Applied Catalysis B: Environmental 218 (2017) 267–276

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Research paper

Vertically-aligned silicon carbide nanowires as visible-light-driven photocatalysts

Jindui Hong*, Seyyed Shayan Meysami, Vitaliy Babenko[1], Chun Huang, Santamon Luanwuthi, Jesus Acapulco, Philip Holdway, Patrick S. Grant, Nicole Grobert*

Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, United Kingdom

ARTICLE INFO

Article history:
Received 29 March 2017
Received in revised form 18 June 2017
Accepted 19 June 2017
Available online 21 June 2017

Keywords:
Aligned silicon carbide nanowires
Large scale
Growth mechanism
Photocatalyst
Visible light

ABSTRACT

Vertically-aligned crystalline silicon carbide nanowires (VASiCs) (1 mm long and 50–90 nm in diameter) were synthesised in gram scale using SiO_2-infiltrated vertically-aligned multi-wall carbon nanotubes (VACNTs) and Si powder. *In situ* residual gas analysis was employed to study their formation and revealed CO to be the main by-product during synthesis. The *in situ* studies also showed that the formation of VASiCs begins at 1150 °C with the growth rate reaching a maximum at 1350 °C. A possible growth mechanism was established based on both, *in situ* and *ex situ* characterisation. The VASiCs have an estimated band gap of 2.15 eV, are photocatalytically active, and show strong light absorbance of up to 577 nm. Under UV–vis light (260–800 nm) as grown VASiCs could remove 90% Rhodamine B (RhB) within 30 min. Over period of 4 h under visible light (400–800 nm) more than 95% RhB was removed demonstrating their potential as visible-light-driven photocatalysts.

1. Introduction

Next generation photocatalysis is considered to be one of the feasible strategies addressing today's emerging energy and environmental challenges [1,2]. Tailored nanomaterials with high surface area, abundant surface state, and controlled morphology are essential to meet the requirements necessary for their efficient exploitation in photocatalytic applications [3]. Uniform, well-aligned one-dimensional nanomaterials facilitate electron transfer in the direction of interest and generally improve mass transfer required in energy and environmental applications [4–11]. For example, vertically-aligned carbon nanotubes (VACNTs) and TiO_2 nanotubes showed superior performance in battery applications [4–6], supercapacitors [7,8], solar cells [5,9], and photocatalysis [10,11]. Moreover, silicon carbide (SiC) is one of most promising photocatalysts due to its variable band gap, high electron mobility (400–900 $cm^2 V^{-1} s^{-1}$), and high conduction band (up to −1.8 eV) [12–21]. Recently, SiC nanowires with random orientation were developed for the photocatalytic reduction of CO_2 and water [12,13,18,22]. Several methods to synthesise well-aligned SiC nanowires were reported including multi-wall carbon nanotube (MWCNT) template growth [23], solvothermal methods [24], pyrolysis of silicon precursors [25–27], chemical vapour reaction [28–31], ZnS-assisted vapour-solid reaction [32,33], and carbonisation of aligned silicon arrays, *etc.* [14,34] Despite these efforts, the production of aligned SiC nanowires in gram scale with tunable diameter and length has not yet been achieved. Yang et al. and Liu et al. have synthesised aligned porous SiC nanowire arrays by the carbonisation of aligned Si nanowires [14,34]. However, due to the confinement of the aligned Si array template, the obtained SiC arrays have fixed diameter (*ca.* 300 nm) and short length (*ca.* 20 μm) [14]. The length and diameters of the resultant VASiC nanowires can be tailored using the carbothermic approach by controlling the thickness of VACNTs carpets and the average diameter of the individual CNTs respectively. Pan et al. prepared aligned SiC by reacting aligned CNTs with SiO [23], yet the yield of SiC was limited due to the small area of the CNTs template (15 mm^2 max.) [35]. Recently, we have developed an aerosol-assisted chemical vapour deposition (AACVD) method for the large-scale synthesis (≤90 cm^2, 14 g/h) of aligned MWCNTs carpets with tunable diameter (25–85 nm) and length (0.1–5 mm) [36–38]. These large-area flexible carpets (600 times of that used by Pan et al. [35] in area) of aligned MWCNTs enable the large-scale production of aligned SiC nanowires with tailored structure. Otieno et al. showed that MWCNTs/aluminoborosilicate composites can be generated by infiltrating MWCNTs with a sol-gel method [39]. Here we used a

