Thermochimica Acta 657 (2017) 163–169

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Full length article

A high energy, reusable and daily-utilization molecular solar thermal conversion and storage material based on azobenzene/multi-walled carbon nanotubes hybrid

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ARTICLE INFO

Keywords:
Reversible isomerization
Solar thermal storage materials
Energy density
Half-lifetime

ABSTRACT

Developing molecular solar thermal storage materials based on the reversible isomerization is an important strategy for future efficient solar energy storage and conversion. A new hybrid system composed of azobenzene chromophore (AZO) and multi-walled carbon nanotubes (MCNTs) nano-templates, is designed and prepared via an organosilane as high-energy molecular solar thermal storage material. External high functional density and bundling effect of azobenzenes on the surface of multi-walled carbon nanotubes enable the intermolecular interactions between neighbouring azobenzenes to bring about a conspicuous increase in energy density (77.1 Wh kg^{-1}) and half-lifetime (14 h), respectively increased 92.5% and 2 order of magnitudes relative to the pure azobenzene molecule. Simultaneously, AZO-MCNTs nano hybrid maintains ultrastable and reusable stored energy ability for 30 cycles. Our results demonstrate this molecular AZO-MCNTs can practically palliate the daily periodicity of sunlight by storing the solar energy during the day and releasing as heat at night, which can be applied as highly customizable energy storage and conversion technology.

1. Introduction

As it is well known, solar energy source is environmentally clean and renewable. Effective utilization of solar energy is one of the greatest challenges to alleviate the pressure of future increasing energy demand [1,2]. Molecular solar thermal storage materials, with the ability of storing solar energy in chemical bonds and releasing it as heat based on the reversible photo-isomerization, are regarded as a closed system to realize the high-energy and stable solar energy storage and conversion without the emission of green-house gas (CO_2) [3–5]. In the past time, scientists have made much effort on different material systems, mainly including norbornadiene–quadricyclane system [6,7], anthracene system [8], stilbene system [9,10], fulvalene diruthenium system [11,12]. and dihydroazulene-vinylheptafulvene system [13,14]. Although the energy densities of above systems have made a great progress (some high up to 300 ~ 600 kJ kg^{-1}), most of these materials are still restricted in practical application due to the properties of molecules themselves, such as low storage capacity, low thermodynamic stability and irreversible degradation at long-time irradiation [15,16].

Recent years, molecular solar thermal storage materials based on azobenzene-system hybrids have attracted much attention because of the unique cycling stability, anti-photo degradation, and highly tuneable absorption wavelengths [17–21]. However, it remains a great challenge to meet the requirements of solar thermal storage due to a quite low energy density (the stored energy per unit mass) and a short storage half-lifetime ($\tau_{1/2}$) of a single molecule mainly caused by a low ΔH (energy difference between *trans*- and *cis*-isomers) and E_a (thermal barrier for the reversion process) [22].

In order to overcome the above servral difficulties, the azobenzene/carbon nano structure hybrids [23–28] based on the molecular interactions, are induced to tune the storage energy density and storage half-lifetime. Grossman et al. [24] first testified that both the ΔH and E_a of azobenzene/carbon nano structure hybrids (including the single-walled carbon nanotube, graphene and fullerene) were remarkably improved at a high functional density (1:4, about one azo molecule supported by four carbon atoms) by optimizing the intermolecular interactions between neighbouring AZO molecules on the surface of carbon nanomaterials via density functional theory (DFT), resulting in a special high theoretical energy density and long-term storage time. Considered from this angle, the increased functional density in AZO/carbon nano-template is essentially important to enhance the energy density and storage lifetime of solar thermal storage materials by intensive molecular

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http://dx.doi.org/10.1016/j.tca.2017.10.002
Received 1 June 2017; Received in revised form 27 September 2017; Accepted 2 October 2017
Available online 04 October 2017

interaction.

More recently, Grossman et al. [25] reported the ground-breaking work about the azobenzene/single-walled carbon nanotubes templated hybrids (AZO-SCNTs) using iterating functionalization by covalent organic radicals with amide-linked azobenzenes to obtain a high functional density about 1:21. Compared with the single azobenzene molecule, the intermolecular interactions and the bundling effect in the solid of AZO-SCNTs increase both the amount of energy stored per AZO molecule by more than 30% and the storage half-lifetime by orders of magnitude. However, an important limitation to this particular AZO-SCNTs hybrid system is its relatively low energy density only 200 kJ kg^{-1}.

Afterwards, Wei Feng et al. [26–28] designed a series of azobenzene/reduced graphene oxide (AZO-RGO) nano hybrids with a high functional density (1:16–19) via repeating radical reaction. They demonstrated that the multiple intermolecular interactions especially the hydrogen bond can remarkably improve both the storage capacity and lifetime. However, this class of nano hybrids needs a long-term ultraviolet radiation (more than several hours) for storing solar energy via the molecule isomerization which limits the practical application.

