Present Advancement in Production of Carbon Nanotubes and Their Derivatives from Industrial Waste with Promising Applications†

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Abstract

An increase in global consumption has led to an exponential increase in industrial production activities which inevitably results in overwhelming remain of industrial waste. Consequently it has driven increasing attentions of research and development teams in various countries to propose and investigate novel methodologies to utilize such industrial waste. Instead of using as alternative energy sources, usage of industrial waste for production of carbonaceous nanomaterials has been examined via various routes, such as catalytic pyrolysis, hydrothermal treatment and so on. Meanwhile, for sustainable and secure continuity of the carbonaceous nanomaterial production, broad spectra of promising applications have also been examined. Among those emerging applications, utilization of carbonaceous nanomaterials in pollution control and prevention has been focused worldwide. Therefore, in this review, relevant research works focusing on catalytic pyrolysis of carbonaceous industrial waste for carbonaceous nanomaterial production were comprehensively analyzed and summarized. In addition, promising applications involving with antibiotic removal, spilled oil handling and pollutant gas detection were also reviewed.

Keywords: carbon, nanomaterial, industrial waste, synthesis, applications

1. Introduction

An increase in global consumption has led to an exponential increase in industrial production activities which has inevitably resulted in overwhelming remain of industrial waste. Such industrial waste management is the major consideration, especially plastics waste like poly-

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R&D efforts have been made toward the synthesis and applications of functional carbonaceous nanomaterials with diverse structures and morphologies, such as nanotubes, nanohorns, nanocapsules, nano-onions, nanofibers, coin-like hollow carbon, and graphenes (Kroto et al., 1985; Iijima, 1991; Bandow et al., 2000; Thostenson et al., 2001; Andrew et al., 2002; Dai, 2002; Sano et al., 2003; Li et al., 2003; Jang and Bae, 2004; Sano et al., 2004; Sun and Li, 2004; Xiao et al., 2006; Yao et al., 2007; Yuan et al., 2007; de Volder et al., 2013). Such carbonaceous nanomaterial has become of interest for many researchers because of its unique and outstanding properties. Table 1 would give an outlook of appropriate method which could provide some specific carbonaceous nanomaterials (Dai 2002; Popov 2004; Bazargan and McKay 2012; Iijima, 2012). Each synthesizing technique would provide a variety of carbonaceous nanomaterials with different advantages and disadvantages with respect to production yield, purity, and handling. For instance, arc discharge method with or without usage of catalyst would be appropriate for production of SWCNTs, MWCNTs and fullerenes but scale-up would be a drawback of this method. Meanwhile, chemical vapor deposition (CVD) technique would be very flexible for producing various carbonaceous nanomaterials except carbon nanohorns (CNHs). In term of synthesized products, besides SWCNTs and MWCNTs, graphene and carbon nanohorns (CNHs) have recently become research topics which also draw attention from many research teams. Anyway, a large variety of products at different synthesizing parameters implies that the so-called self-assembly reactions are complicated. The detailed mechanism has not been fully understood at the present time. Therefore, many of recent research and development efforts have been paid for elucidating the formation mechanism of such carbonaceous nanomaterial with respect to each category because such knowledge could be useful for regulating the production cost and their key characteristics. Unless their actually economic production processes are realized, commercial applications of carbonaceous nanomaterial would not reach their full potential (Thostenson et al., 2001; Dai, 2002; Zhang et al., 2003; Parkansky et al., 2004; Montoro et al., 2005; Kusaba and Tsunawaki, 2006; Guo et al., 2007; Tsai et al., 2009; Lebel et al., 2010; de Volder et al., 2013; Gong et al., 2014). Therefore, there is still much requirement for development of such carbonaceous nanomaterial production from cheaper and stable raw materials of various kinds.

Nevertheless, among those nanomaterials, carbon nanotubes (CNTs) have attracted widespread interest, owing to their unique structures and extraordinary properties in electrical, optical and mechanical properties, which could lead to many highly promising applications including adsorbents, atomic force microscopy (AFM) tips, catalyst or catalyst supports, electrodes for fuel cell and dye-sensitized photovoltaic cells, field emission displays (FED), hydrogen storage, nano-electronic devices, strength reinforcing fillers in polymers (Colomer et al., 2000; Barreiro et al., 2006; Paradise and Goswami, 2007; Arora and Sharma, 2014). In addition, some of their derivatives, such as metal-hybridizing carbon nanotubes are also recognized as novel nanomaterials with some promising applications, such as magnetic recording, medical diagnosis, selective adsorbents and supercapacitors (de Volder et al., 2013). As a result sizable production of CNTs and their derivatives have been continuously proposed and examined for more than two decades. As mentioned above various methods for CNT production would include laser ablation, arc discharge, chemical vapor deposition (CVD), electrolysis, and hydrothermal treatment. A remarkable amount of research attempts have been made toward comparison in various aspects, such as production yield, purity, operating cost, and scalability (Auer et al., 1998; Bandow et al., 2000; Colomer et al., 2000; Serp et al., 2001; Andrew et al., 2002; Sano et al., 2003; Popov, 2004; Barreiro et al., 2006; Xiao et al., 2006; Zeng et al., 2006;

| Table 1 Comparison of typical synthesizing techniques and carbonaceous nanomaterials |
|---------------------------------|-----------------|----------------|-----------|--------|--------|--------|
| **Technique**                  | **SWCNT**       | **MWCNT**     | **Fullerene** | **CNH** | **Graphene** |
| Arc discharge                  | x               | o              | o          | x      | x       |
| Arc discharge with catalyst    | o               | o              | o          | x      | x       |
| Laser deposition               | x               | x              | o          | o      | x       |
| Laser deposition with catalyst | o               | o              | o          | x      | x       |
| CVD (Pyrolysis)                | o               | o              | x          | x      | x       |
| CVD with catalyst              | o               | o              | x          | x      | o       |
| CVD (Plasma with catalyst)     | o               | o              | o          | x      | o       |

Note: o represents “applicable”

x represents “not applicable”
Generally, all of such CNT production methods would require some similar handling process conditions, such as high temperature condition for preparing carbon precursors from decomposition of carbon sources following by the self-assembly processes which could be regulated by various operating parameters. With different controlling parameters, different types of CNTs, which are mainly categorized into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), could be produced (Kim et al., 2003; Qiu et al., 2010; Altalhi et al., 2013).

