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Full paper

Assembling hollow carbon sphere-graphene polylithic aerogels for thermoelectric cells

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ABSTRACT

Aerogels are highly porous bulk materials assembled chemically or physically with various nanoscale building blocks and thus hold promise for numerous applications including energy storage and conversion. Assembling of hollow or porous particles with the diameter larger than 100 nm into hierarchically porous aerogels is efficient but challenging for achieving a high specific surface of aerogel. In this regard, submicron-sized carbon spheres with hollow cores and microporous shells are assembled into bulk aerogels, for the first time, in the presence of two-dimensional graphene sheets as special cross-linkers. The resulting bead-to-sheet polylithic aerogels show ultra-low density (51–67 mg cm^{-3}), high conductivity (263–695 S m^{-1}) and high specific surface area (569–609 m^2 g^{-1}). An application of thermocells is demonstrated with maximum output power of 1.05 W m^{-2} and maximum energy conversion efficiency of 1.4% relative to Carnot engine, outperforming the current simple U-shaped thermocells reported elsewhere.

1. Introduction

Gradual exhaustion of fossil fuels and rapid increase of energy demand may cause a serious energy crisis in the very near future [1]. Either exploiting the new energy options or developing energy recycling is a highly efficient way to overcome increasingly grim energy crisis [2–6]. However, both technologies face the challenge of finding and integrating new materials to meet the demanding performance [7,8]. This constantly motivates scientists to develop novel energy materials [9–12].

An aerogel is a kind of highly porous nanomaterial [13] with many intriguing properties such as the high specific surface area (more than several hundred m^2 g^{-1}), ultra-low density (as low as 3 mg cm^{-3}), large pore volume (several cm^3 g^{-1}), low dielectric constant (approaching that of air), superior thermal-insulating behavior (< 0.015 W m^{-1} K^{-1}), outstanding sound-proofing property (> 100 kg m^{-2} s^{-1}), etc. [14,15]. In recent years, intensive studies and exploitations have been carried out across many fields including environmental remediation, thermal insulation, energy storage and conversion, detection, adsorption, catalysis, and so on [16–18]. From the perspective of chemistry, aerogels are the sol-gel derivatives made via supercritical fluid drying (or other special drying) of various gel precursors, while from the perspective of structure, aerogels are the three-dimensional (3D) interconnected open-packed assemblies of various nano-sized building blocks [19]. 0D nanoparticles (e.g. in quantum dot aerogel [20]), 1D nanofibers (e.g. in carbon nanotube aerogel [21]) and 2D nanosheets (e.g. in graphene aerogel [22]) have been assembled respectively into corresponding 3D aerogel monoliths via covalent bonding (or non-covalent bonding such as electrostatic interaction, hydrogen bonding, hydrophobic effect, π-π stacking, van der Waals force, etc.) together with special drying techniques. Synthesis of various novel nano-sized building blocks and subsequent assembling into 3D bulk materials are at the cutting edge of the nanoscience and nanotechnology [23].

Multiple variables, such as shape, size, density, surface morphology, chemical attributes, etc. of the building blocks play important roles in determining structure and function of the resulting aerogel monoliths [24]. In the case of aerogels assembled with spherical particles, the specific surface area is inversely proportional to both the diameter and density of the individual solid particles under the assumption of no surface overlapping of the particles as shown in Fig. 1a. It is desirable to obtain large specific areas of the aerogel with small diameter and/or

