1. Introduction

The researches on bulk metallic alloys have been widely conducted due to many practical applications such as in electronic, automotive and sports equipments. These materials are reported to have good mechanical strength, strong heat resistance [1], low friction and good oxidation resistance [2]. Developed studies on these materials at nanoscale level expected to offers new promising applications. On the other hand, the researches of carbon-based materials are seemed to an endless study owing to their unique properties and wide range applications.

Only a few studies have focused on the fabrication of metal alloy nanowires [3,4]. To the best of our knowledge, this is the first attempt to synthesise amorphous Al–Cu alloy nanowires decorated with carbon spheres (CS). Most previous studies only successfully synthesised AlCu alloy films [5], Al–Cu composites and coatings [6–8]. Chemical vapour deposition (CVD) has been used for the synthesis of nanomaterials including CS, Al, and Cu nanowires [9–11], whereas electrochemical deposition is a popular technique to synthesise metal and alloy nanowires [4,12–14]. However, this latter method involves many chemicals and unfavourable complex preparation. For example, Fricoteaux and Rousse [4] prepared Cu–Zn–Al alloy nanowires by the dissolution of the chelometric precursors in an ionic liquid solvent. The solution was initially dried in a vacuum for a week before being used. Moreover, additional materials as counter, reference and working electrodes were also needed and required several treatments before being immersed in the prepared solution. The deposition process also needed to be performed in an argon-filled glove-box containing water and oxygen. This technique is not very efficient, time-consuming, expensive and therefore not promising for industrial-scale processing.

Zhao et al. [11] introduced the growth of copper@carbon (Cu@C) nanowires using chemical vapour deposition (CVD) and copper (II)-acetylacetone as a precursor. The temperature is at
least 450 °C then pure Cu nanowires were successfully obtained. Benson et al. [10] also reported the synthesis of Al nanowires using CVD and presented their potential application in energy storage. The use of CVD is beneficial for scaled up production of nanomaterials. Various nanostructured materials can be produced by adjusting the synthesis parameters of CVD. Conventional precursor produces Al or Cu nanowires are copper(II)-acetylacetonate [11,15], aqueous copper(II)sulphate electrolyte [16] and trimethylamine alane [10]. Cu–Al nanocomposite is reported synthesised using Cu and Al nitrate powders [7]. Recently, we reported the use of waste engine oil (WEO) for the production of quasi-aligned CNTs using thermal CVD (TCVD) [17]. It is similar to the use of natural [18,19] and waste oil precursors [20,21] in which high carbon content up to 85% made WEO as a potential alternative source for the production of carbon materials including CS. This can be achieved by varying the synthesis parameters such as catalyst concentration, precursor and synthesis temperatures. Lowering the catalyst concentration may lead to the formation of CS instead of CNTs. This is because of insignificant role of catalyst in producing CS, where it rather plays a role as the template for the nucleation base of CS [22].

Metal contaminants such as Al and Cu in WEO are originated from the oil interactions with engine parts during lubricating process such as bearing, wearing, valve guide, cooler, piston and gear [23]. The presences of Al and Cu contaminants promoted the growth of Al–Cu alloy nanowires from WEO. Inductively coupled plasma–optical emission spectrometry (ICP–OES) is performed for the identification of Al and Cu concentrations in WEO (Table 1). In the repeated identification measurement, the concentrations of Al and Cu in a variety of WEO samples are found to be consistent with average of ~0.94 ppm for Al and ~2.71 ppm for Cu, which were lower than other reports [24,25].

The advantages of the proposed technique are: (i) The use of only one source to produce two different nanomaterials at once, which are amorphous Al–Cu alloy nanowires and CS. (ii) The method is simple and can be easily scaled up for large production of nanomaterials compared to other techniques. In addition, with the use of cheap and abundant waste source as reactants, it provides an opportunity to achieve industrial scale production of nanomaterials. (iii) The use of WEO as a precursor is not only advantageous for nanotechnology innovation, but also environmentally beneficial since it offers a new alternative uses of WEO. Al and Cu are common contaminants presented in WEO, with their concentrations varying depending on the source of the WEO. Concentrations of at least 0.94 and 2.71 ppm for Al and Cu, respectively, must be fulfilled after the filtration and centrifugation processes in order to successfully produce amorphous Al–Cu alloy nanowires decorated with CS. Metal nanowires and CS have been reported to be potentially applied in energy storage devices [10,26]. Here, we also studied the potential application of amorphous Al–Cu alloy nanowires decorated with CS for supercapacitor device. The growth mechanism of the produced material including Al–Cu phase formation is also presented.

