Research Article

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Surface hydrophobicity and oleophilicity of hierarchical metal structures fabricated using ink-based selective laser melting of micro/nanoparticles

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Abstract: Hierarchical structures have attracted considerable interest due to their super-oleophobic/super-hydrophobic behavior. However, it is rare to present a novel additive manufacturing (AM) approach to fabricate hierarchical metal structures (HMSs). A micro/nano mixture ink was deposited on a substrate and a laser was used to selectively scan the ink layer. A new layer of ink was deposited on the previous consolidation layer during manufacturing. The surfaces of the as-sintered HMSs exhibit inherently super-hydrophilic and super-oleophobic behavior with a 155° contact angle (CA) with oil. Furthermore, the HMSs were successfully turned into super-hydrophobic and super-oleophilic mode (with a 152° CA) after surface modification with a solvent-free, electrostatic polychloroethylene particle deposition. They can be used as oil/water separation media by the functional surfaces existing in the pore channels. The experimental study of HMSs shows an effective removal of oil contaminants from water. The developed process also possesses an advantage of AM of HMSs with complex shapes in ambient air under the protection of an organic ink. Importantly, the present approach could be extended to a vast number of HMSs, for the preparation of highly durable functional materials for various applications.

Keywords: super-hydrophobicity, super-oleophilicity, selective laser melting, additive manufacturing, hierarchical metal structures

1 Introduction

Oil contamination is a critical issue that impacts the global environment. For the cleaning of oily wastewater generated in remote and extreme conditions, high performance devices have to be developed for the oil/water separation. A superhydrophobic bulk substrate could be a sound choice due to its light weight, robustness, high strength, and corrosion resistance. The surface properties of such components are critical to their performance. Nanostructures fabricated using nanowires, nanotubes, nanobeams, nanoplates, graphene sheets, and nanoshells could provide unique capabilities for nano-sensors, probes, and surface functionalities [1]. Surface functionalities such as super-hydrophobicity is an interfacial property with a water contact angle (CA) greater than 150°, enabling many applications in industrial and biomedical processes [2–6]. The superwettable property can be used for contaminated oil recovery [7]. In order to achieve a super-hydrophobic surface, usually a low surface energy and a micro/nano hierarchical microstructure are needed [5]. Super-hydrophobicity has been enabled and attracted considerable interest due to its potential of separating oils/organic pollutants from marine ecosystems [8–10]. A highly efficient metal–organic framework (MOF)/carbon nanotube (CN) foam with micrometer-sized pores of CNs for the efficient conversion of CO₂ into cyclic carbonates was fabricated for water/oil separation. The MOF crystals attached on the foam surfaces created a natural shield against water [11]. A NiCrN hydrophobic coating was prepared and deposited on steel and silicon wafer substrates using multi-arc ion plating by Du et al. [12]. With the increase of deposition temperature, the surface morphology changed to a micro-nano hierarchical structure with a CA of over 140°. The adsorption of hydrocarbons on the coated surface presented a unique self-repair capability after wear. Janus particles were used to form aggregates with
hierarchical structures, ranging from the nanometer-scale up to hundreds of micrometers, which exhibited ultra-
hydrophobic behavior [13]. Porous conducting polymers
were synthesized on carbon fiber cloth by electrochemical
polymerization of pyrrole with bipyrrrole and doping of
the polymer with surfactant anions, showing superhy-
drophobic behavior [14]. Chen et al. [15] synthesized 3D
interconnected porous CN/copper composites using pre-
compression, chemical vapor deposition, and spark
plasma sintering. The composites show excellent strength
and corrosion resistance, maintaining good conductivity.
Wang et al. [16] developed 3D hollow quasi-graphite
capsules/polyaniline hierarchical composites by dec-
rating protonated polyaniline on the surface of graphite
capsules. The nanospheres decorated on the inner and
outer surfaces of the graphite capsules provide a large
surface area for NH3 gas adsorption, and a potential gas
sensor application was developed. Jian et al. [17]
developed a ZnN0.4B0.6/SiC nanocomposite using chemical
vapor deposition and chemical vapor infiltration. The
nano/hybrid structures interconnected with the nanofiber
network enhance the interfacial area, thus enhancing the
microwave absorption. Guo et al. [18] developed an
FeSiAl core with an oxidation gradient ceramic coating
composite through a multi-medium plasma method. Due
to strong synergistic magnetic–dielectric effects, the
multistrata core–shell composites show excellent micro-
wave absorption capability and high temperature oxida-
tion resistance. Sorbent materials, such as polyurethane
[19], polyvinyl-alcohol formaldehyde [20], poly aerogel
[21], carbon soot [22], and graphene/polymer aerogels, are
considered as promising media for oil/water separation
[23]. A porous sorbent material usually requires further
treatment such as immobilization of nano-scaled particles
on the surface to achieve hydrophobicity. However, some
of the materials or reagents used in the fabrication
process are environmentally unfriendly, and their manu-
facturing processes are time consuming or have part size
limitation such as tens of micrometers thick thin
films [24].

