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3D-printed electrically conductive silicon carbide

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ABSTRACT

The development of electrically conductive ceramics could achieve robust mechanical strength as well as practically high conductivity, offering applications in structural electrodes, conductors, catalyst supports, etc. However, its operating temperature is limited due to the intrinsic dense structures inevitably hindering the thermal management capability, thus resulting in a temperature-dependent electrical behavior in high-temperature environments. We report an additive manufacturing protocol through vat photopolymerization 3D printing to fabricate the architectured conductive silicon carbide (SiC) ceramics that simultaneously possess high electrical conductivity as well as low thermal conductivity, and demonstrate electric reliability under high-temperature environments above 600° C. The percolation of graphene into the ceramic scaffold establishes a uniform conductive network, exhibiting its electrical conductivity up to 1000 Sm^{-1} . The bulk density of the 3D-printed ceramic is measured from 0.366 g cm⁻³ to 0.897 g cm⁻³, with thermal conductivity ranging from 62 mW m⁻¹ K⁻¹ to 88 mW m⁻¹ K⁻¹. Furthermore, the mechanical performance of conductive ceramic can be effectively reinforced by densifying the microstructures via spark plasma sintering treatment. The proposed additive manufacturing strategy widens the potential of ceramics as a structural and functional material, offering a promising pathway toward high-temperature electronics applications.

1. Introduction

The advent of electrically conductive ceramics, such as high stiffness at elevated temperatures, high corrosion and wear resistance, and high thermal conductivity has led to various applications in gas sensors [1], catalyst supports [2], fuel cells, and batteries [2–4]. The dense ceramic structure enables an increased thermal conductivity, while exhibiting a temperature-dependent electrical characteristic at high temperatures [5–10]. To develop electrical stability with thermal management, the structure of the conductive ceramics has to be designed at multiple length scales from nanoscopic to macroscopic.

However, ceramics cannot be readily machined to complex shapes because of its brittleness nature. Additive manufacturing (AM) provides a diversified platform to fabricate customized 3D architectures and offers significant geometrical flexibility of 3D-printed ceramics [10–12]. Current research on 3D printing conductive ceramics relies on using semi-conductors, such as silicon carbide as the feedstock material [13] and fabricated via direct ink writing process [14,15] or binder jetting [15,16]. The printed sample shows limited resolution and electrical property to realize real-world applications, such as microwave optics [17], and catalyst [18]. Among various AM techniques, vat photopolymerization 3D printing has the outstanding advantages of high-resolution printing of fine features, allowing precise manipulation of the printed macroscopic structures. Lattice or cellular-like ceramics could be 3D-printed using vat photopolymerization process, after post heat-treatment to remove binder materials, the hollow ceramic structure

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demonstrates lightweight with no compromise in stiffness compared to the solid ceramics [19]. Owing to the layer-by-layer configuration of vat photopolymerization printing, the filler material could be uniformly distributed in 3D space during the printing process, which further promotes electrical conductivity. Although a higher filler material loading concentration can improve the end-part performance, it may also incur light attenuation and scattering [20], delamination, and detachment issues during printing [19].

In this study, we report a bottom-up additive manufacturing approach by which porous ceramics can be printed to 3D architectures with high electrical conductivity while achieving low thermal conductivity. Utilizing mesoporous silica, which has high specific surface area and nano-sized porous structures, as the feedstock material can effectively achieve thermal insulation characteristics. Besides, incorporating electrically conductive filler materials, such as graphene into the ceramic matrix can form the conductive network and thus produce electrically conductive ceramics. A customized mask image projectionbased vat photopolymerization printer was used for 3D printing the porous silica-graphene nanocomposites, where the graphene sheet can be wedged into the porous silica scaffold. Followed by the pyrolysis, graphene can percolate into the Si-O-Si network and subsequently forms the robust silica-silicon carbide matrix (Fig. 1 A). Electrical, mechanical, and thermal characterizations are investigated on the 3D-printed ceramics. The porous nature of the building block materials ensures the printed ceramics has lightweight (Fig. 1B) and thermal insulation properties. The electrical conduction is found as a function of the graphene concentration and maintains stability at high temperature (Fig. 1E). In addition, we perform spark plasma sintering treatment on the as-printed samples to further improve its mechanical strength. This distinct AM process could expand the functionalities of ceramics as a structural material and potentially find applications in high temperature or harsh environment catalyst supports, energy storage/convention devices, thermal protection systems, and acoustic metamaterials.



