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Highly Reusable and Environmentally Friendly Solid Fuel Material Based on Three-Dimensional Graphene Foam

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Supporting Information

ABSTRACT: It is a great challenge to find a reusable solid fuel material with both high absorption capability for organic liquids and clean use. In this work, a highly reusable and environmentally friendly solid fuel material based on three-dimensional graphene foam (3D-GF) was prepared, with high absorption capability for organic liquid fuels up to over 900 times its own weight and outstanding fire resistance. This 3D-GF shows high combustion efficiency, exceeding 99%. A rather clean burning was observed without toxic gases and soot particles released, as in the case of the conventional solid fuel materials. More importantly, the reusability and mechanical stability of the material are kept almost unchanged after 10 cycles of adsorption−combustion with organic liquid fuels.

INTRODUCTION

Taking the superiorities of easy to transport, storage, safety, carrying, use, etc., solid fuels have many advantages over liquid and gas fuels in industrial and daily life activities. However, burning solid fuels, especially the traditional solid fuels, such as fossil fuels and solid biofuels or the productions after their treatment, releases a range of health-damaging pollutants and toxic gases in the air,[1−5] which brings many significant human health and environmental problems.[6−8] Therefore, it is of crucial importance to develop and produce clean solid fuels for our society. Many efforts have been devoted to the fabrication of clean solid fuels, such as solid alcohol,[9−12] which produce much less toxic gases and soot particles compared to traditional solid fuels. Thus, solid alcohol is widely used in the occasions such as indoor, catering, tourism, field operations, etc.[13−16] It is important to note that a small amount of extra additives, such as stearic acid, sodium hydroxide, sodium chloride, nitrocellulose, dispersant, etc., is required for the production of solid alcohol.[17−21] These extra additives will lead to incomplete combustion of solid alcohol and create non-recyclable garbage.

Graphene is an exceptional molecular building block for synthesis of three-dimensional (3D) bulk assemblies.[22−24] Recent advances in architecture control of 3D graphene have enabled the successful synthesis of highly compressible graphene aerogels, which possess great promise for a range of applications, such as lightweight structural materials, reinforcing scaffolds, flexible electronics, and organic and solvent sorbents.[22,25−28] 3D graphene and its derivatives with both hydrophobic and organic liquid absorption properties have been reported in many works.[29−33] Recently, we have developed a scalable and three-dimensional cross-linked graphene foam (3D-GF), which exhibits extremely high absorption for organic liquids with great mechanical stability.[34,35] Considering the super mechanical and thermal stability of 3D-GF, in this work, we have explored its application as a reusable solid fuel material and found that the solid fuel material based on this foam material exhibits high reusability with both high absorption capacity and environmental friendliness.

RESULTS AND DISCUSSION

3D-GF was prepared through a solvothermal method described in our previous work[34,35] (see the Experimental Section), followed by annealing under an inert atmosphere at 800 °C for 1 h. Figure 1a exhibit the appearance of the bulk 3D-GF. To measure the performance of 3D-GF for solid fuel material application, the 3D-GF has been cut into an about 10 × 10 × 10 mm cuboid by a laser (inset of Figure 1a). A scanning electron microscopy (SEM) image (Figure 1b) shows that 3D-GF consists of interconnected graphene sheets tiled in a disordered manner to form a cross-linked network (walls), where large micrometer-scale voids were obtained among the walls. This material shows high thermal stability by thermogravimetric analysis (TGA), as shown in Figure 1c, and no weight loss until 450 °C under an air atmosphere. To further evaluate its fire-resistance performance required for solid fuel material, we burned a 3D-GF sample in an ethanol flame for 30 s (Figure 1d). It is noteworthy that no visible change can be observed on the macrostructure of 3D-GF from the SEM analysis (Figure 1e), and the weight of the samples after burning only decrease 1−2 wt %. Raman spectra of the sample before and after the burning test show no difference either, including that of the I_D/I_G value (Figure 1f). These results indicate that the 3D-GF shows high fire-/heat-resistance property, which may be assigned to the quick removal of heat