Additive manufacturing (AM) refers to a rapid proto-
typing technique that uses a layer-by-layer approach to
fabricate digital CAD models [25,26]. The selective laser
melting (SLM) [27] technique has been used to manufac-
ture a variety of materials such as stainless steel [28,29],
aluminum [30,31], and nickel- and titanium-based alloys
with relatively high resolution and geometric accuracy
compared with other AM techniques [32–35]. SLM also
enables the fabrication of lightweight cellular lattices or
porous structures that are difficult to manufacture with
other AM techniques due to the support from the powder
bed [36–38]. SLM generally requires a vacuum or inert gas
protected environment to avoid the oxidization of sintered
materials, which increases the operation costs and
decreases its feasibility. However, an ink-based solution
can act as the protection environment during laser–matter
interaction due to the absence of material oxidation
problems. Guo et al. [39] studied the fabrication of
hierarchical composites using Inconel 718 micro-powder
with irregular-shaped nano-sized TiC particles. The effect
of laser scan speed on the surface wettability and
corrosion resistance was studied, and the water CA
reached ∼151.5° for a laser scan speed of 600 mm/s. Kang et al. [40] fabricated hierarchical composites using
SLM of nickel-coated high-silicon steel powder. Aniso-
tropic magnetic properties were found due to the rod-
shaped structure, and the magnetization saturation pre-
sents a negative correlation with laser scanning speed.
Arakane et al. fabricated Cu-rich and Cu2O-rich micro-
heaters using femtosecond laser-induced reduction of CuO
nanoparticles [41]. An array copper layer with reduced
friction was fabricated by using SLM of Cu nanoparticle-
based organic inks, showing the capability of ink-based
SLM (ISLM) for surface micro-texturing [37], and this
technique was also used to fabricate a nano-scaled
amorphous carbon-coated Cu layer with super-hydro-
phobic behavior by decomposing the polymer in the
solvent [42], showing that ISLM is a potential technique
to fabricate functional structures. A multilayered organic–i-
organic columnar structure was fabricated by Wei et al.
by sequentially assembling rutile titanium dioxide na-
norods, polymers, and graphene oxide in a layer-by-layer
fashion to form an organic–inorganic structure [43]. The
mechanical properties are comparable to those of natural
enamel.

It is of great significance to develop an efficient and
effective method to fabricate hierarchical metal struc-
tures (HMSs) with complex geometries and hierarchical
structures in one step. The flexibility and robustness of
AM methods provide a solid tool to enable fabrication of
such structures with superior surface functionality. In
this work, a novel ink-based AM technique was devel-
oped (Figure 1).