Fig. 1. 3D printing of electrically conductive silicon carbide. A, Graphene and mesoporous silica are used as feedstock materials for 3D printing. The silica-silicon carbide structure is formed after high-temperature pyrolysis. The scale bar is 50 nm. B, Photograph of the lightweight porous conductive ceramic sample placed on a leaf. C, Photograph of 3D-printed porous conductive ceramic parts. The scale bar is 10 mm. D, Comparison of the electrical performance vs. bulk density of this work and related literature [14,21–30]. E, The high-temperature resistance measurement of 3D-printed samples.

2. Results

2.1. Vat photopolymerization printing process and feedstock ink curing behavior

The prepared photosensitive ink is dark due to graphene content significantly absorbing light spanning the visible as well as the near-UV spectrum. This can block the light penetrating through the ink during vat photopolymerization printing, and subsequently affect the printing quality. Therefore, prior to the printing process, we measure the absorption spectrum (Fig. 2B) of the ink to find a preferable absorption behavior for photocuring. The ink for this study composes of PEGDA (Poly (ethylene glycol) diacrylate, MW250), 15 wt% mesoporous silica, and 0.015 wt% graphene. Based on the absorption spectra, which show high absorbance below the wavelength of 400 nm, we utilized an ultraviolet (UV) light source (wavelength = 385 nm) for the mask-image projection-based vat photopolymerization system [31]. Having customized the vat photopolymerization system, we investigate the curing behavior to get an insight for choosing the suitable process parameters and ultimately achieve a high vertical resolution. We measure the single-layer curing depth under different UV intensities and find that higher intensity can cure the ink faster, but a maximum curing depth appears at 0.217 mm (Fig. 2 C). The graphene flakes in the ink could absorb the UV light, hindering the photopolymerization process, which accounts for the plateau value of the curing depth. To determine the layer thickness of vat photopolymerization printing, we further examine

the relationship between the curing depth and the light exposure energy. Jacobs (1993) proposed the curing depth as a function of the exposure energy and the light penetration length, expressed as follows:

$$C_d = D_p \ln(\frac{E}{E_c}) \tag{1}$$

where C_d is the curing depth, D_p is the penetration depth for the given energy, which is directly related to the ink composition and defined as the depth of ink which will lower the irradiance to 1/e (approximately 37%) of the light source irradiance. E_c is the minimum energy required to initiate curing, where a chain of reactions is initiated by the radical photopolymerization. *E* is the exposure energy. A semi-log plot is used (Fig. 2D) to determine the value of E_c and D_p . In which the exposure energy values are on a logarithmic scale, and the curing depth on a linear scale. From the linear-fitted curve, the slope depicts the penetration length D_p and the x-intercept depicts the critical energy E_c . With a UV light intensity of 1.860 mW cm⁻², the resulting critical energy and penetration depth are 2.07 mJ cm⁻² and 0.182 mm, respectively. When increasing the intensity to 2.218 mW cm⁻², the associated critical energy and penetration depth increased to 2.22 mJ cm⁻² and 0.213 mm, respectively.

Based on the present results, the layer thickness should be less than 0.182 mm with a light intensity of 1.860 mW cm⁻². When determining the actual layer thickness, we further consider that the separation force (Figures S3-S5) could cause delamination between the printed layers.



Fig. 2. Vat photopolymerization printing and curing behavior study of the feedstock ink. A, Schematic drawing of the printing process. B, Absorption spectra of the PEGDA (Poly(ethylene glycol) diacrylate) MW250 and PEGDA MW250 with graphene and silica. C, Curing depth as a result of UV light exposure time under different light intensity. D, Curing depth as a function of exposure energy.