2. Experimental

WEO was collected from an automobile servicing workshop. Initial preparations of precursor and synthesis process were similar to previous reports [17,21]. In contrast with previous work [17], only 5.33 wt% ferrocene (C10H8Fe) concentration was consumed in 3 ml of WEO instead of 17.99 wt% in 4 ml. The precursor furnace was set at 450 °C, based on thermogravimetric analysis (TGA) and derivative thermal analysis (DTA) of WEO (Fig. 1) and the synthesis furnace was fixed at 700 °C. Previously, the precursor and synthesis temperatures were 500 and 750 °C respectively for the production of CNTs [15]. The sample was characterized using field emission scanning electron microscopy (FESEM–Hitachi SU8020), scanning tunnelling electron microscope (STEM–Hitachi SU8020), energy dispersive X-ray analysis (Horiba EMAX), high-resolution transmission electron microscopy (HREM – JEOL JEM-2100), micro-Raman spectroscopy (Renishaw InVia microRaman System) and X-ray diffraction (XRD Bruker AXS D9). Cyclic voltammetry (CV) measurements using a Gamry Potentiostat Series-G750 were also conducted on the sample in order to study its potential application for supercapacitor devices. Two films of 1 cm2 area of the prepared sample as electrode materials were sandwiched between a polymeric electrolyte separator [27]. The CV measurement was conducted at a potential window of ~1.0 to 1.0 V with the scan rate of 100 mV/s.

3. Results and discussion

Fig. 2(a)–(d) shows the FESEM images of amorphous Al–Cu alloy nanowires decorated with CS synthesised from WEO precursor. The CS perceived to grow in between the amorphous Al–Cu alloy nanowires. Concentrations of at least 0.94 and 2.71 ppm for Al and Cu, respectively, must be fulfilled after the filtration and centrifugation processes in order to successfully produce amorphous Al–Cu alloy nanowires decorated with CS. Metal nanowires and CS have been reported to be potentially applied in energy storage devices [10,26]. Here, we also studied the potential application of amorphous Al–Cu alloy nanowires decorated with CS for supercapacitor device. The growth mechanism of the produced material including Al–Cu phase formation is also presented.

Micro-Raman spectrum (Fig. 4(a)) shows two dominant peaks at 1351.8 and 1596.8 cm–1 for D and G peaks respectively. G peak represents the graphic structure of carbon material, and D peak corresponded to the disorder or defect mode [28]. IG/ID ratio of the CS was 0.67, which indicated that the CS has a reasonable graphitization degree. XRD pattern in Fig. 4(b) of the sample is matched with AlCu, Al2Cu and Al4Cu16 phases. Peaks at 20.69°, 25.21°, and 29.42° are indexed to Al2Cu (110), AlCu (1 1 1) and Al4Cu (2 0 0). Meanwhile, lower intense peak observed at 38.68° and 66.14° and indexed to Al2Cu (3 2 1) and Al4Cu16 (6 1 1). Low

| Table 1 |
|-----------------|-----------------|
| Al (ppm)        | Cu (ppm)        | Refs.     |
| 0.94            | 2.71            | This work |
| 6               | 23              | [22]      |
| 15              | 40              | [23]      |
intense XRD peaks also revealed the amorphous structure of Al–Cu alloy nanowires produced. Fig. 4(c) presents the CV curve of the sample. The maximum specific capacitance ($C_{sp}$) of the electrode was measured by the expression $C_{sp} = 2I/(SR \times m)$ [29] where $I$ is the maximum measured current (A), $SR$ is the scan rate (V/s), and $m$ is the mass of the electrode. $C_{sp}$ of the sample was calculated to be ~0.28 F/g. The obvious present of oxidation and reduction peaks around potential of 0.2 and ~0.2 V showed that amorphous Al–Cu alloy nanowires decorated with CS synthesised from WEO have a good electrochemical activity. This result paves the way to the development of new and potential production of energy storage devices based on Al–Cu alloy nanowires decorated with CS derived from WEO precursor.

