Materials Research Express

PAPER

Controlling oil/water separation using oleophillic and hydrophobic coatings based on plasma technology

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Keywords: Cu coated mesh, sputtering, hydrophobic, oleophilic, chemical compositions, oil/water separation

Abstract

Disposable and highly efficient device that can separate oil from water is in high demand. This work reveals the concept of oil/water separation using plasma technology. Copper coated, oxygen plasma-treated mesh has been used to separate oil and water from its mixture. At some critical conditions, the prepared coated mesh showed hydrophobic and oleophilic behavior. The coated mesh was used to separate the oil-water mixture, which allowed the oil to pass through, while it repelled water completely. The designed coated mesh maintained separation efficiency as high as 99 percent. Properties of coated and uncoated mesh were examined using various techniques and analyzed to understand the physical changes.

1. Introduction

Oil and/or water pollution is a major environment concern in recent times. Separation of oil/water from oily water is an important task to satisfy this burning worldwide concern. Concentrations have been given toward finding new methods in order to separate oil and water effectively owing to industrial, ecological and environmental needs. Be it treating an oil spill: which poses a huge threat on marine wildlife, waste water treatment: owing to social, environmental and health issues or other industrial applications, oil-water separation finds its way in some form or the other [1–7]. Hence, it has led to an increased demand for developing new ways to separate both oil and water. Given the fact that oil-water separation is an interfacial phenomenon, the use of special wettability to design novel materials is facile and apparently easy way to produce [8–11].

Recent advances in oil/water separation with related super wetting and/or super anti-wetting materials and their design were discussed including anticipated future challenges [8]. In this review article, it is mentioned that because of the presence of surfactants in the aqueous medium, the separation efficiency can be affected and it requires a critical oil surface tension for effective separation processes. Experiments showed that TiO2 coating on native cellulose nano-fibrils resulted in good absorption capacity (~90%) of non-polar liquids and oils when the nano-fibrils were allowed to float on water [9]. TiO2 nano particles and polyurethane mixture spray coating on stainless steel mesh grid was introduced for industrial oil spill clean-up and industrial oily water remediation [12–14]. In this case the coated mesh can separate water from combination of oil/water at separation efficiency of almost 99% with recyclability of 40 times separation cycles. Again various materials like silica aerogels, zeolites, organophilic clays which show properties of hydrophobicity are used as oil absorption materials. Synthesis of these materials and uses of the same in oil spill clean-up are also discussed in detail [15].

Surfaces showing super-hydrophobicity and super-oleophilicity have grabbed a lot of attention in the field of oil-water separation owing to their high oil affinity and water repellence as well as due to their relative ease of
fabrication. Such surfaces are mainly inspired by nature [16]. The concept of spray and the dry method was introduced for the coating to have a contact angle of almost 150° with water. Low surface-energy material like polytetrafluoroethylene (PTFE) as the precursor was used to create nanostructured, craterlike morphology on the microscale rough surface using chemical reaction to attain the property.

A self-cleaning, oil-water separation mesh was prepared using layer-by-layer assembly of sodium silicate and TiO2 nanoparticles for the underwater super-oleophobic conditions [4]. Here TiO2 plays an important role of self-cleaning property and make it possible because of ultraviolet (UV) illumination. In most of the self-cleaning processes, the composite coating processes having layer by layer concept was introduced on mesh grid with considerations (i) uniformly coating all throughout the surface and hence acts as perfect self cleaning membrane, (ii) it allows large scale deposition of functional coating on non-uniform substances and complex morphology etc. However, this process takes relatively more deposition time and since it is chemical deposition processes, hence it is not free from after deposition chemical reactions.

Similarly, CuS2 coating on copper mesh by electrochemical anodization process was initiated by Pihui P et al [7]. The coated Cu mesh shows more water affinity and relatively low adhesion property to the oil and hence it could separate oil water mixture with better efficiency. Interestingly by this technique the same mesh can be used more times without much damage and hence reduces the cost of the same considerably. In this case greater than 95% efficiency was achieved after 50 times uses in laboratory scale.

In this work, for the first time plasma based coating technology has been used to deposit Cu on stainless mesh grid of almost 90% optical transparency (SS 44 μm). Coating processes have been carried out in vacuum conditions and effective efficiency was found out more than 95% even after using more than 10 times. The coated mesh could also used to separate various oil-water mixtures in lab scale and could be used for large scale applications.