Among various synthesizing methodologies, as compared in Table 1 chemical vapor deposition (CVD) or thermal pyrolysis is recognized as an efficient means because of its advantages in large-scale production with relatively low operating costs and excellent controllability in orientation, alignment, length, diameter, purity and density of resultant CNTs. Many technical reports have indicated that the thermal pyrolysis of organometallic compounds, such as ferrocene, iron phthalocyanine, and nickel phthalocyanine can be employed as either reactants or catalysts for production of carbon nanotubes and nanopcapsules (Afre et al., 2006; Liu et al., 2006; Vijayaraghavan and Stevenson, 2007; Charinpanitkul et al., 2009a; Zhuo et al., 2010; Sano et al., 2012; Li et al., 2012; Yang et al., 2012). With the thermal pyrolysis, some metal species, such as Fe, Ni or Co, in those compounds are well recognized to play an important role as catalyst for CNP growth (Auer et al., 1998; Li et al., 2003; Zeng, et al., 2006; Yuan et al., 2007; Morales et al., 2013; Nahil et al., 2015). Many novel methods to incorporate necessary catalyst with carbon sources are also the on-going research issues which have been reported by various research teams around the world. Investigation on tuning of synthesizing parameters for optimized productions of carbonaceous nanomaterials has been one of the most concentrating topics for research teams in many countries.

Meanwhile, it has been well accepted that utilization of alternative carbon sources available in gas, liquid, or solid phase by introducing over catalytic substrates or pre-mixing with catalyst supply would possibly increase production yield, improve CNT quality, or minimize the amount of expensive catalyst usage (Liu et al., 2006; Vijayaraghavan and Stevenson, 2007; Yuan et al., 2007; Zhang et al., 2008; Zhang et al., 2008; Quan et al., 2010; Zhuo et al., 2010; Alves et al., 2011; Sano et al., 2012; Li et al., 2012; Mishra et al., 2012; Yang et al., 2012; Sawant et al., 2013; Bajad et al., 2015). High purity carbon sources (> 99.9 %), such as CO, CO2, alcohols, and various hydrocarbons (methane, ethylene, acetylene, n-butane, hexane, benzene, toluene, xylene) have been extensively utilized for synthesizing CNTs with specific know-how relevant to synthesizing and purifying parameters which are synthesizing temperature and pressure, residence time in reactors, ratio of carbon source to catalyst and so on. However, such carbon sources are still expensive and present in limited supply, resulting in elevating attentions to search for alternative carbon sources, which include industrial wastes, municipal wastes (i.e. plastics wastes), food wastes, and low value-added industrial by-products (red oil, glycerol, slop oil). Instead of using as alternative energy sources, such industrial wastes or by-products could be considered as one of good alternatives for production of carbonaceous nanomaterials (Liu et al., 2006; Vijayaraghavan and Stevenson, 2007; Yuan et al., 2007; Zhang et al., 2008; Quan et al., 2010; Zhuo et al., 2010; Alves et al., 2011; Li et al., 2012; Yang et al., 2012; Altalhi et al., 2013; Acomb et al., 2014; Gong et al., 2014; Bajad et al., 2015). Table 2 summarizes some previous works which have made use of industrial waste as raw material for production of carbon nanotubes (CNTs) and derivatives. It could be clearly observed that some specific catalysts would be essentially required for production of CNTs with different characteristics. Among operating conditions, synthesizing temperature would also be a key parameter for converting raw materials into reactive carbon clusters which would undergo the self-assembly process to generate carbon nanotubes (Lee et al., 2003; Parkansky et al., 2004). Without catalysts, there is high possibility that the resultant products would be carbon black or amorphous carbon nanoparticles (Liu et al., 2006; Zhuo et al., 2010; Li et al., 2012). In addition, because of uncertain compositions, different physical and chemical properties, such industrial wastes or by-products contain some unknown impurities, such as sulfur which is expected to severely affect the synthesizing process, poisoning of catalyst, corrosion of reactor wall and so on. Some counter-measures have been proposed and examined for improving the productivity of carbonaceous nanomaterials from those industrial wastes.

Therefore, in this review, relevant research works focusing on catalytic pyrolysis or chemical vapor deposition of carbonaceous industrial waste for carbon nanomaterial production were comprehensively analyzed and summarized. Synthesizing parameters, such as molar ratio of organometallic catalyst to carbon source, types of catalysts and carbon sources, reaction temperature, were comprehensively examined for improving the synthesis efficiency. Furthermore, some promising applications involving with antibiotic removal, spilled oil handling and pollutant gas detection were also taken into account.
2. Present advancement of carbonaceous nanomaterial production from industrial waste

A comprehensive search of international journal publications was carried out using keywords of carbonaceous nanomaterial, industrial waste, and applications through the SCOPUS database. It should be noted that most of motivations for industrial waste utilization in those previous works are focused on requirement of reducing greenhouse gases (GHGs) in the atmosphere for mitigation of the global warming effect. It is commonly accepted that the combustion of fossil fuels is responsible for 73% of CO₂ emission thereby partial replacement of fossil fuels by bioethanol would enable a reduction in the levels of CO₂ emissions. According to the Renewable Fuels Association (RFA), the world bioethanol production in 2008 was approximately 65.6 billion liters (17.3 billion gallons), representing a 24% increase in the production than the previous year (Yuan et al., 2007; Alves et al., 2011).

