

## Supplementary Information for “Bioinspired steel surfaces with extreme wettability contrast”

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### *XPS and TEM analysis on hierarchical micro/nanostructured steels*

The X-ray Photoelectron Spectroscopy (XPS) analysis was performed on the steel A and B for three different fabrication steps: as-prepared steels, and the CF<sub>4</sub> plasma-treated samples with and without exposure to water immersion. An Al K $\alpha$  (1486.6 eV) X-ray source was used as the excitation source, and the anode was maintained at 250 W, 10 kV, and 27 mA at a chamber pressure of 2.67 x 10<sup>-8</sup> Pa with a beam spot size of 400  $\mu$ m x 400  $\mu$ m. The peak position was calibrated using the C1s peak at 284.6 eV.

The XPS analysis was performed on the hierarchically micro/nanostructured surfaces in Fig. S1. In the wide range of the XPS spectrum, O1s and F1s peaks were enhanced in both steel A and B after the plasma-water treatment procedure (see Figs S1a and b). An F1s peak was not detected while a thin native oxide layer (O1s) was found at ~530 eV. In the Fe2p spectrum of steel A, several distinguishable peaks were observed due to the broadening of a Fe2p<sub>3/2</sub> peak (~711 eV) and the appearance of a shoulder (~709 eV) on the high-energy side of a Fe2p<sub>1/2</sub> peak (~724 eV). This is indicative that those peaks are characteristics of Fe<sup>2+</sup> in Fe<sub>3</sub>O<sub>4</sub> oxide. However the oxide nanostructures may not be identified as Fe<sub>2</sub>O<sub>3</sub> since no satellite peak intensity at about 719 eV was detected, which is a characteristic peak for Fe<sub>2</sub>O<sub>3</sub> oxide.

As steel surfaces are treated with  $\text{CF}_4$  plasma, oxidation on the steels occurred due to exposure to plasma discharge on the metallic surfaces. While the processes for oxidation are not fully understood, the widely accepted explanation involves the dissociation of water released from the surface due to plasma impact. As the surface comes into contact with the water, fluorine reacts with adsorbed water molecules and produces oxygen and hydrogen fluoride that attack the metal surface as a secondary reaction. The appearance of the  $\text{Fe}(\text{OH})_x$  shoulder ( $\sim 713$  eV) observed after  $\text{CF}_4$  plasma (Figs S1a) could be the first step of hydrolysis reaction and/or the dissociation of water into H and OH. The high resolution of the  $\text{Fe}2p$  spectra for the pristine samples and those treated with  $\text{CF}_4$  plasma suggest an increase in the Fe oxide, particularly  $\text{Fe}^{+3}$  and Fe–OH peaks. In this step, the surface of steel A has a mixed oxide state and pristine areas while steel B is fully covered with oxide (see Fig. S1c). The surface oxidation rate could be considered as a factor relating to the tendency of the oxidation reaction. Steel B has more oxidation sites compared to steel A due to the lower Cr content on the surface and bulk, so the nano flake structure was observed to evolve further on steel B. As shown in Fig. S1e, a nanoflake consisting of needle-like structure-forming nanobelt-like structures. A similar increase in oxide peak intensity was also observed on steel B, and it had the crystal structure of a cubic  $\text{Fe}_3\text{O}_4$  with spacings of 0.256 nm and this was consistent with the  $\{311\}$  plane. From this result, it is believed that the formation mechanism for nano-needle or its cluster on steel A is basically same as that for the nanoflakes observed on steel B.

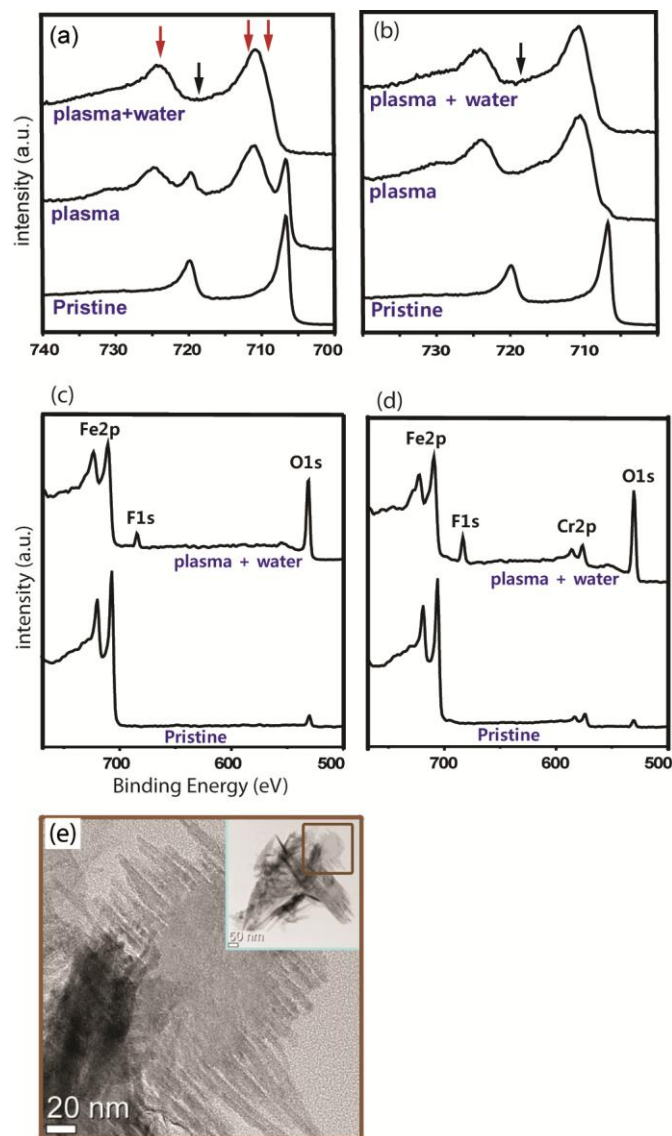


Fig. S1. XPS and HR-TEM analysis of nano needle and flake structures on steel A and B after  $\text{CF}_4$  plasma treatment for 60 min and water immersion for 60 min. XPS analysis was performed on each three fabrication step. Fe2p core level spectra of the steel A surface (a) and steel B surface (b). Wide range scan for steel A (c) and steel B (d). (e) TEM images of nano flake structure from a red-rectangle area of an inset.

**Smovie 1.** Water repellent behaviors on superhydrophobic (left half) and hydrophobic (right half) steel surfaces with and without nanostructuring, respectively.