To explain the wetting behavior on surfaces, especially the super-hydrophobic for water, Wenzel and Cassie-Baxter theories [17] are used. Schematic diagram of the same is shown in figures 1(a) and (b). The former theory takes into account that when a liquid droplet comes in contact with a rough surface, the spaces left between the protrusions on the surface under study are completely filled with the liquid droplet and the liquid remains stick to the surface. Thus it leads to a homogeneous wetting. The latter takes into account that the liquid droplet, rather than filling in the spaces between the protrusions, sits over them. This state reduces the interfacial area between the solid and liquid surface and helps in improving the hydrophobicity of the surface via the introduction of air-pockets beneath the liquid droplet [18, 19]. Thus this leads to heterogeneous wetting.

2. Experimental section/methodology

2.1. Sample preparation

Stainless Steel (SS325) meshes have been used for this experiment. Each mesh of dimension 100 cm² initially cleaned by soaking in acetone bath for 15 min and then immersed in distilled water for 15 min again. The meshes were then dried at room temperature. After it gets dry, meshes are kept inside a plasma system for oxygen plasma treatment. After the placing the mesh in the substrate holder, the experimental system is evacuated to $1.0 \times 10^{-5}$ mbar using a diffusion pump backed by a rotary pump. Once the desired base pressure is achieved, the O2 gas is fed to the system using mass flow controller at a rate of 8.0 Sccm and maintaining the working pressure of the system at $1.7 \times 10^{-2}$ mbar under continuous pumping condition. A DC power supply is used to create plasma between a constricted anode and whole chamber with a DC voltage of 450 V. Under this condition the discharge current is about 1.0 mA. Cu coating was carried out using a DC sputtering system and the schematic diagram of the coating system is shown in figure 2(a). Cu target of 50 mm in diameter and 3 mm in
thickness was kept inside the magnetron. O₂ plasma treated stainless steel mesh grids were placed in a substrate holder which could be heated as per requirement. Sputtering was initiated by introducing Argon gas at a working pressure $2.0 \times 10^{-1}$ mbar and under this condition the desired current and voltages applied to the system were 0.192 Amp and 450 V, respectively. Samples were coated on its either sides. Prepared Cu coated meshes are shown in figure 2(b).

2.2. Characterizations
For studying the surface morphology of the coated mesh, SEM was performed (HR-SEM, Hitachi S-4800 machine). Prior to SEM, samples were gold coated by quorum sputter coater. EDS was used for elemental analysis. FTIR tests were employed using Nicolet Spectrometer (IS10) on the untreated mesh (cleaned with acetone) to investigate the morphology of the coated mesh. X-ray Photoelectron Spectra (XPS) were obtained on PHI 5000 Vera Prob II, equipped with Auger electron spectroscopy (AES) module and C60 sputter gun to analyze the surface chemical composition of the sample. Contact Angle was measured with 20 μl of deionized (DI) water or oil droplets. The images obtained were analyzed using Image J 1.44p (National Institutes of Health, USA). All measurements were carried out at ambient conditions and at least five independent measurements.

2.3. Oil/water separation tests
The coated samples were tested physically for oil/water separation using a custom made separation apparatus. The coated mesh was placed in between the two cylindrical tubes having diameter of 3 cm, as it is shown in the figure 4. A mixture of oil-water was poured from the top and allowed to pass through the coated mesh controlled by gravity to assess the efficiency of the device.

3. Results and discussions
The surface monograph of the plasma treated Cu coated mesh and untreated mesh are shown in figure 3. Figure 3(a) depicts that 60 min O₂ plasma treated mesh has very fine, smooth surface morphology. It shows some coagulation of oxides. Figures 3(b)–(d) shows the surface morphology of the 10 min, 20 min and 30 min of Cu coating on each mesh after 60 min of O₂ plasma treatment.

Figures 3(c) and (d) indicate that the Cu coating is uniform on top of the mesh with increasing surface roughness. Now as per Cassie-Baxter state [17], it is clear that enhancing the surface roughness, increases the hydrophobicity of the surface and as a result, more and more water droplets sit on the top of the protrusions present on the surface and hence, the affinity of the water molecules for the surface decreases. From figures 3(c) and (d), it is evident that these two samples have the highest roughness amongst all the tested samples. However, from the 1 μm magnification image, it has been found that the 30 min Cu treated mesh has 50% larger protrusions in comparison to 20 min coated mesh and thus shows more hydrophobicity.
To understand the nature of hydrophobicity and oleophilicity more quantitatively, the physical tests were conducted with the samples in the custom made apparatus (Figure 4). During the experiments tap water, saline water and distilled water were used which were mixed in different combinations with five different types of oils-almond oil, coconut oil, engine oil, diesel and petrol. Fifty trials were conducted to measure the separation efficiency of the coated mesh and the samples were re-tested after a period of two weeks and one month to investigate their reusability.
The separation efficiency of the meshes are found in the order, 30 min Cu > 20 min Cu > 10 min Cu > Oxygen Plasma treated mesh. Although 30 min Cu and 20 min Cu have the same separation efficiencies, the time taken for the separation of the mixture of oil and water (mixture of almond oil and tap water 50 ml each, mixed thoroughly) for 30 min Cu mesh (∼13 s) is less as compared to 20 min Cu mesh (∼17 s).

