Inorganica Chimica Acta 468 (2017) 49–66

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Review article

Carbon nano-onions: Unique carbon nanostructures with fascinating properties and their potential applications

Olena Mykhailiv, Halyna Zubyk, Marta E. Plonska-Brzezinska *

Institute of Chemistry, University of Bialystok, Ciolkowskiego 1K, 15-245 Bialystok, Poland

A R T I C L E I N F O

Article history:
Received 27 February 2017
Received in revised form 9 July 2017
Accepted 12 July 2017
Available online 22 July 2017

Special Volume: Protagonists in Chemistry Dedicated to Professor Luis Echegoyen

Keywords:
Carbon nano-onion
Multi-layered fullerene

A B S T R A C T

This article presents a short review of the knowledge concerning carbon nano-onions, also known as onion-like carbon or multi-layered fullerenes. Currently, these nanostructures are some of the most fascinating carbon forms. We can only find approximately 2000 articles under the entry of "carbon onion" in the Web of Science. Surprisingly, there have been ~40,000 citations since their discovery, and the interest in these nanostructures is still growing. In the last three years, 5000 citations per year have been reported. This means that researchers have noted the unusual nature of these carbon nanostructures. In this article, we review the most important literature reports in this area, which in a condensed way, present these nanostructures, their production methods, their unusual physical and chemical properties and their potential uses.

Contents

1. Introduction . . . 49
2. Production, structures and physical properties of the onion-like structures . . . 50
3. Structural modification of CNOs via physical methods . . . 53
4. Doping of CNOs with metals and heteroatoms . . . 53
   4.1. Doping of CNOs with metals . . . 53
   4.2. Doping of CNOs with heteroatoms . . . 55
   4.3. Doping of CNOs with metals and heteroatoms . . . 55
5. Covalent and non-covalent functionalisation of CNOs . . . 56
6. Potential applications of CNOs . . . 58
   6.1. Electrochemical properties of CNOs and their composites as charge collectors . . . 60
7. Conclusions . . . 62
   Acknowledgements . . . 62
   References . . . 62

1. Introduction

Recently, materials chemistry has been one of most intensively developing fields of science. It mainly involves the synthesis of new materials or the modification of their surfaces so that new properties can allow for their practical application. Much attention has been devoted to nanoparticles, which can form bigger micro- and macromolecular systems. Since the discovery of fullerenes in 1992 [1], carbon nanoparticles have been quite commonly used in such systems. Recently, larger morphological variations of fullerene-like all-carbon nanostructures (CNs) have received enormous attention. Carbon nano-onions (CNOs) are a member of the fullerene family, and they consist of quasi-spherical- and polyhedral-shaped graphitic layers close to one another. The distance between the graphitic layers is 0.335 nm, and it is approximately equal to the distance between two graphitic planes (0.334 nm) [2]. The

* Corresponding author.
E-mail address: mplonska@uwb.edu.pl (M.E. Plonska-Brzezinska).