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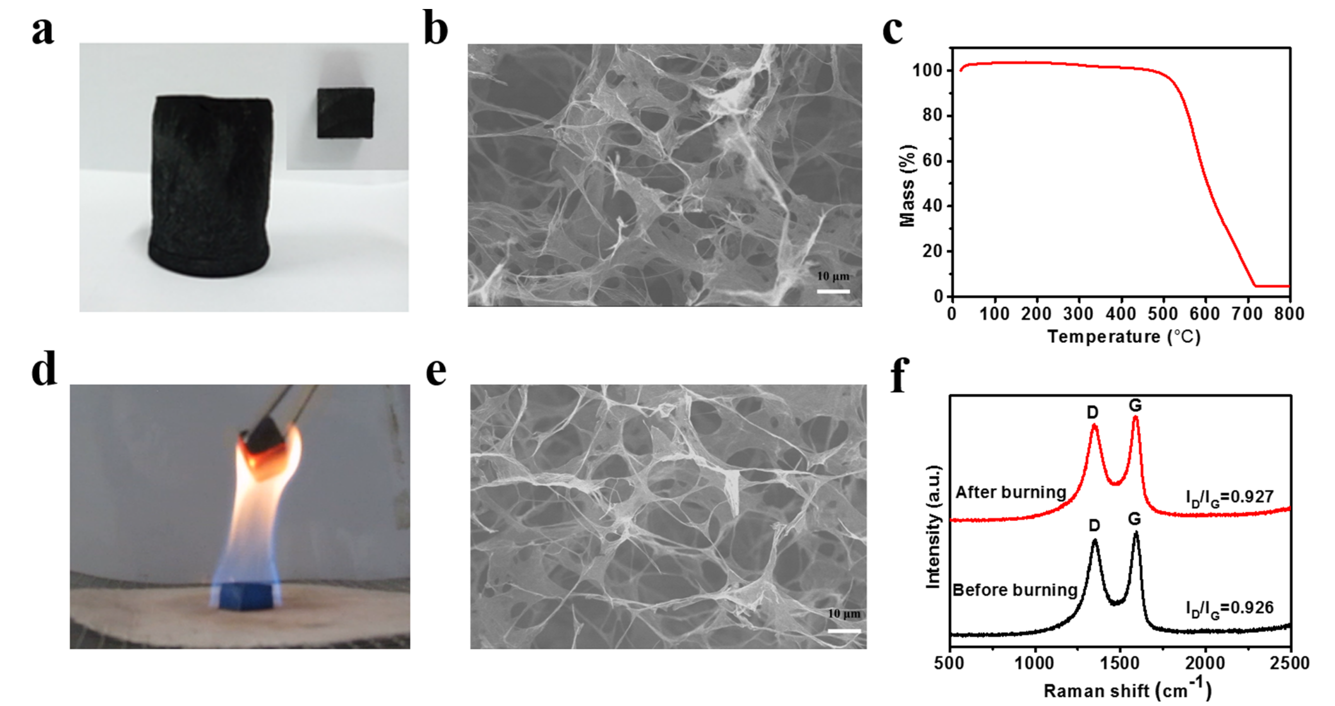

Figure 1. (a) Photograph of a 3D-GF and a 10 × 10 × 10 mm cuboid (inset). (b) SEM image of 3D-GF (scale bar of 10 μm). (c) TGA curves of 3D-GF in air with the heating rate of 10 °C min^{-1}. (d) Photograph of 3D-GF was burning in the ethanol flame. (e) SEM image of 3D-GF after burning in an ethanol flame for 30 s. (f) Raman spectra of 3D-GF before and after burning in an ethanol flame for 30 s.