Therefore, although the single layer curing depth can reach 0.22 mm, but when the layer thickness is 0.2 mm, the resulting layer bonding is not strong enough to overcome the separation force-induced delamination (Figure S6). On the other hand, due to the presence of the thermal gradient during the subsequent pyrolysis process, it could further magnify the delamination issue. When we decrease the layer thickness from 0.2 mm to 0.1 mm, although the as-printed part has good structural integrity, but the sintered part still shows the delamination issue, and the cracks coincide with the inter-layer bonding (Figure S6). Therefore, we set the layer thickness at 0.05 mm, and the printed sample shows good structural integrity.

2.2. Structural property

The scanning electron microscope (SEM) and transmission electron microscopy (TEM) images of the sintered conductive ceramics are shown in Fig. 3A-C, where internal porous structures are revealed. The percolation of graphene into the porous particles can be observed in the TEM image (a TEM image of pure graphene is shown in Figure S7). XRD (X-ray diffraction) characterization (Figure S8) reveals that the samples

show an amorphous structure when the sintering temperature is less than 1400°C. When sintering at 1400°C, the diffraction peaks occur and correspond to the SiO₂ cristobalite and β -phase SiC (Silicon Carbide). Sorarù et al. (1996) proposed that the re-distribution of C and O atoms accounts for the origination of SiC [32]. In a high-temperature and inert environment, a portion of the Si-O bonds are replaced by the Si-C bonds. On the other hand, the presence of SiO₂ cristobalite peaks indicates that high temperatures also induce the crystallization of the porous feedstock silica. In this regard, those carbon substances that do not form the Si-C bond are percolated on the silica skeleton and form lots of porous. Besides, due to the volatilization of methylene and carbonyl groups as gases, it promotes the formation of new pores. Together, these two factors play a significant role in limiting large shrinkage under high-temperature [33-35]. Figure S9 shows the photographs of the as-printed sample and the sintered sample, demonstrating no significant shrinkage.

The Barrett-Joyner-Halenda (BJH) tests are performed on the sintered conductive ceramics to study the porous structures. Fig. 3D shows the N_2 adsorption-desorption isotherm curves, which matched the type IV isotherms based on the IUPAC classification, indicating its



Fig. 3. Structural analysis of the 3D-printed porous conductive ceramics. A and B, SEM images of the 3D-printed porous ceramics. C, TEM image of the 3D-printed porous ceramics, showing the percolation of graphene into the porous particles. Scale bar represents 50 nm. D, BET-BJH Nitrogen-sorption isotherm curves. E, Pore size distribution diagram. F, Thermal conductivity measurements of 3D-printed samples with various graphene/silica ratio. G, An infrared (IR) image of a 3D-printed UB logo placed on a hot plate. The image is taken after keeping the sample for 30 min on the hot plate. H, Stress-Strain curves of uniaxial compression tests. I, Summary of the compressive strength of 3D-printed samples. The SPS treated samples demonstrate 96.19% enhancement in the compressive strength.

mesoporous structures. The pore size distributions are shown in Fig. 3E, the pore size ranges from 10 to 150 nm. Also benefiting from the porous structure, the 3D-printed conductive ceramics show a low thermal conductivity, measured from 62 to 88 mW/mK (Fig. 3 F). The increasing graphene concentration leads to a slightly increased thermal conductivity due to graphene having strong in-plane bonding, which accounts for the high thermal conduction. Fig. 3 G shows an infrared (IR) image of a 3D-printed conductive ceramic sample placed on a hotplate (234°C). The porous sample can well insulate the heat transfer, and the temperature on the sample is at 89.2°C, indicating its excellent thermal insulation performance.

The stress-strain behavior under compression load for the conductive ceramics are shown in Fig. 3H with graphene/silica loading from 0.02 wt% to 0.10 wt%. The compressive strength is summarized in Fig. 3I. The 0.02 wt% graphene/silica loading ceramic could withstand maximum stress of 46.625 MPa, and the corresponding compressive strain at failure was 0.106. In contrast, with a higher graphene/silica loading, the 0.10 wt% graphene/silica sample could only withstand the stress of 29.546 MPa. However, the ultimate compressive strain increased to 0.142, and a fluctuated stress increase was observed. This is due to the higher graphene/silica loading resulting in a lower bulk density and higher porosity. During the compressive tests, pores were first condensed, leading to a fluctuating increase in the stress, and the ultimate compressive strength was reached at the end of the pore condensation process. We further optimize the mechanical performance

of the composites through the spark plasma sintering (SPS) treatment to densify the conductive ceramics. The SPS treated sample found a maximum compressive strength of 57.947 MPa, which accounted for a 96.19% increase in strength.