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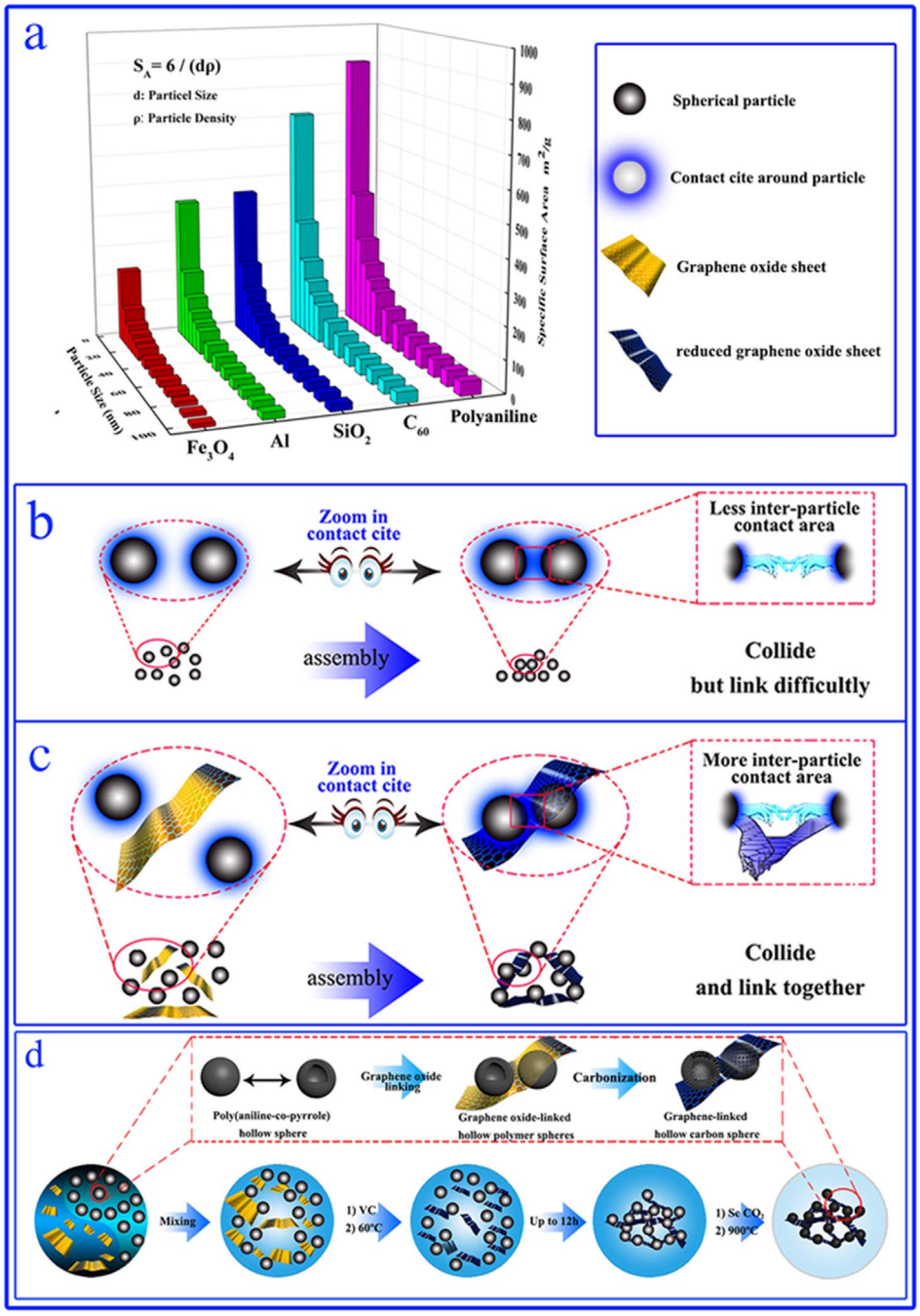

Fig. 1. (a) Particle size vs specific surface area curves of different materials, schematic diagram on stacking spherical particles in the absence (b) and presence (c) of 2D sheets, and (d) synthetic route of graphene-cross-linked hollow carbon sphere polylithic aerogel.

low density particles [25]. However, only a small range of diameters of the building blocks, from a few to several tens of nanometers is particularly of interest for an aerogel as its specific surface area decreases substantially when the diameter of the solid spherical particles is larger than 100 nm (Fig. 1a). For example, polyaniline with the density of 1.36 g cm^{-3} (the lightest shown in Fig. 1a) and particle size of 100 nm has an aerogel monolith which only possess maximum specific surface area of less than 44 m^2 g^{-1}. Such monoliths have lost the unique high-specific-surface-area property of the aerogels.

On the other hand, assembling particles with a high porosity (i.e. weight-lightening) can also achieve the aerogel with a high specific area. For each chosen material with its bulk density as a constant, creation of hollow or porous structure within the particles can substantially reduce the apparent density [26]. Therefore, assembling those hollow or porous particles will generate a hierarchically porous structure in combination with nano to micro voids. Small sized (e.g. several nm) particles are prone to be assembled via wet chemistry approaches [27]. However, assembling relatively larger particles, like hollow or porous spheres, with the diameter larger than 100 nm is not trivial (except close-packed photonic crystals [28]) due to much smaller inter-particle contact area (see Fig. 1b) and thus far fewer reaction sites in comparison with those with diameters smaller than 100 nm [29]. Furthermore, assembling heterogeneously structured aerogels using particles with different size, shape and composition is an effective approach to achieve multi-functionality of an aerogel [17,18]. Despite more variables being involved, the above limitations related to competing dimension scales of the building blocks are fundamentally the same. No matter which type of aerogel is made, it is challenging to produce high performance aerogels consisting of hollow or porous building blocks with the diameter larger than 100 nm.

Herein we report an ingenious strategy to assemble carbon hollow spheres using graphene as a nano-crosslinking agent to produce unique