Different from the strategy of both high energy density and long-term storage, a suitable solar thermal storage material with high energy density and short half-lifetime may be more beneficial for practical solar thermal application in daily life. Recently, Si Wu et al. [29] demonstrated an integrated azo-polymer system that could efficiently store energy under full-spectrum solar irradiation for both ultraviolet and visible light with a short half-lifetime about 12 h. Although this result opens a new gate for daily-utilization solar thermal application, the practical energy density 125 kJ kg^{-1} is relatively low that severely limit the development of azo-polymer solar thermal storage materials. As a result, exploiting other structure material with high energy is very important for daily-use solar thermal storage.

In this paper, we present an effective approach to obtain a solar thermal storage material based on the azobenzene/multi-walled carbon nanotubes (AZO-MCNTs) nano hybrids (as shown in Fig. 1) with a high energy density and a suitable half-lifetime, which would allow solar thermal storage on a short-term basis for peak power shifting during a single day. Furthermore, we demonstrate the AZO-MCNTs shows a relatively high functional density on the surface of the MCNTs, leading to an increasing intermolecular interactions and the bundling effect in the solid of AZO-MCNTs that can remarkably improve the storage capacity up to 277.2 kJ kg^{-1} and a short-term lifetime about 14 h with an excellent cycling stability for 30 cycles. Our work develops a promising class of solar thermal storage materials with high energy density and suitable short lifetime for daily-utilization.

Table 1
Sample table.

Chemical Name	Source	Purification Method	Final Mole Fraction Purity	Analysis method
AZO	Synthesis	recrystallization	0.95	NMR
MWCNTs	Shenzhen Nanotech Pord Co., Ltd.	none	0.99	TGA[a]
KH550[b]	Aldrich	none	0.9990	HPLC[c]
dichlorosulfoxide	Aldrich	distillation	0.9991	HPLC
toluene	Aldrich	distillation	0.9992	HPLC
dichloromethane	Aldrich	distillation	0.9994	HPLC

[a] TGA = Thermogravimetric analysis.
[b] KH550 = (3-Aminopropyl)triethoxysilane.
[c] HPLC = High Performance Liquid Chromatography.

2. Experimental section

2.1. Materials

Azobenzene and AZO-MCNTs were synthesized according to the refs. The MCNTs was bought from Shenzhen Nanotech Pord Co., Ltd. (China) and all other main materials be supplied by Aldrich. The detailed information of the materials including purification method, final mole fraction purity and analysis method was shown in Table 1. The purity of MWCNTs was conducted by the authors and other chemicals

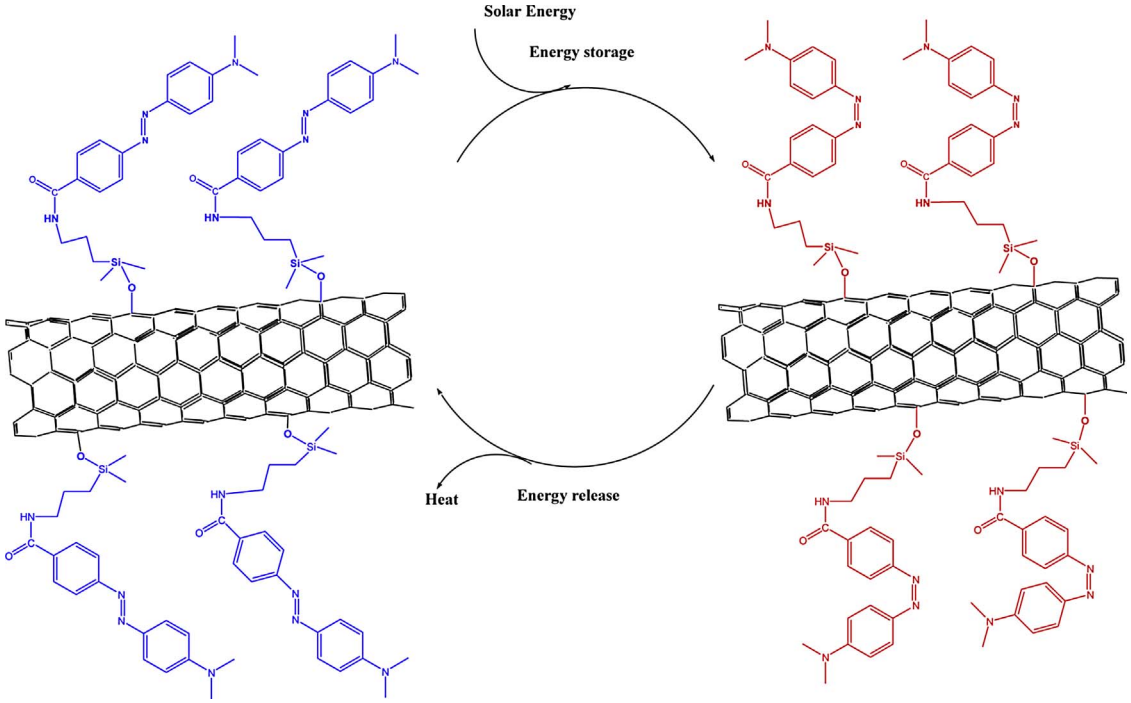

Fig. 1. Schematic illustration of the AZO–MCNTs for solar thermal storage. Energy from sunlight can be stored in the form of chemical bonds by photo-chemically induced *trans*-to-*cis* transformation and be released as a heat source tuned by *cis*-to-*trans* reversion.