaluated for their oil water separation efficiency using a simple laboratory setup. This consisted of two circular discs of Teflon with a circular cavity in the center and O-rings on one side. The mesh was placed between the discs and tightly secured with the help of nuts and screws. Glass tubes of thickness ~1 mm and length ~25 cm were attached to central cavity region of both discs and the setup placed vertically with the help of clamps. The oil water mixture was poured into the upper tube and collected in a small beaker placed at the bottom.

3. Results and discussion

3.1. Surface morphology of synthesized nanoparticles

Since particle morphology (size, shape and distribution) is known to strongly influence surface properties e.g. wettability, the synthesized ceria nanoparticles were analyzed using electron microscopy. Fig. 1