3.2. EDS
From the EDS Spectrum of all the samples, it is observed that Carbon (C), Iron (Fe) and Chromium (Cr) constitutes the majority amount in terms of atomic percentage in all the samples. This is mainly because of Stainless Steel (SS) material itself composed of mainly Fe, C, and Cr. Untreated SS mesh shows the presence of Oxygen atoms (6%). This may be due to the exposure of mesh to air before treatment and at the same time, maybe due to the base pressure of the system being not very less. Further, the O₂ plasma-treated mesh (60 min) shows an increase of the oxygen atoms (12%). When the O₂ plasma-treated mesh is coated with Cu for different timings as mentioned earlier, the corresponding percentage of oxygen atoms, increases to 16%, 18%, and 20%, respectively for 10 min, 20 min, and 30 min Cu coating. Details of elements present in the coated and uncoated mesh are shown in figure 5. Cu treated meshes showed a gradual increase in the atomic percentage of copper with increasing treatment time. EDS results imply that, increasing percentage of CuO (due to reaction between the coated oxygen and coated copper) is leading to increased surface roughness. The SEM images show that an increase in CuO leads to more protrusions on the surface (figures 3(a)–(d)). There were more crystal-like protrusions with increasing treatment time. This lies in complete agreement with the Wenzel and Cassie-Baxter equations [17].

3.3. FTIR
ATR-FTIR spectroscopy peak positioned at 3398 cm⁻¹ is attributed to the vibration in the O–H group (figure 6). Peaks at 1604 cm⁻¹ and 1487 cm⁻¹ are due to symmetric and asymmetric vibration bending of C=O, while the peak at 2190 cm⁻¹ corresponds to C–O bond. The peak positioned at 700 cm⁻¹ is attributed to FeO.

FTIR figure clearly shows the increase or decrease in intensity of the peaks between untreated, treated and Cu coated plasma. An initial increase in the intensity of the C–O bond, when the sample is treated in O₂ plasma, can be explained by the fact that ionized condition of oxygen molecules in the atmosphere always attack the membrane surface, causing bond scission of C=O and C–O. On the other hand, C–O group can be formed due to the reaction of O₂ species particularly in the presence of plasma. Effect of plasma treatment and Cu coating on the surfaces reduces the intensity of the peak, as few microns thickness of the coating is allowing the light to pass through. Even the FTIR is working on attenuated reflectance mode.

3.4. XPS
The XPS analysis was done on the acetone cleaned mesh (SA1), oxygen plasma-treated mesh (SA2) and Cu coated O₂ plasma-treated mesh (SA3). The raw spectrum of the same is shown in figure 7(a). Spectrum analysis of Cr present in the uncoated mesh is shown in figure 7(b). After de-convoluting the XPS scan of 2p₃/₂ orbital of Cr, two peaks have been seen which represent the Cr metal and Cr₂O₃ in its binding energy level 574.23 eV and 575.3 eV energy levels, respectively. The peak at 574.23 eV is due to 2P₃/₂ electrons of chromium atom in Cr⁺³.
Figure 6. FTIR Spectroscopy results of the untreated, O\textsubscript{2} plasma treated and O\textsubscript{2} plasma treated along with Cu coated meshes.

Figure 7. (a) XPS Spectrum of the meshes of SA1: Uncoated mesh, SA2: Oxygen treated mesh SA3: Oxygen and Copper coated mesh, Raw and de-convoluted XPS data when it is analyzed for (b) Cr atom as a function of wave number, (c) O\textsubscript{2} atom as a function of wave number, (d) Cu atom as a function of wave number.
The peak at 575.3 eV is attributed to the 2P_{3/2} electrons of chromium atom in Cr_{2}O_{3}. At the same time, deconvolution shows that it contains iron peaks at 708.3 eV and 710.2 eV level, respectively. Iron peaks observed at 708.3 eV binding energy is due to the 2P_{1/2} electrons of Fe^{3+} states as an oxide in the form of Fe_{2}O_{3}. Again the peak at 710.2 eV is corresponding to the 2P_{1/2} electrons indicates γ-FeOOH states.

