At the origins of nanotechnology. Discoveries and tough competition in the field of the carbon nanotubes

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Abstract: The present paper discusses some aspects of the research landscape related with nanotechnology, starting from Kroto's announcement of the discovery of fullerene and Iijima's seminal work on carbon nanotubes. In particular, we analyse the issue of competition within the nanotechnology research field, as regards both physical properties and performance of CNTs and the commitments of national states in boosting this research field. We also discuss the inherent interdisciplinary character of nanotechnological research and we offer some reflections on the looseness of disciplinary boundaries.

Keywords: Carbon nanotubes, nanotechnology, competition, interdisciplinarity

1. Introduction

The nanotechnology field is so wide and varied that its boundaries can hardly be described by a precise definition. In the USA, within the awesome National Nanotechnology Initiative (NNI), the following definition has been proposed: "Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometers" (National Nanotechnology Initiative 2015a). This statement suggests that any scientific practice applicable to systems or objects of nanometrical size is part of "nanotechnology"; if so most chemistry would fall within the perimeter of nanotechnology. In using the word nano-technology emphasis should be put not only on the *nano* prefix, but also on *technology*, because the budgetary effort that fuels research is explicitly aimed at the *technological innovation*. Actually, there is some alarm among American funding agencies as regards the "delay" in developing relevant applications, at least in the carbon nanotubes (CNTs) field. This concern underlines the importance of CNTs research. The historical analysis presented hereafter is justified by the relevance of the collective effort focused on CNTs; we also discuss some epistemological aspects, namely those regarding disciplinary boundaries that are a constant aspect of the history of CNTs' research.

2. The discovery of carbon nanotubes

The scientific context wherein the discovery of CNTs took place was dominated by the interest towards another discovery, occurred 6 years earlier. On November 1985 *Nature* published a letter with a bizarre title: "C_{60}: Buckminsterfullerene", and an intriguing image alongside the title. The figure legend was: "A football (in the United States a soccer ball) on Texas grass". Then, the text clarified the nature of the reported discovery: "The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom" (Kroto *et al*. 1985). The name of the new substance contained an indirect reference to the structure of its molecules, as the American architect Richard Buckminster Fuller (1895-1983) was known for having spread the use of geodesic domes, whose structure is precisely icosahedral. No doubt, the name of the substance, the picture of a soccer ball and the figure legend are by Harold Kroto, a very ironical man, and an excellent chemist.

The experimental procedure applied by Kroto and colleagues was very elegant, as the mass spectra reported in Fig. 1a clearly show. Spectrum *a* was obtained under a low-pressure Helium gas flow: it shows the presence of many Carbon *clusters*. Spectrum *b* was obtained under 1 atm pressure; the increase in the number of collisions favors the more stable structures, C_{60} and C_{70}. Spectrum *c*, where species C_{60} predominates, was obtained by lengthening the pathway swept by the Carbon *clusters* before entering the spectrometer. In this preliminary communication, Kroto and colleagues remarked that the C_{60} molecules were hollow. Hence they were able to host other atoms: this opened new interesting structural perspectives. The name proposed by Kroto was quickly simplified in "fullerene", and the structure of the C_{60} molecule became an icon, capable to compete with the centennial icon of benzene.

The discovery of fullerene disclosed the fact that stable molecular structures with a high number of Carbon atoms could be easily obtained; in addition, the existence of C_{70} molecules foreshadowed the possibility – for the perfect structure of fullerene – to grow towards still unknown directions. In any case, this was an interdisciplinary research since the very beginning: in fact, the five coauthors of the *Nature* communication were representative of the disciplinary domains of quantum physics, chemistry and engineering.

Sumio Iijima, the discoverer of CNTs, was born in 1939 in the Saitama prefecture, next and partly integrated to the "big Tokyo" area. Date and place of birth were unlucky, but Iijima was spared from the deadly incendiary bombing carried out by the American B29 and managed to get an engineering M.Sc. in 1963 and Ph.D. in solid-state physics in 1968. For a long time, from 1970 to 1982, he was in the USA at the Arizona State University, where he undertook research on electronic microscopy applied to crystalline materials. In 1982 he was back to Japan, where he covered different roles in various sites of the Nippon Electric Company (NEC), an illustrious enterprise founded in 1898, that later become a powerful multinational specialized in informatics technologies.