A micro/nanoparticle-based organic ink was depos-
itied layer by layer during an SLM process to fabricate
HMSs in ambient air. The organic solvent prevents the
oxidation during the ISLM process where Cu-NPs
covered the surfaces of stainless steel micro particles
(SS-MPs) due to the surface tension difference among the
melt, surrounding Cu-NPs and organic solvent. Due to
the laser-induced self-assembly behavior, Cu-NP-shelled
HMSs with a hierarchical structure were successfully
fabricated in ambient air in a single step. Furthermore, the HMSs were successfully switched to super-hydrophobic and super-oleophilic mode after surface modification by using a solvent-free, electrostatic polytetrafluoroethylene particle deposition technique. The water/oil CAs were measured to analyze the surface hydrophobicity and oleophobicity. Both static and dynamic oil/water mixture separation experiments were conducted. In addition, the surface morphology and microstructure of the particles and HMSs were characterized using a scanning electron microscope (SEM) and X-ray diffraction (XRD). Durability tests of the HMS surface functionality in the pH range of 1–13 were conducted as well.

2 Experimental section

2.1 Materials

Cu-NPs (Guangzhou Hong Wu Material Technology Co., Ltd, China) with a size range of 70–100 nm and 316L SS-MPs (HLPOWDER, Changsha Hualiu Powder Metallurgy Co., Ltd, China) with a size range of 10–38 µm were used in this work. Oils of n-heptane and trichloromethane (TCM) served as organic oils for the oil/water separation tests. Polyvinylpyrrolidone (PVP, MW = 10,000) was adopted to stabilize the NPs in the solvent mixture. 1H,1H,2H,2H-Perfluoro-decyl-triethoxysilane (PFDTS; Sigma-Aldrich Co. LLC, USA) was utilized for the surface modification. ANSI 304 stainless steel plates with a thickness of 2 mm were cleaned three times in an ultrasonic bath with an ethanol/water (1:1) solution for 5 min before being used as substrates.

2.2 ISLM process

In order to obtain the solvent mixture of micro/nanoparticles, organic solvents PVP (8.19 wt%) and ethylene glycol (27.4 wt%) were prepared to prevent the agglomeration and oxidation of Cu during SLM. The Cu-NPs (17.56 wt%) were dispersed in the mixed organic solvent and stirred with ultrasonic waves for 25 min. Then, the ANSI 316L SS-MPs (46.85 wt%) were added in the solvent mixture and homogenized using ultrasonic waves for another 15 min.
One of the typical methods of SLM is to use a mixture of two functional materials which contains a structural material and a binder material with a lower melting point to stabilize the structural material [44]. The binder material can fill up the micro-pores and create a high capillary force for rearrangement of the structural particles [45]. Our previous work illustrates that this method can fabricate a pure copper layer in ambient air [46]. This motivates us to use Cu-NPs as a binder material in SLM of SS-MPs in ambient air, fabricating hierarchical and surface functional composites. In this ISLM process, a fiber laser was used to heat the solution with the mixture of ANSI 316L MPs and Cu-NPs. Thus, pure copper could be formed under the protection of a reduction solvent. Furthermore, under the irradiation of the laser, SS-MPs and Cu-NPs will simultaneously melt and react with the surrounding chemicals.

A continuous ytterbium fiber near-infrared laser (wavelength of 1,070 nm) with a fast scanning optical system (focal length ∼255 mm) was developed for the ISLM process. The experimental setup is illustrated in Figure 1b. An optimized slot die was designed and applied to deposit the organic solvent mixture. The layer thickness of the solvent layer was kept as 40 µm. Each newly deposited solvent layer is kept at 70°C through a radiation heater, and the layer deposition time is 0.5 s. A laser power of 25 W, a laser spot size of 18 µm, a scan speed of 35 mm/s, and a hatch space of 0.1 mm were used for fabricating the HMS samples. After the first layer of the organic solvent was deposited and sintered, another layer would be spread on the previous sintered layer, and this process was repeated until a solid HMS part was fabricated, and the 3D parts were manufactured with a slicing space of 0.04 mm.