Figure 7(c) shows the chemical composition of O_{2} plasma (SA2) treated mesh grid. In this case, along with 2P_{1/2} peaks of electrons of Fe^{3+} and Fe_{2}O_{3} at 708.0 eV and 710.2 eV, respectively, two more predominant (81%) compositions of Fe have appeared. Fe oxide peaks significantly shifted to higher binding energies even at lower excitation energy. This results in multiple splits of Fe2P spectra as Fe compounds are described by high-spin metal [18]. The peak intensity at 529.3 eV binding energy of the electron is related to 1s_{1/2} of Fe_{3}O_{4} atoms and 527.7 eV corresponding to Fe^{2+} states as oxide. Figure 7(d) shows the XPS spectra of treated mesh grid coated with Cu using sputtering process. Peak intensity of Cu_{2}O at 932.5 eV binding energy is related to 2p_{3/2} of Cu_{2}O atoms.

### 3.5. Contact angle (CA)

Figure 8 shows the contact angle of water for the five samples of mesh. It was seen that the effective CA (considering both Left Contact Angle (LCA) and Right Contact Angle (RCA)) values for the untreated sample came out to be 103.59 ± 14°. Similarly, when the mesh was treated in O_{2} plasma for 60 min (sample SA2) the CA value had increased slightly to 109.43 ± 11.5°. The 10 min Cu coated, 60 min O_{2} plasma-treated mesh (SA3) showed less hydrophobicity as compared to both SA1 and SA2. In this case, the average CA came out to be 78.25 ± 9°. However, SA4 and SA5 i.e., 20 min and 30 min Cu coating on O_{2} plasma-treated mesh showed hydrophobic nature, with an average CA 130.77 ± 6.5° and 126.78 ± 11°, respectively.

The contact angle results are in correlation with the SEM results as discussed earlier. For O_{2} plasma-treated mesh, the percentage of O_{2} is 12% having a Water Contact Angle (max value) of 124.75°. For 20 min Cu treatment with O_{2} and Cu percentages are 17.54 and 8.59 and having a WCA (max value) of 138.75°. Whereas for 30 min Cu, it is 20.34 and 9.15 respectively with a WCA (max) of 140.6°. This increase in O_{2} and Cu (further forming CuO) leads to more protrusions which in turn lead to more surface roughness (figure 3) and hence the surface shows improved hydrophobicity.

For the untreated cleaned mesh, the Oil Contact Angle was 55.4°. It reduced to 51.05° when it was treated with 60 min O_{2} plasma. However, with 20 min Cu coating O_{2} plasma-treated mesh, the measured average Oil
Contact Angle was approximately 43.3 ± 15.5° whereas, with 30 min of Cu coating, it was impossible to measure the OCA, as the oil droplet passed through the mesh within a fraction of time. The time-lapse has been shown in figure 9. Oleophilic nature of the mesh for automobile oil was evident from the OCA analysis.

When the mixture of almond oil and water was allowed to pass through the Cu coated O2 plasma-treated mesh (30 min) in the custom made apparatus (figure 4), it has been observed that oil slips through the mesh completely. 50 trials were conducted which gave the consistent results. As the mesh was hydrophobic in nature, water remained on the top of the mesh and the efficiency of oil-water separation was almost 100%. To test the stability of device, the experiment was conducted two weeks and four weeks after coating and gave the same results and efficiency as earlier.

The contact angle results showed that the cleaned untreated mesh had little hydrophobicity and as we increase the treatment time, the water droplet sticks to the surface due to the development of surface protrusions according to Wenzel Theory. However, on further treatment, as the surface roughness increases, the droplet now rather sits on top of the surface protrusions. This exhibits superhydrophobic nature owing to Cassie Baxter equation.

**4. Conclusions**

We have designed an inexpensive device to separate oil and water. Copper coated, oxygen plasma treated stainless steel mesh is cheap, flexible and reusable material. The SS 325 mesh when treated with O2 plasma for 60 min along with 30 min Cu coating on the top, showed the best properties of hydrophobicity as well as oleophilicity. Increased time of treatment increases the surface roughness. In our case, combined effect of O2 plasma and Cu coating increased the mesh roughness. The fabricated device could efficiently separate oil from water. Therefore, the copper coated mesh might a promising substitute for the conventional oil water separation methods.

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