* Corresponding authors.
E-mail addresses: jindui.hong@materials.ox.ac.uk (J. Hong), nicole.grobert@materials.ox.ac.uk (N. Grobert).
[1] Present address: Centre of Advanced Photonics and Electronics, University of Cambridge, 9 JJ Thomson Ave, Cambridge CB3 0FA, United Kingdom.

http://dx.doi.org/10.1016/j.apcatb.2017.06.056
0926-3373/

similar sol-gel process but the SiO_2 was used as Si source for the conversion of MWCNTs to aligned SiC nanowires using a carbothermal reaction.

Previous reports speculated that both, CO and CO_2, are formed as by-products influencing the evolution of the SiC nanowires during the conversion reaction [40–42]. For example, Han et al. reported that CO may react with SiO to form SiC nanowires epitaxially while CO_2 may etch the MWCNTs leading to SiC nanowires with a wider range of diameters [40]. Chiu et al. explained the shorter length of the SiC nanowires compared to the template of CNTs by the CO_2 etching of the MWCNTs [42]. Despite these past findings and theoretical explanations, the effect of CO and CO_2 on the structure of VASiCs has not been experimentally investigated yet. Monitoring of these gaseous by-products in real time and *in situ* diagnostics of the production line are essential in order to understand and propose possible growth scenarios for the VASiCs. Herein, we analysed the chemistry of a VASiCs CVD reactor using a quadrupole mass spectrometer to monitor the formation of residual by-product gases. These profiles of gas evolution and furnace temperature were then used to study and establish the growth mechanism of VASiCs.

Studies of aligned SiC nanowires were focused on the synthesis [25,28,29,31–33], structure or their field emission properties [23,24,26,30,34], while their application in photocatalysis is still limited. The aligned structure facilitates the electron transfer, hence improving the solar energy conversion efficiency [43]. Aligned SiC nanowire arrays with enhanced activity in water splitting were reported by Liu et al. [14]. It is well known that the photophysical/electrochemical properties and photocatalytic/photoelectrochemical performance of nanowires are highly dependent on their structure, *i.e.* diameter, length and aspect ratio [44,45]. As such, previously reported methods with fixed SiC nanowire dimensions did not have the flexibility in the applications due to their limited in control of their length and diameter. In addition, previous photocatalytic studies of aligned SiC were limited to UV light only. Considering the narrow band gap of SiC nanowires (2.2–2.8 eV) [12,20,42,46], they are expected to be visible-light-responsive, hence being capable of harvesting solar energy more efficiently than the UV-responsive photocatalysts. In order to verify this, we conducted the photocatalytic studies with VASiCs to degrade dye pollutant (RhB) using both UV–vis light and visible light, demonstrating that the developed VASiCs are efficient and visible-light-driven photocatalysts.

2. Experimental

2.1. Material synthesis

Individual steps of the preparation of the VASiCs are described below and illustrated in Fig. 1. These include: a) Synthesis of VACNTs, b) infiltration of a SiO_2-sol within the VACNTs matrix, c) conversion of the VACNTs into VASiCs, and d) removal of unconverted VACNTs through calcination in air. With a production rate of 14 g/h for VACNTs [38], the scale of production for VASiCs simply depended on the quantity of VACNTs used for the conversion to VASiCs. For example, 0.9 g (3.9 g) VASiCs were collected by loading 1.6 g (6.8 g) of SiO_2-VACNTs in a 5 ml (20 ml) alumina boat allowing gram scale production of aligned SiC nanowires. For SiO_2-VACNTs, both step c) and d) were omitted and for the semi-converted VASiC/CNTs only step d) was not applied.