### 2.3 Characterization

SEM tests were performed on a field-emission SEM (FEI Helios Nanolab 600i). Powder XRD patterns were recorded using a D/MAX-RB diffractometer (RIGAKU Corporation, Japan) with Cu Kα radiation. EDS mapping data were obtained by using an AZtecEnergy Standard X-MaxN 50 instrument (Oxford Instruments). X-ray photoelectron spectroscopy (XPS) data were measured using an ESCALAB 250Xi instrument (ThermoFisher, USA). The CA was measured by using a CA system (OCA20; Data Physics, Germany) using a droplet (3 µL) of water or oil as an indicator. For in-water CA measurements, the HMS samples were first fully immersed in water, and a droplet (3 µL) of TCM was carefully dropped on its surface. Three measurements of each CA test were conducted, and the average value was recorded. The surfaces of the fabricated HMS samples were then modified to decrease their surface energy by immersing them in an ethanol solution (1 wt%) of PFDTs at a temperature of 40°C for 24 h, followed by washing with ethanol and drying at 130°C for 1 h. Water CA tests using the modified HMS samples were then conducted. The pH durability test was conducted by immersing the samples in an aqueous HCl or NaOH solution with a pH range of 1–13 for 12 h, and then the CA tests were carried out on the dried samples.

### 3 Results and discussion

#### 3.1 Morphological and XRD analyses of the HMS samples

The composition of Cu-NPs only fabricated using ISLM was characterized (Figure S1, Supplementary material). The dynamic formation of the Cu-shelled-SS hierarchical structure during the ISLM process is very complex, due to the existence of ethylene glycol and differences of specific weight, surface tension, solidification rate between stainless steel and copper. The absorptivity of copper for the near-infrared laser radiation is much lower than that of iron. When copper and stainless steel were exposed to the same laser irradiation conditions, the heating rate of stainless steel would be higher than that of copper. Since the melting point of Cu-NPs is lower than that of SS-MPs, they would melt almost simultaneously under a high laser power intensity. During the ISLM process, the solvent was heated as well. Ethylene glycol near the top of the ink would evaporate, which leads to a faster cooling rate. The SS-MPs and Cu-NPs in the ethylene glycol solvent would be protected during laser irradiation from oxidation. Additionally, the oxidized of Cu-NPs can be further suppressed by their reaction with ethylene glycol.

Figure 2a shows a coral-like structure of an HMS sample surface. The formation of the hierarchical structures was attributed to the fusion of aggregates. The open pores were formed from the space trapped within the loose SS-MPs. The result from XRD is presented in Figure 2b, indicating that pure copper was formed during the ISLM process. However, based on the observation, the black color of the sintered composites
indicates that some of the materials on the surface are oxidized to CuO. The XRD tests possess a specific depth of penetration where the CuO formation on the surface has not been detected, which further implied that only a very thin layer of CuO was formed due to the evaporation of the reduction solvent on each layer surface. In the meantime, the organic solvent in the adjacent areas would enter the laser irradiation region through the capillary effect, and the CuO would be deoxidized into Cu due to the reaction with the organic solvent. Some of the CuO on the top surface of each layer would be saturated by the next layer of ink and turned into Cu as a result.

Figure 2c shows the surface morphology of the HMS sample. A detailed micro-graph is shown in Figure 2d. It can be observed that due to the surface tension and wettability, a nano-size copper structure would uniformly cover the surface of HMS samples, which shows self-assembly behavior. This autonomous organization of Cu-NPs into patterns or structures is further investigated in the next section for its wetting behavior. Energy dispersive X-ray spectroscopy mapping of Fe and Cu on the as-sintered HMS sample illustrated the growth of the Cu-NPs over the entire HMS surface after the ISLM process (Figure 2e and f).
Small amounts of CuO and Cu$_2$O as well as carbides were found on the surfaces of Cu-NPs using XRD and XPS analysis. Figure 3 shows a typical cross-section morphology of the cut HMS samples obtained using SEM secondary electron mode, in which the steel shows a darker color and the copper shows a lighter color. The compositions of both were characterized by using EDS (Figure S2, Supplementary material). It can be seen in Figure 3 that during the sintering process, alloying of the SS-MPs and Cu-NPs occurred, and the copper layers were covered on the stainless steel agglomerates (lighter color on the boundaries). Further agglomeration/bridging occurred among these aggregates and formed the closed micro-pores. Full melting of the powders due to the laser irradiation can be observed.