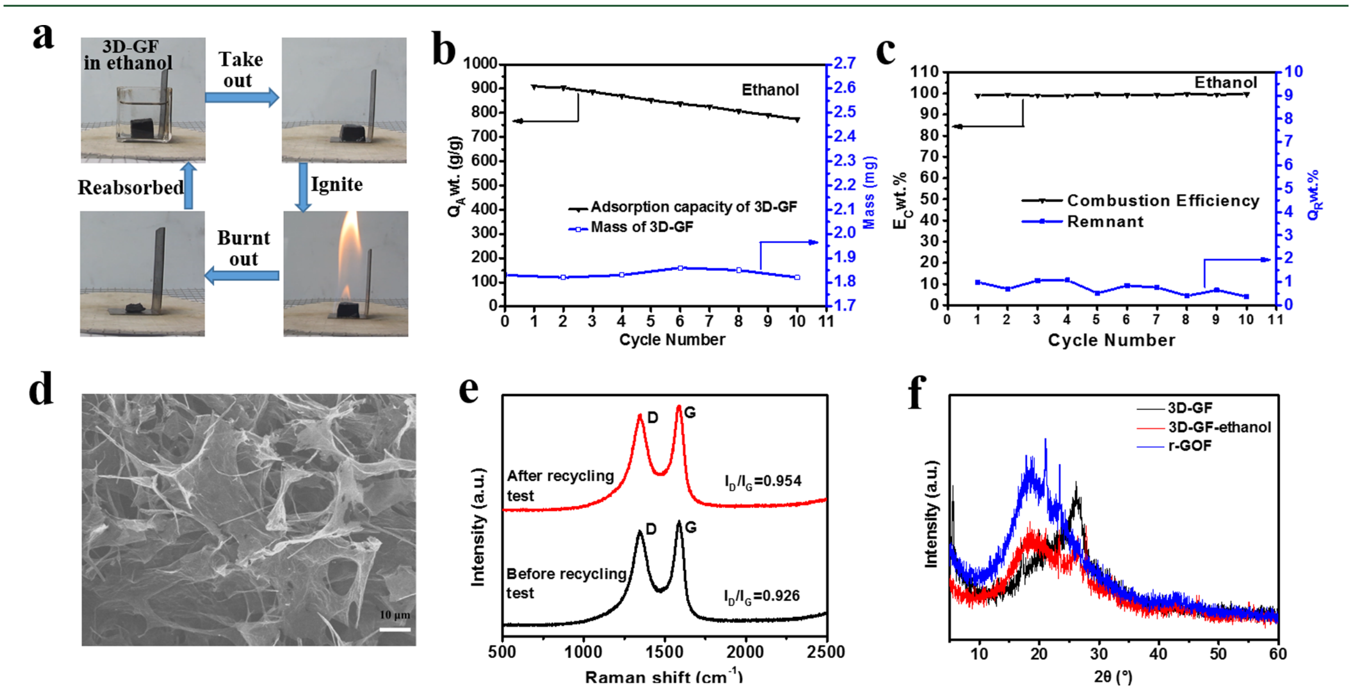

Figure 2. (a) Photographs show an absorption−combustion cycle of 3D-GF with ethanol. (b) Recording of the adsorption capacity of 3D-GF and the change of its mass during 10 absorption−combustion cycles with ethanol. (c) Combustion efficiency of the 3D-GF with ethanol and the remnant weight percentage under 10 absorption−combustion cycles. (d) Typical SEM images of 3D-GF after 10 absorption−combustion cycles with ethanol. (e) Raman spectra of 3D-GF before and after 10 absorption−combustion cycles with ethanol. (f) XRD patterns of the r-GOF (as prepared from the solvothermal process), 3D-GF (annealing of r-GOF at 800 °C in Ar), and 3D-GF−ethanol (3D-GF after 10 absorption−combustion cycles) .

during combustion, owing to the high porosity of the 3D-GF.[36,37]