Among various environmental concerns, management of plastic waste has posed a serious challenging issue for our society because they make up a significant proportion of municipal waste, typically around 10 wt% (Altalhi et al., 2013). Even though recycling rates for waste plastics have recently increased there is still a large remaining amount which ends up by being unsustainably disposed in landfill sites (Zhang et al., 2008; Mishra et al., 2012; Bajad et al., 2015; Nahil et al., 2015). In almost every country, the governmental sector has enforced more serious criteria for such industrial waste handling, such as limitation or avoidance of landfilling while encouraging promotion of waste management techniques are provided. In order to develop a more economically competitive usage, it is necessary to develop new methods to use industrial waste as replaced resources. Therefore, one of promising alternatives is to utilize such industrial waste containing carbonaceous content as feed stock for CNT production. If a feasible process could be developed for transforming those available carbon-rich wastes into high value-added products like CNTs, economic benefits could be made through simultaneously solving the plastic wastes and CNT production shortcomings. It seems that the amount of published studies attempting to synthesize CNTs from such industrial wastes were scattered and limited because most of them were exclusive projects or

| Source | Feed | Catalyst | Reactor Type | Temperature (°C) | Carrier Gas | Reaction Time |
|--------|------|----------|--------------|-----------------|-------------|--------------|
| Afre et al., 2006 | Chemical process waste | Turpentine Oil | Co and Fe | Quartz Tube | 500–900 | N₂ | NR | 2.5 nm |
| Liu et al., 2006 | Petroleum refining process waste | Deoiled Asphalt | Ferrocene | Quartz Tube | 700–1200 | Ar | 20–50 min |
| Bajad et al., 2015 | Plastic waste | Polypropylene | Ni/Mo/MgO | Muffle Furnace | 700–900 | | 10 min |
| Charinpanitkul et al., 2009 | Chemical process waste | Naphthalene | Ferrocene | Quartz Tube | 600–1000 | N₂ | 15 min |
| Zhuo et al., 2010 | Plastic waste | HDPE | 304 Stainless steel with Co, Ni or No | Quartz Tube | 800 | | 1 min |
| Sano et al., 2012 | Petroleum refining process waste | Ethylene | 316 Stainless Steel | Quartz Tube | 700 | H₂ | 30 min |
| Li et al., 2012 | Petroleum refining process waste | Heavy Oil Residue | Fe, Co, Ni, Au and Pt | Quartz Tube | 900 | H₂ | 20 min |
| Yang et al., 2012 | Automobile waste | Scrap Tyre Rubber | Co, Mg, Mn, Al | Quartz Tube | 650 | H₂ | 60 min |
| Morales et al., 2013 | Petroleum refining process waste | Acetylene | FeAl₂O₄ | Quartz Tube | 730 | H₂/N₂ | 60 min |

Note: NR represents “not reported”
announced in limited venues. So far serious issues including the variety and fluctuation of chemical compositions within such waste have been explored. It seems that the broad spectra of carbon-containing compounds, such as CH₄, C₂H₆, C₂H₄, C₂H₂, CO, CH₃OH, and so on, would involve as carbon sources for productions of CNPs (Bai et al., 2003; Lee et al., 2003; Chaisitsak et al., 2007; Zhang et al., 2008; Gong et al., 2014; Bajad et al., 2015). Furthermore, regarding to a common issue on using specific reactor system which would be promising for scalable production, some typical reports available in the public domain could be summarized in Table 2. It should be noted that various types of raw materials existing in gas, liquid and solid phases could be utilized for CNT synthesis with the assistance of various kinds of catalysts, such as ferrocene, nickel, cobalt and iron (Afre et al., 2006; Liu et al., 2006; Vijayaraghavan and Stevenson, 2007; Charinpanitkul et al., 2009b; Zhuo et al., 2010; Sano et al., 2012; Li et al., 2012; Yang et al., 2012; Morales et al., 2013). Those information would be good evidences that utilizing chemical vapor deposition or catalytic pyrolysis is a promising method because of its advantages on practical scalability and handling (Colomer et al., 2000; Grobert, 2007; Bazaegan and McKay, 2012; Mishra et al., 2012). In addition, it has been recognized that the industrial CNT manufacturing processes become sustainable and inherently safe though it would be sensible to use readily-available alternative fuels, such as existing waste streams. At the moment, since the production of CNTs has been successfully transferred from laboratory-scale to industrial-scale, their worldwide market is expected to grow from $215 million in 2009 to over $9 billion by 2020 (Iijima, 2012; Li et al., 2012; Nahil et al., 2015).

### 2.1 Gaseous carbon source

Hydrocarbons, such as methane, acetylene, ethylene, ethane, propane and some of gaseous hydrocarbons have been experimentally confirmed as carbon sources for CNT synthesis (Satishkumar, et al., 1999; Endo, et al., 2001; Bai, et al., 2003; Emmenegger, et al., 2003; Lee, et al., 2003; Liu, et al., 2003; Kim, et al., 2003; Lu et al., 2005a; Paradise and Goswami, 2007; Morales, et al., 2013). As a category of CVD synthesis, combustion or pyrolytic synthesis has the advantage of being an exothermic process which such carbon source can be utilized for in situ synthesis by means of decomposition and catalytic growth of CNTs. The composition of hydrocarbon gasses from those industrial processes would be varied from process to process. For example, in petrochemical downstream processing, the hydrocarbon gasses from the methane reformer would contain high content of CH₄, CO and CO₂, while those from refining units would consist of large compositions of BTEX, propane and ethylene. The current strategy for using these hydrocarbon gases is to install the carbon-material production unit on-board where the hydrocarbon sources are produced (Alves et al., 2011; Bazargan and McKay, 2012; Mankhand et al., 2012; Yang et al., 2012; Acomb et al., 2014). The use of suitable combustion equipment and catalyst as well as implementation of appropriate operating conditions, such as carbon source, flow of inert gas, and operating pressure, could realize controllable synthesis of CNTs with specifiable characteristics, such as diameter, length and purity (Liu, et al., 2003; Paradise and Goswami, 2007; Prasek, et al., 2011; Morales, et al., 2013).