During sintering, the interaction among aggregates was non-uniform and different bridging behaviors were found. Four different alloy regions can be observed in Figure 3a–d. The first type is the separately distributed copper (SDC). SDC covered isolated stainless steel melt without interrupting the surrounding materials. The second type is the stainless steel bonded (SSB) aggregate. The successive heating by laser irradiation connects the melt of stainless steel along the scan path, which results in fusion among the adjacent stainless steel aggregates. The third type is the copper bonded (CB) aggregate. Since the Cu-NPs are uniformly adhered around the SS-MPs, the copper melt could finally result in the fusion among other Cu-NPs. The last type is the aggregate fused by stainless steel and copper bonding (SSCB), which resulted from the melt copper being drawn inside the adjacent stainless steel and forming a close bond with another aggregate. By the combination of these four types of fusion, the Cu-shelled-SS hierarchical structure of the HMSs was formed. The morphology of the HMS structure showed a clear Cu-NP melt pattern along the laser scanning direction (Figure 3e and f and Figure S3, Supplementary material).

### 3.2 Wetting behavior and oil/water separation capability of HMS samples

In order to examine the wetting behavior of the as-built HMS samples with water and oil, an in-water CA experiment was carried out. Figure 4a shows the in-water CA test with TCM, and Figure 4b presents the in-water wetting behavior with Oil-Red O dyed TCM. A nearly 0° water CA and ~155° in-water oil CA were obtained, indicating its super-hydrophilic and in-water super-oleophobic functionalities. These functionalities are attributed to the micro/nano hierarchical structures formed by the Cu-NP self-assembly phenomenon during the ISLM process. The hydrophilic behavior of the HMS structure resulted from the high surface energy and capability of wetting the
surfaces. When an HMS sample was immersed in water, the structure would be fully infiltrated, which forms a water membrane at the boundaries.

For the purpose of investigating the wetting ability of the HMS material, the fabricated samples were surface modified to decrease the surface energy by immersing the samples in an ethanol solution of PFDTS. The surface morphology after the modification can be found in Figure S4, Supplementary material. The wetting behavior of the modified samples is shown in Figure 5a, and a 152° CA with water and a nearly 0° oil CA were found. The wetting behavior was completely switched after surface modification. This demonstrated that the ISLM-fabricated HMS samples could switch from super-hydrophilicity to super-hydrophobicity by suitable surface modification.

Furthermore, based on the surface functionality changes, the HMS samples were tested for their oil collection capability from water as shown in Figure 5. Oils of n-heptane and TCM were selected as the organic oils to test the super-oleophilicity of the modified HMS sample. Figures 5b–d show the process of separating TCM (Oil-Red O dyed) from water. The water was repelled from the sample surface, which allows the sample to collect the majority of the oil in the water surface. Figure 5e–h shows the process of separating n-heptane (dyed orange) on the
surface of water; the n-heptane was completely removed from water by the HMS sample. The collected oil can be removed from the samples afterward through nitrogen gas cleaning. The unique hierarchical structure of the HMS sample shows its superior performance for oil/water separation under both in-water and on-the-surface-of-water conditions.

The magnetic actuation behavior of the HMS samples was also investigated. Figure 6 shows that the fabricated HMS sample moves under the control of a permanent magnet. The oil/water separation experiment was conducted in a curved glass tube. A surface modified cylindrical HMS sample with a diameter of 12 mm and a height of 6 mm is fabricated for the test. A total of 300 µL n-heptane and 300 µL TCM are dripped into the tube slightly. Four times collection were conducted to separate the oil from water thoroughly, as shown in Figure 6. The HMS material fabricated using the ISLM technique shows a promising performance in oil/water separation with its super-oleophilicity.