Because ethanol is the most commonly used organic liquid fuel, we choose ethanol as the typical representation of organic liquid fuels to investigate the combustion efficiency and recyclability of 3D-GF-based solid fuel material. At the beginning of the absorption−combustion experiment, a bulk 3D-GF was used to fully absorb ethanol (3D-GF−ethanol), and then the 3D-GF−ethanol was combusted directly in air. The recycling procedure of 3D-GF with ethanol in the absorption−combustion cycle is illustrated in Figure 2a. It can be seen that the apparent volume of the 3D-GF−ethanol shrinks gradually

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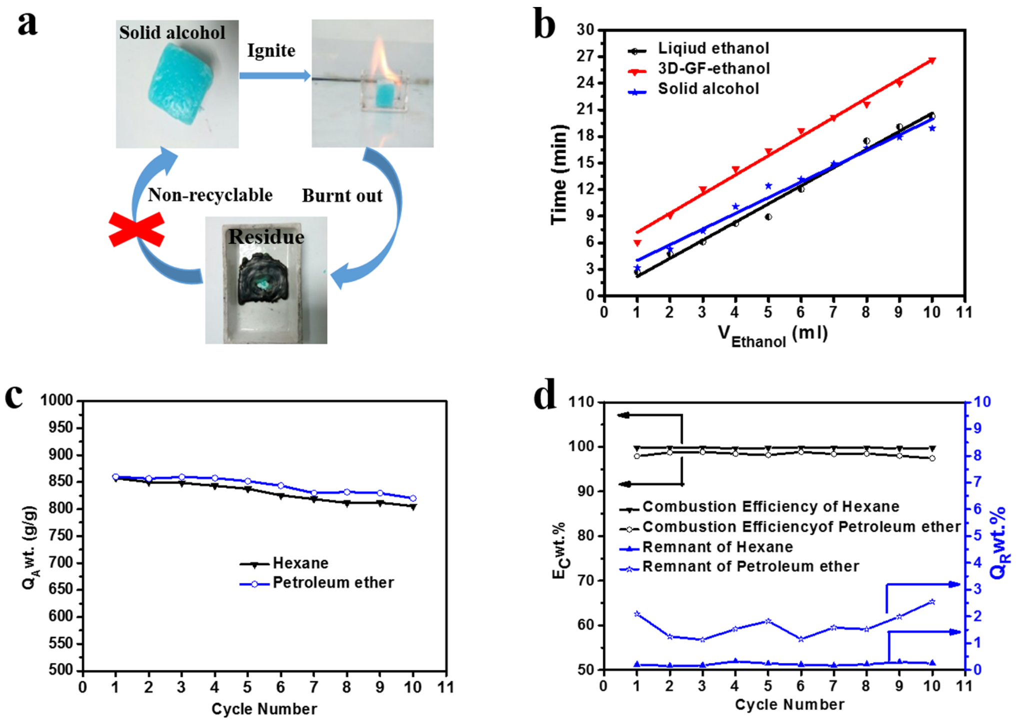

Figure 3. (a) Procedure of burning solid alcohol. (b) Curves of the burning period versus volume of ethanol for the 3D-GF−ethanol, solid alcohol, and pure ethanol liquid from 1 to 10 mL of ethanol combusted in the same conditions. (c) Absorption capacity of 3D-GF for hexane and petroleum ether during 10 cycles of absorption−combustion, separately. (d) Recyclability and efficiency of the 3D-GF with hexane and petroleum ether and their remnant weight percentage under 10 absorption−combustion cycles.

with the burning and then expands rapidly once put into ethanol again (movie S1 of the Supporting Information). We have measured the temperatures around the surfaces of the 3D-GF−ethanol upon burning and find that they are around 400 °C (335−410 °C), which are lower than its decomposition temperature (∼500 °C) and much lower than the outer flame temperature (around 700 °C); thus, burning of 3D-GF−ethanol will do no severe harm on the framework of 3D-GF. The absorption ability of 3D-GF for ethanol is up to 908 times its own weight (Figure 2b). After an absorption−combustion cycle, the absorption capacity of 3D-GF for ethanol decreased a little to 903 times its weight. The absorption capacity of the 3D-GF for ethanol can still maintain more than 772 times its own weight after 10 cycles of combustion (black line in Figure 2b), which is even several times higher than other reported 3D carbon materials.[29,32,38,39] The combustion efficiency of 3D-GF−ethanol in 10 cycles of absorption−combustion is exhibited in Figure 2c, which shows the high combustion efficiencies larger than 99% (black line). A very small amount of ethanol has been left in 3D-GF after a cycle (blue line in Figure 2c).