Satishkumar et al. (1999) proposed to synthesize MWCNT bundles using pyrolysis of methane, acetylene or butane with the presence of ferrocene as catalyst precursor. The MWCNT bundles associated with nominal diameter in a range 2–13 nm contain iron nanoparticles inside their walls. As a result, such MWCNTs exhibit ferromagnetic behavior showing low saturation magnetization when compared to bulk iron. Meanwhile, Emmenegger et al. (2003) have synthesized MWCNTs from decomposition of C₂H₂ over a thin catalytic film of iron-oxide substrate. C₂H₂ concentration, time of deposition, temperature and ratio of C₂H₂ to N₂ are regulated to control the resultant MWCNT length. It is found that Fe₂O₃ is reduced to FeO₄ and FeO after contacting with C₂H₂:N₂ flow, resulting in formation of MWCNTs with tips anchoring on iron carbide clusters. Later, Lee et al. (2003) could synthesize well-aligned MWCNTs with high purity by pyrolysis of C₂H₂ at 800 °C with the presence of iron (II) phthalocyanine. The synthesized MWCNTs exhibit a bamboo-like structure with good crystallinity. It is also reported that the growth rate of well-aligned MWCNTs could be enhanced with an increase in C₂H₂ concentration. With those typical examples, such pyrolytic method has been recognized as one of the most practical routes appropriate for mass production of MWCNTs. As a result, most of commercially available MWCNTs are synthesized by many manufacturers, such as Hyperion Catalysis International, Inc. (Cambridge, MA). Meanwhile, Carbon Nanotech Research Institute (CNRI), a subsidiary of Mitsui Chemical has planned to develop a large scale production of 120 t of MWCNTs per annum. In addition, Applied Sciences, Inc. (API) and Showa Denko (SDK), have been successful in a large scale production of MWCNTs with relatively large diameters and a wide distribution in the range 70–200 nm. However, it should be noted that synthesis of those carbon nanomaterials from such gaseous raw materials would possibly be upset by the unstable supply.

### 2.2 Liquid carbon source

Instead of gaseous raw materials, various kinds of liq-
some kinds of liquid carbon sources would be intentionally prepared while others would be available as liquid by-products or wastes received from some specific industrial processes (Ago et al., 2000; Endo et al., 2001; Afre et al., 2006; Alves et al., 2011; Li et al., 2012). For investigation of formation mechanism, Ago et al. (2000) used a vertical flow reactor for synthesizing single and multi-walled carbon nanotubes by the catalytic reaction of colloidal solutions of metal nanoparticles. They made use of a reverse micelle solution of Co–Mo nanoparticles dissolved in toluene as raw material and injected the solution directly into a reactor of which temperature was maintained at 1200 °C. Therefore, it could be implied that such liquid precursor would be vaporized to provide clusters of carbon atoms as building blocks (Sun and Li, 2004; Yuan et al., 2007; Sovichai et al., 2012). The growth of SWCNTs was observed when the small amount of thiophene was added in the colloidal solution (1 wt.%). However, when they added 10 wt.% of thiophene, only MWCNTs could be grown from the self-assembly process. For mechanism investigation, it was found that carbon nanotubes contained metal nanoparticles encapsulated at the tip so that the tip-growth model was discussed.

Meanwhile, in many countries petrochemical industries have also produced some useful products necessary for our daily life but they also generate some hydrocarbon wastes which are mainly in liquid form. In general, as-received heavy hydrocarbon residue which is a highly aromatic material received as a bottom product after the distillation of petroleum could also be fed into a furnace or boiler for the generation of heat or “lighting up” facility in many coal-fired power plants. Certainly, such by-product of petroleum industries has great potential as feedstock in making carbon materials because it contains a large amount of carbon-rich molecules. As a typical example, slop oil which is a residual waste obtained from a petrochemical plant in Thailand was fractionated using a laboratory distilling unit could be separated into some fractions based on their boiling points as shown in Fig. 1. Light fraction contains hydrocarbons with boiling point lower than 170 °C while the middle and large factions are separated at 150–320 and > 300 °C, respectively. It could be clearly observed that the fractionated hydrocarbons exhibit different appearance because of their compositions which could be decomposed for generating carbon clusters after subject to sufficient thermal energy (Endo et al., 2001; Andrews et al., 2002; Dai, 2002). Anyway, the main drawback of residual hydrocarbons is its high initial viscosity. In addition, it usually contains relatively high amounts of pollutants and particularly sulfur which forms sulfur dioxide upon combustion. Li et al. (2012) reported that the growth temperature plays an important role in determining the formation of SWCNTs. However, different characteristics of SWCNTs synthesized from heavy oil when compared with the small hydrocarbons would be attributed to the formation process which did not proceed through C2 carbon units. It should also be noticed that effects of impurities in such waste on the synthesis of CNPs would be of concern so that many current strategies have been explored by adapting from some existing technologies. For example, the bottom product of a crude distillation unit in a petroleum refinery process usually contains high contents of sulfur and mercury compounds (Mohammed et al., 2012; Zubaidy et al., 2013; Khairi et al., 2015). Typically, various methods including chemical adsorption, gas stripping and chemical precipitation are employed for removing mercury from crudes and other hydrocarbon liquids to avoid the problems of poisoning. Meanwhile, sulfur removal with sorbent beds or chemical scrubbing has also been used with new supporting methods, such as microwave irradiation, for scavenging the sulfur content from liquid hydrocarbons in prior to their processing. In addition, effect of hydrocarbon chain length on the synthesis and the final quality of CNTs is also important issue though it is still ambiguously understood. Basically, the longer chain hydrocarbons would possibly be decomposed, resulting in formation of a broad spectrum of small hydrocarbons and carbon clusters with different specific molecular weights. Such hydrocarbons would undergo different reaction routes, resulting in formation of either arranged graphitic nanostructures or amorphous forms (Alberts 1997; Endo et al., 2001; Andrews et al., 2002; Dai 2002; Prasek et al., 2011; Mishra et al., 2012). In comparison with other carbon sources, such as methane, acetylene and ethanol, those hydrocarbons with broad molecular weight distribution would provide both crystalline and amorphous carbon nanostructures as could be confirmed by Raman spectroscopic analyses (Lee et al., 2003; Liu et al., 2003; Puengjinda et al., 2009).
Therefore, some pre-treatment would be essential for controlling the final quality or purity of CNPs which are synthesized from those hydrocarbon wastes.