2.3. Electrical performance

The electrical properties are presented in Fig. 4 A, B, and S12. The current-voltage (I-V) curves of the 3D-printed conductive ceramics are shown for graphene content increase from 0.02 to 0.10 wt% with the corresponding conductivity in the range of 207-680 S m⁻¹. The conductivity curve initially increases exponentially with the increasing graphene concentration, denoting that the conductive pathways begin to form as a result of graphene percolation [36]. As more graphene is doped into the sample, the pathways form a conductive network that spans inside the printed sample, and the corresponding conductivity curve saturates to a plateau value. The highest electrical conductivity (680 S m^{-1}) is three times higher than those of traditional conductive ceramic composites [25,37,38]. This is because the porous feedstock silica provides a high specific surface area for the graphene percolation and thus exhibits preferable electrical conductivity. The bulk density of the conductive ceramics was in the range from 0.366 g cm^{-3} to 0.897 g cm^{-3} . Compared to the silicon carbide density of 3.21 g cm $^{-3}$. the 3D-printed sample demonstrates an outstanding lightweight structure (Fig. 1 and Figure S11). We construct a demonstration of the



Fig. 4. Electrical properties and high-temperature performance. A, Electrical measurement of 3D-printed porous conductive ceramics. B, Summary of electrical conductivity and bulk density as a function of graphene/silica concentration. C, An electrical performance demonstration of a 3D-printed UB logo made of porous conductive ceramics. With the low resistivity of the porous conductive ceramic, a 64-LED matrix panel could be lighted in parallel. D, Electrical performance under high-temperature environment.

electrical performance as shown in Fig. 4 C. The circuit is composed of a micro-controller board powdered by a 5 V DC (direct current) source, a 64-LED (light-emitting diode) matrix panel, and a 3D-printed conductive ceramic sample. All the 64 LEDs can light up simultaneously, and the video (Supplementary Video) shows a stably running circuit with the printed conductive ceramic as conductor. Fig. 4D shows the resistivity measurement under high temperature in the nitrogen environment. The result indicates that the resistivity of 3D-printed conductive ceramic can maintain a constant value from room temperature to 500°C. A slight resistivity increase is found higher than 500°C but remains in a practically low range. The high-temperature stable behavior is attributed to the good thermal management capability making the 3D-printed silicon carbide less prone to temperature change. As shown in Section 2.2, the average pore size is less than 150 nm, which effectively limits the free path of the gas molecule and thus limits the heat conduction. As a result, when placing the sample in high-temperature environments, the porous structure creates a thermal barrier to protect the conductive network and maintains stable electrical conductivity. These results showed that the 3D-printed conductive ceramic could find promising applications operating in high-temperature environments.

Supplementary material related to this article can be found online at doi:10.1016/j.addma.2022.103109.

3. Conclusion

In conclusion, we demonstrate vat photopolymerization 3D printing of porous conductive ceramics, which exhibit notably lightweight, high electrical conductivity, and low thermal conductivity. The curing behavior study provides insights into print graphene/silica loaded ink to high-resolution 3D structures and regulates the macroscale porous structures. Combined with the mesoporous silica feedstock, the printed sample demonstrates low thermal conductivity of 62 mW m^{-1} K⁻¹, and a low density of 0.366 g cm⁻³. The mechanical properties of the 3Dprinted sample could be tuned by varying the graphene loading and effectively reinforced using the spark plasma sintering treatment, showing a robust strength of 57.947 MPa. The percolation of graphene into the porous ceramic matrix creates an electrically conductive network that shows practically high conductivity. The conductive ceramic also features outstanding electrical properties and maintains stability in high temperature environments above 600°C. Our findings represent a new 3D-printed conductive ceramic conductor and promising strategies to address the temperature-dependent electrical property of conventional metallic conductors.