Fig. 5 shows the schematic diagram of the growth of amorphous Al–Cu alloy nanowires decorated with CS. Heating the precursor furnace to 450 °C decomposed the WEO molecules into vapour elements. Ferrocene molecules were decomposed during the heating of precursor furnace, formed nanosized Fe catalysts and deposited in the synthesis region via Ar gas flow. Besides the role of catalytic activity for precursor decomposition [30], Fe catalysts also play a role as a template for the growth of amorphous Al–Cu alloy nanowires decorated with CS. Since a lower temperature of 125 °C is required for the growth of Al nanowires [10], the Al nanowires were expected to grow first as compared to Cu nanowires which required temperature at least 450 °C [15]. Moreover, the formation energy of Al (0.59 eV) is lower than Cu (1.14 eV) [31]. Next, since the diffusivity of Cu in Al is greater than Al in Cu [32], Cu then diffuse into Al nanowires forming the Al–Cu core nanowires with thickness of ~25.1 nm. Amorphous Al–Cu alloy nanowires continued to grow outside the core with larger thickness (48.5 nm). From
the weight and atomic percentage of the sample in EDX analysis (Fig. 3e) seen that Al intensity inside the core is higher than the outside. This confirmed the initial formation of Al nanowires and also supported with intense Cu outside the core.

Phase formation of amorphous Al–Cu alloy nanowires are based on the STEM, EDX and XRD observations also suggested. Three phase formation reactions of amorphous Al–Cu alloy nanowires are proposed as follow:

\[
\begin{align*}
2\text{Al} + \text{Cu} & \rightarrow \text{Al}_2\text{Cu} \\
2\text{Al}_2\text{Cu} + 7\text{Cu} & \rightarrow \text{Al}_4\text{Cu}_9 \\
\text{Al}_4\text{Cu}_9 + 5\text{Al} & \rightarrow 9\text{AlCu}
\end{align*}
\]

Al\(_2\)Cu phase is initially believed formed at lower synthesis temperature between 130 and 160 °C [33]. After the formation of Al\(_2\)Cu, the simultaneous formation of Al\(_4\)Cu\(_9\) and AlCu phases are suggested due to the continuous diffusion of Cu and Al into the nanowires. The detail of reactive phase formation in Al–Cu system was also suggested by Haidara et al. [33]. When the temperature reached 450 °C, precursor elements dissociated into carbon and hydrogen atoms. Carbon atoms are precipitated on the surface of Fe catalyst and formed graphitic structure, which led to the growth of carbon spheres. The growth of amorphous Al–Cu alloy nanowires decorated with CS terminated once the supply of vapour elements from precursor discharged.

4. Conclusions

In this study, synthesis of amorphous Al–Cu alloy nanowires decorated with CS has been done using WEO as the starting material. Different Al–Cu phases are observed during the growth process. This study is killing two birds with one stone where it is not only diversifying the use of WEO in nanomaterial field but also reduces the negative effect of illegal disposal of WEO. It is cheaper and also as one of the alternative ways to recycle WEO which can be harmful to the environment. The produced amorphous Al–Cu alloy nanowires decorated with CS have potential applications in energy storage devices, such as supercapacitors.
Fig. 4. (a) XRD pattern of Al–Cu alloy nanowires, (b) micro-Raman spectrum of CS and (c) CV curve of amorphous Al–Cu alloy nanowires decorated with CS.

Fig. 5. Schematic of the growth mechanism of Al–Cu alloy nanowires decorated with CS.
Acknowledgments

The authors are grateful to Malaysia Toray Science foundation (MTSF: 2012-0137–102-112), Research Acculturation Collaborative Effort – Malaysia (2012-0147–102-62), PRGS (2013-0097-102-32) grants and Universiti Pendidikan Sultan Idris for financial and facilities support of this work.

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