In general, a typical set-up employed for synthesizing carbonaceous nanomaterials from such hydrocarbons would consist of a reactor equipped with raw material feeding and product collection as shown in Fig. 2. Feedstock would be introduced into the reactor by many means, such as spraying nozzle, ultrasonic nebulizer or even static container (Vilatela et al., 2015; Chaisitsak et al., 2007; Charinpanitkul et al., 2009b). Some inert carrier gas would be supplied into the reactor for carrying the hydrocarbon precursor which would be vaporized by regulated heating with a designated ramp rate for ensuring the steady flow of carbon sources into the reaction zone. The self-assembly reaction would be stimulated by a control of sufficiently high temperature zone within the reactor (Colomer et al., 2000; Barreiro et al., 2006; Charinpanitkul et al., 2009b; Puengjinda et al., 2009; Sano et al., 2012). During the formation of carbonaceous nanomaterials within the reactor, complicated phenomena, such as convective diffusional flow, thermophoresis and decomposition, would play a competitive role in regulating the production yield and characteristics of the resultant products. As a typical example, SEM micrographs of carbonaceous nanomaterials synthesized from fractionated hydrocarbon wastes and its mother liquor (slop oil) were depicted in Fig. 3. It could be clearly observed that synthesized products collected from different location of the reactor exhibit different apparent characteristics. Carbonaceous nanomaterials collected from Zone 1 where temperature was a little bit higher than the boiling point of slop oil mainly consist of spherical carbon nanocapsules (CNCs) which contain metal nanoparticle inside. Meanwhile, the highest thermal energy supply in Zone 2 would result in formation of well aligned MWCNTs with rather uniform diameter because of enhanced self-assembly reaction. However, at Zone 3 where the remaining precursors would further undergo the self-assembly reaction but would be discouraged by the convective flow, resulting in formation of a mixture of MWCNTs and amorphous carbon nanospheres (CNSs). Further analyses on characteristics of resultant products obtained from different location in the reactor in cooperation with synthesizing conditions (temperature, ratio of feedstock and catalyst, flow rate of carrier gas and so on) would be taken into account for elucidating the formation mechanism of such carbonaceous nanomaterials. Most of previous works agree with a postulation that metal catalysts which would be intentionally supplied into the reactor would exist in active liquid form which would adsorb carbon molecular clusters onto its surface and then catalyze the self-assembly reaction, resulting in formation of carbonaceous nanostructures which contain those catalytic metal nanoparticles inside (Bai et al., 2003; Emmenegger et al., 2003; Barreiro et al., 2006; Prasek et al., 2011). However, other concrete evidence from in situ characterization would still be required for clear understanding on such phenomenon.

2.3 Solid carbon source

In general sense, plastic is considered as a nuisance which could provide many negative consequences, such as destruction of mangrove ecosystem due to its non-dissociation property in nature. Thin plastic bags have no recyclable value and are abandoned or by packing refuse in it (Tarig et al., 2013). Converting such plastic wastes into valuable products, such as carbon nanotubes (CNTs) could be an important and profitable option for industry and for environmental protection. Recently many research works focusing on synthesis of CNTs and other nanostructure derivatives through thermal decomposition of
plastic wastes, such as polypropylene (PP), low density polyethylene (LDPE), high density polyethylene (HDPE), polyacrylate (PC), polyvinyl chloride (PVC), polystyrene (PS) and polyethyleneterephthalate (PET) with the presence of specific catalysts have been reported (Zhang et al., 2008; Quan et al., 2010; Zhuo et al., 2010; Mishra et al., 2012; Yang et al., 2012; Savant et al., 2013; Acomb et al., 2014; Bajad et al., 2015; Nahil et al., 2015). Within those previous works, usage of low-cost alternative feedstocks which are post-consumer plastic wastes for CNT production has been demonstrated. Sufficient concentrations of carbon-containing species (either hydrocarbons alone or a mixture of hydrocarbon, CO and CO₂) as well as hydrogen and water molecules could be generated from the thermal decomposition of those plastic wastes. Then stand-alone pyrolysis of such plastic wastes or pyrolysis followed by premixed combustion of resulting gaseous pyrolyzates leads to CNT growth on catalytic surfaces. For example, Zhang et al. (2008) used combustion method for synthesis of CNTs using Ni compound/organic-modified montmorillonite and polypropylene (PP) as a source. They reported that with the increment of temperature, PP began to decompose to form carbon clusters which would diffuse around Ni nanoparticles, which could facilitate the growth of CNTs due to root-growing mechanism (Liu et al., 2003). Later, Mishra et al. (2012) have tried to use PE and MA-PP as precursor for synthesis of CNTs by mixing PE with PP using ferrocene or Ni as catalyst in a stainless steel autoclave heated at 700 °C for 100 min. They reported that CNTs with average diameter of about 160 nm were synthesized with negligible generation of toxic or corrosive reagents. In addition, effect of synthesizing temperature on catalytic conversion of those plastic wastes to carbonaceous nanomaterials could be manifested through changes of catalyst particle size which is intentionally loaded into the synthesizing reactor (Bazargan and McKay, 2012; Altalhi et al., 2013). As a result, it should be noted that effluents of such plastic waste treating system are gases with substantial amounts of carbon monoxide, light hydrocarbons and hydrogen (Acomb et al., 2014). Therefore, it may be possible to utilize such gaseous by-products for power generation. Some new gas turbine technologies, such as Siemens G-class Gas Turbines, could work under flexible load conditions which such gaseous by-products with CO content could be effectively controlled (Engelber et al., 2004). In addition, the conversion of such gaseous by-products to reactive chemicals, such as alcohol and liquid hydrocarbons would be achievable by chemical reactions prior to its utilization as feed materials for CNT production (Andrews et al., 2002). These previous works would reveal that usage of such commodity plastic wastes with appropriate catalysts is a potential mean for synthesizing CNTs with competitive cost. However, due to the complexity of experimental

Fig. 3 SEM micrographs of CNTs prepared from (a) low boiling point hydrocarbon (LHC), (b) medium boiling point hydrocarbon (MHC), (c) high boiling point hydrocarbon (HHC) and (d) slop oil under a synthesizing temperature of 900 °C.
process, exact formation process of CNTs still needs further research.

Meanwhile, because of the increasing demand of electronic applicant usage, printed circuit board (PCB), which typically consists of 15 % epoxy resin, 30 % glass cloth filament, 22 % copper coils, metal (Sn, Pb, Fe, Ni, etc.) and Br, has become a serious social problem. One possible method for recovering both organic and non-organic fractions from PCB is pyrolysis technique so that some research works on conversion of PCB wastes have been reported (Jie et al., 2008; Quan et al., 2010; Mankhand et al., 2012). It is demonstrated that PCB waste pyrolysis could provide liquid products containing high concentrations of phenol-group species. Hollow-centered and straight CNTs with outer diameter of ~338 nm could be directly synthesized by pyrolysis of PCB pyrolysis oil using ferrocene as catalyst at 900 °C under nitrogen atmosphere. CNTs with nominal length of several microns could be observed with the presence of amorphous carbon nanoparticles (Quan et al., 2010). The external surface of porous carbonaceous nanomaterials prepared from carbonization of KOH-treated resin at 700 °C is full of cavities with BET specific surface area of 1214 m²/g and micropore volume of 0.41 cm³/g, respectively.