A test apparatus was also made to test the flowing/dynamic oil/water separation capability of the fabricated HMS samples. An HMS sample with a thickness of 0.5 mm was sintered and covered on an acrylic tube. A mixture of water and n-heptane was prepared and put into the acrylic tube with a small inclination that allows the liquid to flow through the porous sample as shown in Figure 7a. Due to the super-oleophilicity and super-hydrophobicity of the HMS sample after the surface modification, the n-heptane flowed through the sample completely.

### 3.3 Durability tests of the HMS surface functionality

The durability of surface functionalities such as super-oleophobicity and surface-modified super-oleophilicity of the ISLM fabricated HMS samples was investigated. The fabricated samples were all cleaned in an ultrasonic bath for 1 h to wash away the unmelt particles after being manufactured. The samples showed a stable behavior that endures through in the presence of acid or alkali. Although a few surface scales of CuO have been observed in the presence of an acid solution, the surface structures still demonstrated an excellent performance of in-water oil CA as shown in Figure 7c. The HMS sample surfaces maintain an in-water oil CA above 150° after being immersed in an aqueous HCl or NaOH solution in the pH range of 1–13 for 12 h. After surface modification, the HMS samples were treated in the aqueous HCl or NaOH solution in the pH range of 1–13 for 12 h as well. The water CA of the surface-modified samples is shown in Figure 7d, indicating the excellent acid and alkali resistance as expected. In all, the prepared samples demonstrate a strong durability and robustness under acid or alkali conditions.

### 3.4 ISLM of HMS samples with complex geometries

The ISLM technique developed in this study shows an advantage of fabricating micro/nano hierarchical structures that can switch from in-water super-oleophobicity to super-hydrophobicity and super-oleophilicity after appropriate surface-modification. In the ISLM process, the laser scans and sinters the M/N particle solvent mixture layer by layer under the control of X–Y galvanometers. In order to demonstrate the capability of the developed ISLM process to fabricate HMS samples with complex geometries, several different CAD models were designed. Figure 7b shows the fabricated 3D parts with a dimension of about 5 mm using the ISLM method with various shapes such as cylinder, cone, tetrahedron, and...
twisted cuboid, respectively. It can be seen that the ISLM technique was successfully applied for the fabrication of complex geometries of HMSs. These findings shed light on the application of HMSs in the field of bioengineering, sensors, fluid flow control, water purification, and so forth [47]. By adjusting the contents of micro/nanoparticles as well as the organics, the ISLM technique provides a tool for customized hierarchical structure fabrication in a single step without any requirement for post-processing. Importantly, the present approach could be extended to a vast number of HMS structures, by adjusting the materials and concentration of NPs and MPs, for the preparation of highly functional materials for various applications.

4 Conclusions

In this work, we demonstrated a novel method using ISLM of stainless steel micro-particles and copper nanoparticles to fabricate micro/nano hierarchical metal composites in ambient air. The major findings are listed as follows:

1. The hierarchical structures of the fabricated composites were formed by the connection of micro/nanoparticle aggregates with an outer shell of copper. Due to a high surface energy of the as-sintered surfaces, they showed super-hydrophilic behavior with a nearly zero water CA, expressing a good in-water super-oleophobicity with an oil CA of about 155°.

2. The HMSs were successfully turned into super-hydrophobic/super-oleophilic mode after surface modification by using a solvent-free, electrostatic polytetrafluoroethylene particle deposition method. The surfaces showed a water CA of 152° and a nearly zero oil CA, which allows the composite samples to collect oil from water even through a curved tube using magnetic actuation.

3. Pure copper was formed during the ISLM process due to deoxidization. Part of the composite surfaces was oxidized to CuO. The XRD tests showed that a very thin layer of CuO was formed due to the evaporation of the reduction solvent. The CuO would be deoxidized into copper due to the reaction with the organic solvent.

4. By using the ISLM technique, hierarchical metal composite parts with complex shapes were successfully fabricated. Both static and flowing oil/water separation tests showed excellent super-hydrophobic and super-oleophilic behavior of the surface-modified hierarchical metal composite samples.
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