During 10 absorption−combustion cycles, the mass of 3D-GF is kept almost unchanged (blue line in Figure 2b). Also, no significant changes on the microstructure of the 3D foam can be observed by SEM images after 10 absorption−combustion cycles (Figure 2d). This result is also in agreement with that obtained from Raman analysis (Figure 2e), where I_D/I_G values of 3D-GF between the original and that after 10 cycles are barely changed and are 0.926 and 0.954, respectively. X-ray diffraction (XRD) spectra are suggested to determine whether there exists changes of the stacking structure of graphene during the cycle. It can be seen from Figure 2f that the main diffraction peak moves from 20° (r-GOF) to 26° (3D-GF) after annealing, which means the reduction of defeats and some restacking of graphene sheets upon annealing. After 10 absorption−combustion cycles, the diffraction peak at 26° decreases, while the diffraction peak at 20° increasea, which indicates the increase in the defeats and the interlayer spacing. Because this 3D-GF is constructed by graphene sheets mainly via chemical bonding, each absorption−combustion cycle will introduce small damage to the chemical bonding and the surface structure; thus, the content of defeats will increase and the pore volume will decrease, of which the former leads to the change in XRD patterns and the latter results in the decrease of the absorption ability after each cycle. All of these results indicate that the absorption−consumption cycles bring about some injury to the structure of 3D-GF, but the majority of the 3D-GF framework is still kept unchanged.

The characteristics of a 3D-GF−ethanol remind us of solid alcohol fuel, which is a popular solid fuel that has been widely used in the occasions such as indoor, catering, tourism, field operations, etc. Therefore, a side-by-side comparison test was carried out for this 3D-GF-based solid fuel material with a conventional solid alcohol. The results show 3D-GF-based solid fuel material the following advantages. First, the conventional solid alcohol cannot be reused after burning out (Figure 3a), while 3D-GF not only can be reused but also retain high absorption capability, even after 10 cycles of absorption−consumption (Figure 2b). Second, with equivalent absorbed ethanol and burning under the same conditions, the outer flame temperature (around 700 °C) of 3D-GF−ethanol is higher than that of pure ethanol liquid (around 650 °C) and much higher than the conventional solid alcohol fuel (around 550 °C) (movies S2, S3, and S4 of the Supporting Information). Furthermore, the combustion of 3D-GF−ethanol lasts longer than that for solid alcohol fuel and pure ethanol liquid (Figure