4. Experimental section

4.1. The silica/graphene ink slurry preparation

The porous silica was synthesized following the published protocol [39]. The printable ink was prepared by mixing Poly (ethylene glycol) diacrylate (PEGDA, MW250, Sigma-Aldrich), graphene (ACS Material), and porous silica particles at 15 wt%. 0.5 wt% Phenylbis (2, 4, 6-trimethylbenzoyl) phosphine oxide (Irgacure 819, purity \geq 97%, Sigma-Aldrich) was added as the UV light photoinitiator. The light absorber, 2-Nitrophenyl Phenyl Sulfide (MW231.27, purity≥ 98%, TCI), was added by 0.04 wt% to facilitate the high-resolution printing. The photoinitiator and light absorber were used as purchased without further recrystallization. The weight ratios between graphene and porous silica vary from 0.015 wt% to 0.1 wt%. A dispersing agent (Darvan 811, Vanderbilt) was added by 2 wt% of the PEGDA250 to prevent solid particle aggregation and sedimentation. The precursor was mixed using a sonicator for 2 h.

4.2. Vat photopolymerization printing process

A custom-built mask image-based vat photopolymerization printer

with a bottom-up building configuration was used to print the various objects. The 3D CAD models were sliced to mask images using a customprogrammed slicing software with layer thickness of 50 µm. A customprogrammed control software was developed to synchronize the mask image projection and the build-platform motion. The light source of the projector was 385 nm ultraviolet (UV) light, with a 1080 P projector (Wintech PRO4500, Texas Instruments).

4.3. Post-heat treatment process

The as-printed 3D parts were sintered in forming gas environments (95% nitrogen and 5% hydrogen). The temperature profile was shown in Figure S10 (c). A HP D 25 system (FCT GmbH) was used for the Spark Plasma Sintering (SPS) process with previously published protocol [40].

4.4. Characteristic analysis

The microstructures of printed conductive ceramics were imaged using Carl Zeiss AURIGA scanning electron microscopy (SEM). A thin layer of gold was sputter-coated to avoid charging effect. TEM images were recorded on a JEOL-2100 high resolution transmission electron microscopy (TEM) at 200 kV. BET analysis is performed on a Tristar II 3020 (Micromeritics Corp. Atlanta, GA). The density of ceramics samples was measured using Archimedes' principle. The electrical conductivities were tested by Ossila Four-point probe system. Mechanical properties were measured using a compression test machine (SSTM 20KN, United Testing System). UV intensity was measured using a digital light meter (UV513AB, General Tools). Thermal conductivity measurement was carried out using a custom-built instrument with heat flux sensors. The heat flux and thermal conductivity relationship was given bv



 $q = \frac{\lambda \Delta T}{\Delta x}$

where *q* is the heat flux value collected by the sensors, λ is the thermal conductivity, ΔT is the temperature difference between the surfaces, and Δx denotes the thickness of the measured samples. Thermogravimetric analysis (TGA) was carried out using a TA Instruments SDT Q600 Differential Calorimeter/Thermogravimetric Analyzer (DSC/TGA). The high temperature-resistance characterization was conducted in a tube furnace under nitrogen environment. A ceramic tube was utilized to secure the Nichrome 80 wires in the furnace with alligator clips at the end to establish a connection with the sample. The resistance was monitored using Keithley 2450 Sourcemeter and the temperature was monitored using the furnace thermocouple.

Author statement

This manuscript is approved by all the authors for publication. The authors declare that the work described is original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part. The authors also declare no competing financial interest, and disclosed the financial support in the "Acknowledgement" section.

CRediT authorship contribution statement

Ren Shenqiang: Writing - review & editing, Writing - original draft, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. Armstrong Jason: Resources, Methodology, Investigation, Data curation. Hu Yong: Methodology, Investigation, Data curation. Chivate Aditya: Methodology, Investigation, Data curation. Khuje Saurabh: Validation, Methodology, Investigation, Data curation. Wu Yiquan: Writing - review & editing, Resources, Funding acquisition, Conceptualization. Li Jiao: Methodology, Investigation,

Data curation. **Zhou Chi:** Writing – review & editing, Writing – original draft, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **An Lu:** Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Guo Zipeng:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization, Conceptualization. Guo Zipeng: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.addma.2022.103109.

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