2.1.1. Synthesis of VACNTs

VACNTs were prepared using an AACVD setup as described previously [37]. Briefly, an aerosol consisting of 95 wt% ethylbenzene (99%, Sigma–Aldrich) and 5 wt% ferrocene (purified by sublimation from ferrocene 98%, Sigma–Aldrich) was generated by an aerosol generator and introduced into a quartz reactor located in a standard tube furnace. The VACNTs synthesis was carried out at 850 °C in Argon (1000 sccm) for 1 h.

2.1.2. Infiltration of SiO_2 in VACNTs

SiO_2 was infiltrated in VACNTs using a sol-gel method [39]. The sol was prepared by combining tetraethyl orthosilicate (98%, Sigma-Aldrich, TEOS, 2.2 ml) with a mixture of ethanol (absolute, Fisher, 2.2 ml), deionised water (0.5 ml) and nitric acid (70%, Sigma-

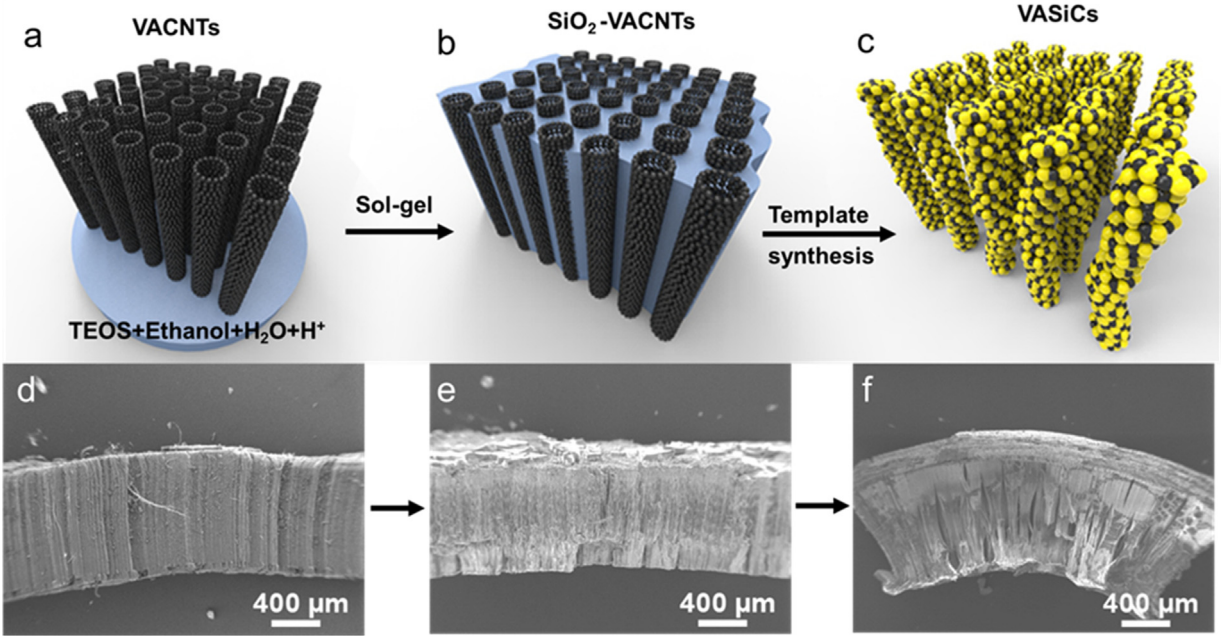

Fig. 1. Schematic illustration on the synthesis of VASiCs. Sol-gel: VACNTs placed in the mixture of tetraethyl orthosilicate (TEOS), ethanol, nitric acid (H^+) and deionised water; Template synthesis: heating at 1350 °C in Ar for 3 h then calcination at 900 °C in air for 2 h. Corresponding SEM images of (d) VACNTs, (e) SiO_2-VACNTs and (f) VASiCs showing the structure of VACNTs remained intact for all samples except that VASiCs were slightly bent following calcination due to a difference in concentration of the infiltrated sol between the bottom and top end of the VACNT matrix.