http://dx.doi.org/10.1016/j.ica.2017.07.021
0020-1693/

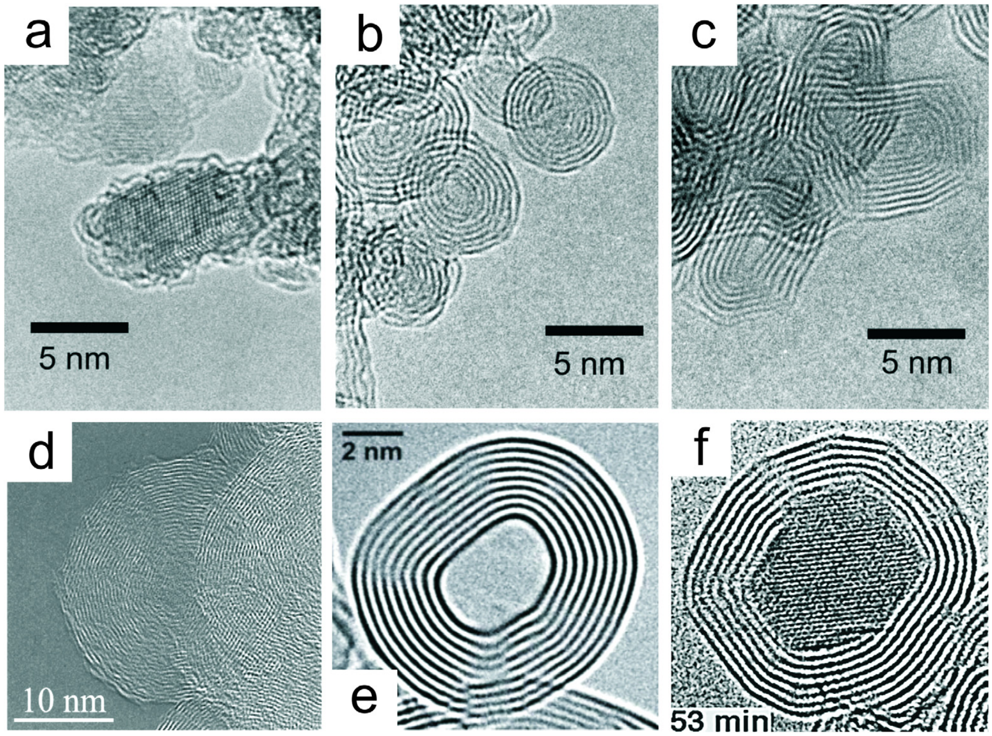

Fig. 1. HRTEM images, high resolution of (a) NDs [19], (b) spherical "*small*" CNOs [19], (c) polyhedral CNOs [19], (d) spherical "*big*" CNOs [13], (e) spherical hollow-core CNOs [21], and (f) metal-core CNOs [23]. Adapted with permission from Refs. [13,19,21,23]. Copyright 2017 AIP Publishing LLC, John Wiley and Sons, and Elsevier.

Table 1
Methods of CNO synthesis.

Method	Substrate	Condition	Size and shape	Yield	Ref.
Electron-beam irradiation	Amorphous carbon soot	–	Pristine dense-core spherical CNOs, ca. 6–50 nm	Low yield	[17,22]
Annealing	NDs	800–2100 °C	Pristine dense-core spherical CNOs, 5–10 nm	High yield	[10,19,24,25]
Arc-discharge	Amorphous carbon soot	Arc discharge between 2 graphite electrodes, water	High-quality spherical hollow-core CNOs, 15–25 nm	Large quantities	[13,29]
	Ni/Al catalyst	5000–6000 K Under water	Pristine hollow-core spherical CNOs 5–50 nm	Low yield	[11,12]
Chemical vapour deposition	CH_4, N_2 CH_4 (60 mL min^{-1}) N_2 (540 mL min^{-1})	Ni/Al catalyst, Ni content >60 wt%	Pristine hollow-core spherical CNOs, 5–50 nm	Large quantities	[16,39]
Ion implantation	carbon into Cu, Ni substrate	600–1000 °C	Pristine dense-core spherical CNOs, 15–200 nm	Low yield	[15,30–32]
	Ag substrate	>600 °C	Pristine dense-core spherical CNOs, 5–100 nm	Low yield	[33–35]
Pyrolysis	Phenol-formaldehyde	Ferric nitrate catalyst, 1000 °C	Pristine dense-core CNOs, ca. 40 nm	Large quantities	[14]
	Propane	Propane/Oxygen flame (1.8 stoichiometric coefficient), Al	CNOs with many by-product, 10–25 nm	Low yield	[40]
	Plastic wastes (polyethylene, styrene, ethylene terephthalate	–	CNOs with many by-product, 50–70 nm	Low yield	[41]

number of carbon atoms forming a corresponding layer is calculated according to the formula:

$$C_{x(n)} = C_{60} \cdot n^2 \quad (1)$$

where n is the subsequent number of the corresponding layer; $x(n)$ defines the number of carbon atoms comprising the layer [3,4]. The structure of CNOs contains hexagonal and pentagonal rings with carbon atoms located at the vertices forming two single bonds and one double bond with neighbouring carbon atoms with delocalized π-electrons across the molecule [5,6]. Graphitic layers in the structure of this nanomaterial consist of a significant number of defects and holes [7]. The holes can be filled in a variety of ways with heptagonal and pentagonal carbon rings, creating amorphous or crystalline quasi-spherical onions [8]. However, CNOs discovered by Sumio Iijima in 1980 [9], did not garner as much interest as carbon nanotubes (CNTs) discovered at the same time. It is surprising, but the interest in them dates back to the beginning of 2000, modifications of these nanostructures began to be addressed.

2. Production, structures and physical properties of the onion-like structures

Although various methods have been published for the synthesis of CNOs, the main synthetic methods have been thermal