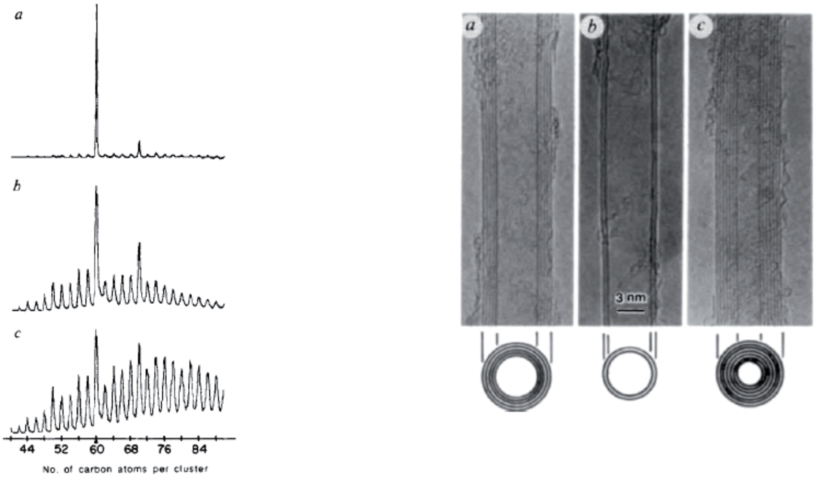

Fig. 1. Left: experimental data by Kroto *et al.* (1985, p. 163). Right: experimental data by Iijima (1991, p. 56)

The paper that made Iijima popular was published in *Nature* on November 1991. The Japanese physicist places his work in the frame of the "intense interest in the structures accessible to graphitic carbon sheets" raised by Kroto's and Smalley's discovery (Kroto *et al.* 1985). Experimental data were obtained through a transmission electronic microscope (TEM) and the author reports the high-resolution images of "typical needles" (Fig. 1b). The dark parallel lines correspond to images of graphite reticular plane (002); for the sake of clarity, Iijima added the drawings of the *tubules'* sections: tube *a* is made up of 5 graphitic sheets, tube *b* is made by 2 sheets and tube *c* by seven sheets. Based on a further set of diffractometric data, Iijima states that these objects are actually chiral, a phenomenon justified by the model that describes the formation of CNTs through the "winding" of a monoatomic graphitic sheet.[1] Iijima's paper has become one of the most cited papers in the recent history of physics: according to Google Scholar, it counts 37715 citations (October 20th 2015).

Iijima's 1991 work was based on excellent instrumentation; nevertheless the Japanese physicist did not mention the specific TEM technical model that he used: he just reported a 200 KeV electron energy. The data was sufficient, to disciplinary experts, for identifying Iijima's instrument as a Topcon 002B, produced by the Japanese firm Topcon from 1986 on.

As regards the theoretical aspects, both chemists and physicists had studied structures made of pure Carbon well before the fullerene's discovery (Rao 1995); hence, the reaction of theoretical scientists to the CNT's discovery was prompt (Table 1). Hamada's and Harigaya's groups worked at NEC, so they were within the same institution as Iijima; oddly enough, the first theoretical contribution to be published was from

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[1] The model is based on graphene, the allotropic form of Carbon discovered in 2004.

the Naval Research Laboratory in Washington, and the *Physical Review Letters* received it *before* Iijima's paper was published.

(Iijima 1991)	(Mintmire 1992)	(Hamada 1992)	(Harigaya 1992)
August 27th 1991			
	October 9th 1991		
November 7th 1991			
			November 25th 1991
		December 9th 1991	
	February 3rd 1992		
		March 9th 1992	
			May 15th 1992
Italics: submission date of the paper; **bold**: publication date of the paper			

Table 1. Chronology of (Iijima, 1991) and the first theoretical works on CNTs

Another interesting aspect of the papers cited in Table 1 is the uncertainty on the name to be given to the new objects discovered by Iijima. The discoverer himself calls them: *needle-like tubes*, *needles*, *tubes*, *graphitic carbon needles*, *microtubules*, *tubules*, *tubular needles*. In (Mintmire 1992) the privileged term is *fullerene tubules;* Hamada (1992) uses the term *graphitic microtubules*, and Harigaya (1992) writes of *fullerene tubes*. Lexical uncertainty discloses the newness of the discovery and the "elusive" nature of the new objects. The name of CNT, later adopted by the scientific community, appeared for the first time in a paper entitled "Large-scale synthesis of carbon nanotubes". This work was published in *Nature* on July 1992, and once again it was signed by NEC researchers (Ebbesen, Ajayan 1992).

3. The developments of competition and an up-to-date reflection

Data in Table 1 already show that CNTs research could not have been a *made in Japan* enterprise. Many labs immediately set as a goal the production of single-wall CNTs. In fact, this would have simplified the experimental and theoretical investigations of these objects; in addition, the standardization of mass production would have been a (future) realistic task. The competition was immediately manifest, and it was gained on *Nature* by the Japanese NEC researchers against the Americans IBM scientists. The editorial data show that the Americans were beated to the punch: the communication by Iijima and Ichihashi (1993) was received on April 23rd, accepted for publication on June 1st and finally published on *Nature* on June 17th 1993. Donald Bethune's communication (1993) was received on May 24th, accepted on June 3rd and published on June 17th 1993, in the same issue reporting Iijima's work.