Eventually, it should be noted that scaled-up industrial system has also been explored especially for utilization of useful energy released during the synthesis of carbonaceous nanomaterials from such industrial wastes. Such exothermally released energy will offset the energy required to pyrolyze the industrial waste and to preheat the synthesizing system, resulting in a great improvement of the overall energy-efficiency. Thus, it would possibly help minimize the production cost of carbonaceous nanomaterials (Thostenson et al., 2001; Paradise and Goswami, 2007; Prasek et al., 2011; de Volder et al., 2013). As mentioned above, comprehensive analyses of synthesized products within those different synthesizing process would still be required for ensuring the economically justifiable production of such carbonaceous nanomaterials.

3. Present advancement of carbonaceous nanomaterial applications

As mentioned above, applications of carbon nanotubes (CNTs) including their derivatives, such as carbon nanocapsules (CNCs), carbon nanohorns (CNHs) and graphenes have been an emerging subject of considerable research attempts owing to their unique mechanical, thermal, electrical and optical properties (Andrews et al., 2002; Zeng et al., 2006; Paradise and Goswami, 2007; Iijima, 2012; de Volder et al., 2013). Owing to those advantages, CNTs hold great promise as fundamental building blocks for nanoelectronics, field emitters, drug delivery system, sensors and energy storage devices. For sustainable and secure continuity of the carbonaceous nanomaterial production, broad spectra of promising applications have been examined by many research teams around the world. Therefore, a substantial number of works done for exploring what might be the key characteristics of such carbon nanomaterials for each specific requirement of their usage are available. Using a comprehensive collection of literatures, promising applications involving with some specific technical requirements, such as antibiotic removal, spilled oil handling and pollutant gas detection were summarized in this review.

3.1 Fundamental applications

As fundamental applications, carbonaceous nanomaterials could be employed in their primitive form as they are produced or in modified form as other composites, which would require additional processing (Andrews et al., 2002; Yang et al., 2005; Zeng et al., 2006; Xu et al., 2007; Tusi et al., 2010; Iijima, 2012). Applications of such carbonaceous nanomaterials with specific purposes would be metal catalyst support, pollutant removal and so on. Based on our search through SCOPUS database, it seems that there are a variety of fundamental applications but three main categories have drawn attentions of many researchers because of some specific emerging needs from industrial and environmental viewpoints (Dai, 2002; de Volder et al., 2013).

3.1.1 Catalyst supports

Industrial sector generally requires robust catalysts made of precious metal species which are generally embedded onto the surface of some supporting materials. Among various materials, carbon is recognized as an excellent candidate due to its stability and compatibility (Bazargan and McKay, 2012; Nahil et al., 2015). For example, Yang et al. (2005) prepared spherical carbon particles or carbon spherules for accommodating Pt nanoparticles which was employed as electrocatalyst in direct methanol fuel cells (DMFCs). Their microscopic analyses revealed that K₂PtCl₆ with ethylene glycol could reduce size of the Pt nanoparticles with faceted crystalline structure. Aggregation and activity of the Pt nanoparticles are dependent on the surface properties of the carbon spherules. It should be noted that with cyclic voltammetry and galvanostatic polarization analyses the Pt/HCS catalyst could exhibit a higher catalytic activity in the electrooxidation of methanol than that of commercial ones. Then Xu et al. (2007) had also tried to deposit Pt or Pd on carbon microspheres (CMS), which could be used for methanol and ethanol oxidation in alkaline media. The results show that noble metal electrocatalysts supported on carbon microspheres give better performance than that supported on
Carbon black. It is well known that Pd is not a good catalyst for methanol oxidation, but it shows excellently higher activity and better steady-state electrolysis than Pt for ethanol electrooxidation in alkaline media. The results confirmed a synergistic effect by the interaction between Pd and carbon microspheres which could exert a great potential in direct ethanol fuel cells application. Meanwhile, Tusi et al. (2010) examined hydrothermal carbonization process for preparing composite of CNTs and PtRu nanoparticles, which were respectively generated from starch as carbon source and platinum and ruthenium salts as catalysts, with the presence of KOH or TPAOH (tetrabutylammonium hydroxide) for pH control. Based on comprehensive analyses using SEM/EDX, TGA, XRD and cyclic voltammetry, they reported that carbon PtRu nanocomposites prepared from TPAOH were more active for methanol oxidation than those prepared from KOH due to the pore volume and mesoporous structure. More recently Nahil et al. (2015) has reported that the pyrolysis with catalytic reforming of waste polypropylene with the presence of Ni-composite catalysts could provide multi-walled carbon nanotubes as a by-product of hydrogen production. They found that injection of steam with the presence of Ni–Mn–Al catalyst and MWCNTs would play a crucial role for achieving an optimal hydrogen production. Because of abundant surface area available for accommodating metal catalysts and the presence functional groups, MWCNTs could provide preferable yield of hydrogen as well as promoting decomposition of pollutants, such as phenol (Sano et al., 2012; Nahil et al., 2015). With such typical examples, it could be implied that carbonaceous nanomaterials would be a good candidate for supporting catalyst but clear understanding on their synergistic functions is still under investigation.