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3b), indicating a better energy efficiency for our solid fuel material. This could mainly be attributed to the 3D porous structure of 3D-GF. The 3D pores (channels) in 3D-GF are like countless capillary tubes, and the absorbed ethanol molecules distributed evenly in 3D-GF. Thus, the ethanol molecules can be gradually released during burning, which makes the burning of 3D-GF−ethanol more thorough and even than solid alcohol. Once burning, along with the quick consumption of the organic liquid molecules near the opening of the channels of 3D-GF, the organic liquid molecules in the inner pores of 3D-GF diffuse quickly to the outer surface via the channel. Because the opening of the pores is occupied by organic liquid molecules, air molecules cannot enter the pores of 3D-GF. Thus, a pressure difference between the inside and outside of 3D-GF is formed, which lead to the shrinking of the 3D-GF with the progress of burning (movie S1 of the Supporting Information), and the ethanol molecules can be combusted more violently and thoroughly than solid alcohol. It is similar to the mechanism of why alcohol blow lamps can gain a higher flame temperature than an ordinary alcohol lamp. Therefore, the burning of 3D-GF−ethanol can gain higher combustion efficiency than solid alcohol, such as a higher flame temperature and longer time. Third, there are additives in the conventional ethanol alcohol solid fuel, such as stearic acid, sodium hydroxide, nitrocellulose, sodium chloride, dispersant, etc., which could produce toxic gases and leave a solid residue of more than 10 wt % of its own weight after burning. However, there are no extra components in 3D-GF−ethanol; thus, during or after burning, there are no toxic gases and soot particles released in the air and no remnant waste left behind. Last, there is only about 90 wt % ethanol in the solid alcohol fuel,[11,40] while the take up of ethanol is up to 99.9 wt % of the weight of 3D-GF-based solid fuel material. Here, 3D-GF−ethanol has shown the advantages over solid alcohol at many aspects, such as a higher flame temperature, longer combustion time, no residue garbage after burning, and, particularly, recyclable use. Therefore, it would be cost-effective and environmentally friendly to replace solid alcohol by 3D-GF−ethanol in the cases that highly frequently use solid alcohol, such as catering, tourism, field operations, etc.

Besides ethanol, other common organic liquid fuels, such as hexane and petroleum ether, have also been used to investigate the recyclability and combustion efficiency performance of 3D-GF in absorption−combustion cycles, and they all show similar excellent performance, as shown in panels c and d of Figure 3. They also show a relatively lower surface temperature (370−390 °C) and a higher outer flame temperature (650−695 °C).

In addition, as a popular lame wick, cotton could be burned out gradually. Thus, on the basis of the above excellent absorption−combustion cycling results, the 3D-GF could be used as a lame wick, as showed in Figure 4. The wick can keep a rather stable and continuous combustion before ethanol has been consumed. The alcohol burner can be reused by simply adding ethanol into the container.

CONCLUSION

As a result of the high thermal and mechanical stability of 3D-GF and its unique microstructure, the solid fuel material based on such a material exhibits high reusability with high absorption capacity for organic liquids. Both the chemical and structure of the solid fuel material are kept almost unchanged after 10 absorption−combustion cycles. The graphene foam enables ethanol to be stored in a solid form, which greatly facilitates transportation and employment. Furthermore, this graphene-foam-based solid fuel material offers several advantages over the conventional solid alcohol material, such as reusability, environmental friendliness, and high absorption capacity.

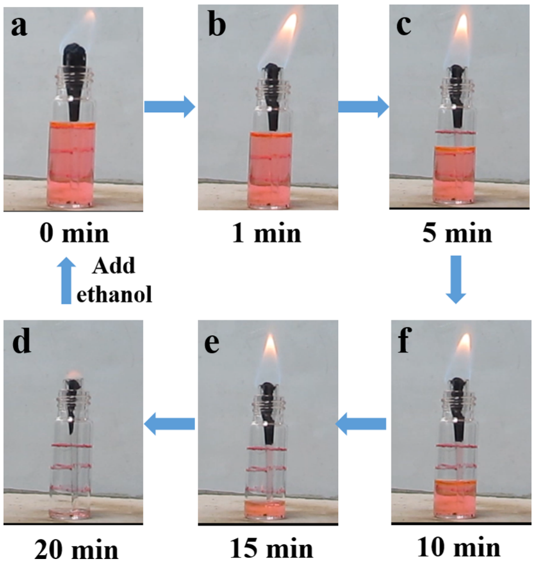

Figure 4. 3D-GF used as a lame wick of an alcohol burner (3 mL, pure alcohol). The alcohol burner can be reused by simply adding ethanol.