The competition on CNTs may be analyzed from different standpoints. A survey of bibliometric data shows that the landscape of CNTs' research is very dynamic and has changed along the years as regards a number of aspects, e.g. the relations between disciplines (in terms of competition and/or collaboration), the national states commitments towards the CNTs research field (in the last few years, nations like Iran and India have gained prominent positions in the field, overriding many European countries), the change in research trends within the nanotechnology area (since 2008, graphene has overtaken CNTs as research topic). A detailed analysis of all these aspects would take too long. We will briefly comment the data in Table 2, that show the changes occurred in the distribution of the contributions to CNTs research from distinct disciplinary subfields. Data are extracted from the SCOPUS bibliographic database.

Subject area	Physics and Astronomy	Materials Science	Chemistry	Chemical Engineering	Engineering	Energy	Biochemistry, Genetics and Molecular Biology
1991-2004	53.8 %	36.1 %	26.1 %	4.8 %	9.7 %	1.0 %	0.9 %
2005-2014	39.8 %	52.9 %	44.9 %	17.9 %	30.3 %	6.1 %	5.8 %
The percentages in each line sum up to more that 100%, because SCOPUS may assign a same article to distinct subject areas, depending on the interdisciplinary character of the corresponding journals. Hence each article may count for more than one contribution, depending on the disciplinary tags assigned to it.							

Table 2. Distribution of the disciplinary contributions over the 67,726 papers published on CNTs in the time ranges 1991-2004 (9137 articles) and 2005-2014 (58589 articles)

In the 1991-2014 period, a total of 67,726 articles on CNTs have been published. Each article is associated with one or more disciplinary field. Data in Table 2 show that, in the earliest time of CNTs research, physics played the main role; but, over the years, it was outclassed by materials science and chemistry. Chemistry and chemical engineering almost doubled their contributions in the later period with respect to the earlier one. The level of inter-disciplinarity of CNTs research has grown over time: SCOPUS data show that, shifting from the 1991-2004 to the 2005-2014 period, the average disciplinary contributions *per article* grew from 1.37 to 2.13.

As far as the physical properties of CNTs are concerned, an important issue seems to be their length. Different labs seem to be engaged in an “athletic” competition. At present, the pole position for the longest CNT is held by a Chinese team of the Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Dept. of Chemical Engineering, Tsinghua University, Beijing, China (Zhang *et al.* 2013). Conversely, the smallest diameter was obtained by researchers of the Dept. of Materials Science and Engineering, Meijo University, Nagoya, Aichi, Japan. This record was established in 2004 and still holds: in fact, it seems hardly possible to go lower than 3 Å diameter, due to the inherent size of Carbon atoms (Zhao *et al.* 2004).

Despite its many records, CNTs research has not yet delivered the output expected by the funding agencies In the USA, an alarm has been raised on the delay in commercializing CNTs-containing products (National Nanotechnology Initiative 2015b). The main obstacles are the standardization of CNTs production and the present impossibility to assure a mass production (Aldrich CNTs samples are 20-fold more expensive than gold). A further criticism is the delay in the investigation of the interaction between nanotechnological products, environment and health. This issue is so critical that 10% of the $1.5 billion budget assigned to NNI have been recently redirected towards nanotechnological risk assessment (Morrison 2015).

4. A hint of epistemic analysis

We have seen that CNTs research is inherently inter-disciplinary. Scientometric data confirm that it is the object of research[2] that attracts the researchers' commitment. Scientists have not become transgressive, by trespassing their own disciplinary boundaries; they have rather fully exploited all the available cognitive tools, regardless of their academic labels. Let's consider the experimental data that led to the discovery of fullerenes and CNTs. In both cases, instrumentation is "physical" (a time-of-flight mass spectrometer and a powerful TEM). The expert that examines Fig. 1a being aware of the instrument employed to get it, infers the presence of distinct entities with a well defined mass, i.e. molecules. Even an inexperienced person that looks at Fig. 1b would notice the reference scale (3 nm) and could not avoid thinking that the figure reports nanometric objects, whose structure is clarified by the section reported at the bottom of the figure. No chemical investigation could possibly demonstrate that Iijima's objects are tubes. This might uphold the separation between chemistry, that infers properties from collective behaviors, and physics that sees the microscopic objects. History shows that this was not the case. A recent paper by Zhang et al. (2013), appeared on Physical Review Letters, foreshadows the production of CNTs of macroscopic length and states – in the title – the use of the Schulz-Flory function. This function describes the molecular weight distribution of linear condensation polymers obtained through a kinetics-controlled reaction, where the monomers are assumed to be equally reactive. The application to CNTs of a statistic function aimed at modeling polymer synthesis indicates that – in the nanotechnological field – it is impossible to discern whether one is doing "physics" or "chemistry".

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[2] These are "social objects" whose ontology is enriched by the network of connections built around them by the scientific community, by the heads of funding agencies, by the press, etc.

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