3.1.2 Water pollutant removal

Leakage of some chemicals employed in many human activities including agricultures and health remediation has been recognized as one of emerging threats to the world. Among those pollutants, it happens that antibiotics lead to tremendously serious consequence to the eco-system (Lu et al., 2005b; Grobert, 2007; Ji et al., 2009; Wang et al., 2009; Sowichai et al., 2012; Zhang et al., 2012). Though some conventional adsorbents, such as activated carbon or zeolite, are commercially available there are some drawbacks related to post-handling would draw research attentions to explore other new candidates. Therefore, some carbonaceous nanomaterials with special properties have been developed as novel adsorbent. From a viewpoint of adsorption kinetics, CNTs with ordered pore structure could make it easier for the diffusion of pollutants to adsorption sites when compared to conventional activated carbon (AC) with random pore structure. It should be noted that ACs generally contain micropores, which are seldom available for the access of relatively large organic molecules. Lu et al. (2005b) studied the adsorption of trihalomethanes to CNTs and powdered activated carbon (PAC). They reported that CNTs reached adsorption equilibrium much faster than PACs, which would be attributed to the different porous structures of CNTs and PAC. The more uniform pore structure of CNTs would be beneficial for the diffusion of pollutants into the inner pores. Based on experimental investigation on adsorption of tetracycline to CNTs, graphite and activated carbon done by Ji et al. (2009), the adsorption affinity of tetracycline decreased in the order of graphite/ SWNT > MWNT >> AC upon normalization for adsorbent surface area. These finding results would be attributed to the weaker adsorption of tetracycline to AC of which adsorption affinity was greatly influenced by the accessibility of available adsorption sites. Meanwhile, the remarkably strong adsorption of tetracycline to CNTs can be attributed to the strong adsorptive interactions (van der Waals forces, π-π EDA interactions, cation-π bonding) with the graphene surface of CNTs.

Then Sowichai et al. (2012) synthesized magnetic carbon nanoparticles (M-CNPs) from a mixture of glycerol and ferrocenes. The synthesized nanomaterials which mainly consisted of CNTs were used as an adsorbent for removal of tetracycline dissolved in simulated waste water. It was found that the adsorption capacity on M-CNPs was strongly dependent upon contact time and adsorption temperature. The increase in the adsorption temperature would result in the increase in both adsorption capacity and rate. However, the adsorption equilibrium would be achieved within 180 min regardless of adsorption temperature. Meanwhile, Zhang et al. (2012) examined the adsorption kinetics of phenanthrene and biphenyl on granular activated carbon (GAC) and CNTs. They reported that external mass transfer controlled the adsorption of organic compound to CNTs, while intraparticle diffusion dominated in the adsorption of organic compounds onto ACs. As a result, in well mixed systems, CNTs are superior to ACs in terms of sorption kinetics. Based on those typical examples of previous investigations, there are sufficient evidences revealing that regardless of their morphology, carbonaceous nanomaterials would be a good candidate for water pollution removal.

3.1.3 Spilled oil handling

More recently spreading news of many incidents of damaged pipeline and liner containing hydrocarbons which were spilled into the environment would clearly reveal that such spilled oil pollution could exert tremendously serious destruction of the eco-system. Spreading of spilled oil layer on natural water resources usually occurs after the oil discharge from emission sources and starting contact with water-surface. Rate of spreading
would be dependent upon oil characteristics, such as surface tension, viscosity, density, speed and environmental conditions, such as direction of wind, and water currents. Spreading would increase the oil covering surface area which would prevent the exposure to the sunlight and air, resulting in serious collapse of the ecosystem. Therefore, development of effective adsorbent technology for handling such problem has gained an increasing interest from many research teams in many countries (Walkup et al., 1969; IPIECA, 1991; Albert, 1997; Wei and Molloy 2003; White and Molloy, 2003; Wang et al., 2007; Ren et al., 2011; Liu et al., 2015).

In general, natural inorganic sorbents, such as clay, glass, perlite, sand, vermiculite, wool, and volcanic ash would be employed for adsorbing those spilled oil. Those adsorbents would be able to absorb from 4 to 20 times their weight of oil. On the other hand, organic materials can be used on land and are not adaptable to water use for oil spill cleanup. More recently some synthetic sorbents includes man-made materials that are similar to plastics, such as polyurethane, polyethylene, polypropylene, and nylon fibers, which could exhibit superior adsorption capability as much as 70 times their weight of oil. However, those synthetic sorbents possess some drawbacks, especially their reusability and difficulties in their handling until they are disposed of properly (IPIECA, 1991). It appears that carbonaceous nanomaterials could be suited to adsorb spilled oils that can permeate or Wick within their tortious surface (Wang et al., 2007; Ren et al., 2011; Liu et al., 2015). Such adsorbents could be employed like sponges to collect oil by capillary action or suction, attributed to large surface area, the chemical affinity of the sorbents for the spilled oil, and chemical constituents including their porosity, molecular structure and change in volume (Ren et al., 2011). Absorbents work best on light, less viscous oils, while adsorbents work best on heavy, sticky, more viscous oils. For actual demonstration, the authors have also employed a freeze drying method to prepare sponge composites made of polyvinyl acetate (PVA) and MWCNTs. Fig. 4 illustrated the appearance of 2 different sponge samples which the first was prepared from a mixture PVA and MWCNTs and the other from a similar mixture with addition of carboxymethyl cellulose (CMC). It could be clearly observed that the sponge prepared from the PVA/MWCNT/CMC exhibited stable porous structure with only insignificant shrinkage. Such stronger structure could be explained by the evidences obtained from microscopic analyses as shown in Fig. 5. With the presence of CMC, MWCNTs were uniformly dispersed within the PVA matrix, resulting in formation of fibrous network which could endure the external forces and could recover to its initial dimension after the external forces were released. Finally, with oil adsorption test, both sponge samples could exhibit impressive performance in collecting spilled oil within their porous structures. Fig. 6 is a typical example of slop oil adsorption using the PVA/WMCNT/CMC sponges. In good agreement with other previous works, such composite sponge could exhibit a superior adsorption capability of about 60 times their weight of oil. Therefore, based on these evidences, it would be considered that carbonaceous nanomaterials could be a good alternative for many fundamental applications.

### 3.2 Novel applications

Different from fundamental applications, transformation of carbonaceous nanomaterials into distinguishable forms would lead to some novel applications which would hardly be achieved by using their primitive forms. It could be expected that derivation of novel applications of carbonaceous nanomaterials by integration with other technologies, such as sensor or quantum electronic technology, would cover much broader perspectives (Bittencourt et al., 2006; Espinosa et al., 2007; Balazsi et al., 2008; Hashishin and Tamaki, 2008). In this review, some typical examples of novel applications of carbonaceous nanomaterials are summarized.

#### 3.2.1 Pollutant gas detection

Various gaseous pollutants have been emitted from many sources which are related to industrial manufacturing or daily living of human. Preventive actions against natural or artificial emission of some toxic exhausted gas have been accomplished by many research teams around the world (Bittencourt et al., 2006; Espinosa et al., 2007; Balazsi et al., 2008; Hashishin and Tamaki, 2008; Ghasempour and Zad, 2009). In this review, some typical examples of novel applications of carbonaceous nanomaterials are summarized.