EXPERIMENTAL SECTION

Preparation of 3D-GF. 3D-GF was fabricated by an *in situ* solvothermal method. First, graphene oxide (GO) was synthesized by the oxidation of natural graphite powder using modified Hummers' method.[34] Then, GO ethanol solution (≈1.0 mg/mL^{-1}) was solvothermally treated in a Teflon-lined autoclave at 180 °C for 12 h. The obtained ethanol-filled intermediate was carefully and gradually solvent-exchanged with water, followed by freeze-drying. Finally, the material was annealed at 800 °C for 1 h in an argon atmosphere to obtain the 3D-GF. The densities of the 3D-GFs were 0.75−1.5 mg cm^{-3}. The obtained 3D-GF was cut into an about 10 × 10 × 10 mm cuboid by a laser for experiment.

Combustion Efficiency and Recyclability Test of the Solid Fuel Materials. The cuboid 3D-GF was fully soaked in ethanol (hexane or petroleum) and then taken out and directly burned in air. When it shrank and began to strip from the support, the burning sample was put out. The solid fuel material can be reused by simply reabsorbing organic liquid fuels in the next cycle. The burning period of each sample was recorded, and the flame temperatures were measured during burning. We performed 10 absorption−combustion cycles with ethanol, hexane, and petroleum ether, separately. The weight of the solid fuel materials was recorded before and after each absorption−combustion cycle, and the combustion efficiency (EC) was calculated according to the following equation:

$$\mathrm{EC}\ (\mathrm{wt}\,\%) = (\mathrm{WA} - \mathrm{WR})/\mathrm{WA} \times 100\%$$

where WA is the weight of organic liquid fuel absorbed in 3D-GF and WR is the weight of the remnant of organic liquid fuel in 3D-GF after burning.

Contrast Experiments. A total of 10 blocks of conventional solid alcohol (solid alcohol, alcohol content of 92 wt %, Ku Pai Hu Wai, China) and 10 parts of pure ethanol liquid containing 1−10 mL of ethanol were prepared, separately. Then, they were put into the same quartz container as used by the 3D-GF−ethanol test, burning them one by one and investigating their combustion performance in the same way as the 3D-GF−ethanol. The time interval of each test is about 10 min to decrease the temperature of the quartz container to room temperature. The burning period of the flame temperatures was measured and recorded during each test.

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Fabrication of a Simple Alcohol Burner with 3D-GF as the Lamp Wick. A cylindrical 3D-GF was piled in a little quartz tube as the lamp wick and then put into a small-opening container with 3 mL of ethanol to obtain a simple alcohol burner. After ethanol was burnt out, ethanol was added to the wick and burner, and it can be used again.

Characterization. The 3D architecture of 3D-GF was observed by SEM (JSM-7500F, JEOL, Japan). The Raman spectra were obtained on a Renishaw inVia Raman microscope using a laser excitation at 514.5 nm. X-ray diffraction (XRD) measurements were conducted on Rigaku D/Max-2500 diffractometer with Cu Kα1 radiation (λ = 1.54046 Å) at 40 kV. TGA was obtained using a Netzsch STA 409 PC analyzer, with a heating rate of 5 °C/min. The annealing treatment under an argon atmosphere was realized using a tube furnace at a ramp rate of 5 °C/min from room temperature to 800 °C (SK-G6123K, CTJZH, China).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.6b01867.

Process of 3D-GF used as solid fuel materials in our combustion efficiency and recyclability test by the method of absorption−combustion with ethanol (movie S1) (AVI)

With equivalent ethanol, 3D-GF−ethanol burned in the same conditions as solid alcohol and pure ethanol liquid one by one, with the ranking of their flame temperatures being 3D-GF−ethanol > pure ethanol liquid > solid alcohol (movie S2) (AVI)

With equivalent ethanol, solid alcohol burned in the same conditions as 3D-GF−ethanol and pure ethanol liquid one by one, with the ranking of their flame temperatures being 3D-GF−ethanol > pure ethanol liquid > solid alcohol (movie S3) (AVI)

With equivalent ethanol, pure ethanol liquid burned in the same conditions as 3D-GF−ethanol and solid alcohol one by one, with the ranking of their flame temperatures being 3D-GF−ethanol > pure ethanol liquid > solid alcohol (movie S4) (AVI)

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Notes

The authors declare no competing financial interest.

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