![Fig. 4](image-url) Appearance of MWCNT sponge prepared by freeze drying with (a) 1 wt% of PVA and (b) 1 wt% of PVA/CMC mixture.
be hybridized with some semi-conductor nanoparticles for improving sensing capability. Here are some typical examples of previous works which made of carbonaceous nanomaterials which could detect some toxic gaseous pollutants (NOx, Sox and VOC).

Bittencourt et al. (2006) prepared active layers for gas sensing applications by adding oxygen plasma functionalised multi-walled carbon nanotubes (MWCNTs) to WO3 and using the drop-coating deposition method. Two different ratios of MWCNTs in WO3 (1/100 and 1/1000) were considered and the response of these sensors towards toxic gases such as nitrogen dioxide, carbon monoxide...
and ammonia was compared with that of WO$_3$ and MWCNTs gas sensors. It was found that the addition of a suitable quantity of MWCNTs in a WO$_3$ film can lower the sensor operating temperature to room temperature. The response of the hybrid films to NO$_2$ could be enhanced when only a few MWCNTs were added into the WO$_3$ films. Furthermore, hybrid films were able to detect ammonia which is very difficult to detect by using pure WO$_3$ and MWCNTs gas sensors, when operated at 150 °C.

Then Espinosa et al. (2007) investigated response to NO$_2$ of three different type of metal oxide (SnO$_2$, WO$_3$ or TiO$_2$) prepared with the presence of a low amount of oxygen-functionalized MWCNTs. It was reported that the responsiveness towards NO$_2$ of these metal oxide/MWCNT hybrid films could considerably be improved. Meanwhile, the sensors based on hybrid SnO$_2$/MWCNTs films present excellent sensitivity towards NO$_2$ when operated at room temperature. The results suggest that there should be an optimum amount of carbon nanotubes to be added to each specific metal oxide in order to enhance sensitivity.

Later, Hashishin and Tamaki (2008) also prepared MWCNT-WO$_3$ composite by directly growing MWCNTs on Au electrode by means of thermal CVD following by an impregnation by a suspension of H$_2$WO$_4$ on the surface of as-grown MWCNTs. After calcinations in argon at 400 °C for 3 h, the composite was fabricated as sensor for testing its responses to NO$_2$. The MWCNTs-WO$_3$ composite sensor could exhibit good sensor response (Ra/Rg = 3.8 at 200 °C, whereas Ra is the resistance of sensor in air and Rg is that in NO$_2$-containing atmosphere). The sensor response was greatly improved with MWCNT-WO$_3$ composite, comparing with that of MWCNT sensor (Ra/Rg = 1.05) which would be ascribed to formation of p-n junction, between MWCNT(p) and WO$_3$(n), and thus improvement of NO$_2$ adsorption.

### 3.2.2 Electrode material

As promising novel applications, electronic devices have been proposed and developed for various purposes, such as supercapacitor, dye-sensitized solar cell, hydrogen fuel cell and so on (Yoon et al., 2000; Soneda et al., 2003; Liu et al., 2005; Lee et al., 2008; Ramasamy et al., 2008). In those devices, electrode materials have been considered as a key issue for improving such device performance. Among various carbonaceous materials, such as activated carbon, disordered carbon, mesoporous carbon and MWCNTs are under close scrutiny for use as a promising electrode material. For instance, in electrical double layer capacitors (EDLC), composites involving, carbon or CNT and RuO$_2$ or MnO$_2$ compounds, have been developed for usage as electrode materials. In some preliminary studies involving MWCNTs and MnO$_2$ composites focused on optimal composition of MWCNTs and their rate capability for few cycles, and showed their promising performance (Yoon et al., 2000; Liu et al., 2005). It is well recognized that long cycle and high rate stability of an energy storage system are very important criteria for its applications as supercapacitors. However, long cycle performance at a considerably higher charge–discharge current has not been reported so far. Meanwhile, for counter-electrode of dye-sensitized solar cell application, carbon based materials, i.e. fullerene and SWCNTs have also been investigated as cost-effective and simpler alternatives. Catalytic activity towards iodine ion reduction has been investigated on carbon based counter-electrodes (Soneda et al., 2003). So far, an overall energy conversion efficiency of such solar cell device has still been below that of conventional Pt counter electrode DSSCs. However, it has also been suggested that Pt counter electrode in DSSC could be replaced by carbonaceous nanomaterials without affecting the energy conversion efficiency. Despite high catalytic activity towards iodine ion reduction, carbonaceous counter-electrode would probably exert some risk to the stability of DSSCs (Ramasamy et al., 2008). Since the electrodes made up of carbonaceous nanomaterials, prolong exposure in corrosive iodine redox electrolyte would be expected to result in the detachment of loosely bounded particles from rest of the electrode.
Therefore, promoting the dark current and degrade the overall device performance. Nevertheless, the stability of carbon counter-electrode in DSSC through optimization of electrolyte composition and device fabrication process would be further explored.

4. Summary

Because of the increasing global consumption, an exponential increase in industrial production activities inevitably results in overwhelming remain of industrial waste. As a result, increasing attentions of research and development teams in various countries have led to development of novel methodologies to utilize such industrial waste for production of carbonaceous nanomaterials instead of using as alternative energy sources. Meanwhile, for sustainable and secure continuity of the carbonaceous nanomaterial production, broad spectra of promising applications have also been examined. Among those emerging applications, utilization of carbonaceous nanomaterials in pollution control and prevention has been focused worldwide. Therefore, in this review, relevant research works focusing on catalytic pyrolysis of carbonaceous industrial waste for carbon nanomaterial production were comprehensively analyzed and summarized. In addition, broad spectra of promising applications involving with antibiotic removal, spilled oil adsorption, pollutant gas detection and electrode materials were also reviewed. Based on comprehensively reviewed literatures, it would be considered that carbonaceous nanomaterials could be potentially produced from various industrial wastes and they would be a good alternative for many fundamental and novel applications. Linkages between their characteristics and dominating phenomena taking place in those applications would be important research issues for further exploration.

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