Linear carbon chains: ultimate 1D crystals

Alexey Kavokin
International Center for Polaritonics
This work has been done by

A. Kucherik
V. Samyshkin,
A. Osipov,
S. Arakelyan

Stella Kutrovskaya

M. Portnoi, R. Hartmann

A. and A. Povolotsky

M. Scarselli
M. De Crescenzi

P. Lagoudakis, A. Zasedatelev, S. Baryshev
The outline

• Carbyne: an elusive allotrope of carbon
• Laser ablation and stabilisation of C-chains
• Deposition on a substrate
• TEM and X-ray analysis, Raman spectra
• Low-temperature photoluminescence reveals strong exciton features!
• Conclusions
Carbon hybridization and resulting nano-objects

Carbyne: the ultimate one-dimensional crystal

An elusive allotrope of carbon
The most robust of all known crystals!
Carbyne: high expectations

Bei der vollständigen Reduction der Tetraacetylen dicarbonsäure müsste Sebacinsäure erhalten werden. In der That bildet sich auch bei der Behandlung derselben, zuerst mit Zink und Schwefelsäure, dann mit Natriumamalgam eine sehr schwer lösliche, bei 200° schmelzende Säure, welche durch sehr energische Reduction mit Natriumamalgam in eine bei 180° schmelzende übergeführt wird, die die Eigenschaften der Sebacinsäure zu besitzen scheint. Bei der geringen Menge von Substanz konnte indess die Identität beider Säuren nicht vollkommen festgestellt werden.

Diacetylen, H ---C≡C---C≡C---H.

Bei der grossen Übereinstimmung zwischen der Acetylendicarbonsäure und der Diacetylendicarbonsäure konnte man erwarten, aus der letzteren in derselben Weise das Diacetylen abscheiden zu können, wie das Acetylen aus der ersteren.


Zweite Mitteilung.)
(Eingegangen am 14. August.)

In der ersten Abhandlung 1) über diesen Gegenstand ist die Diacetylen dicarbonsäure genauer beschrieben worden, während die Abkömmlinge derselben nur kurz erwähnt werden konnten. In der folgenden Mitteilung soll nun diese Lücke ausgefüllt werden.

УСПЕХИ ХИМИИ

УДК 661.66, 661.97/99

СТРОЕНИЕ ПОЛИМЕРНОГО УГЛЕРОДА

Мельниченко В. М., Сладков А. М., Никулин Ю. Н.

С позиции науки о полимерах проведен критический анализ экспериментальных работ и модельных представлений по структурной организации различных форм конденсированного углерода. Подчеркнута роль химических межмолекулярных связей (услов разветвления), ламеллярных и других надмолекулярных образований в многоступенчатом процессе пространственного структурирования полимерного углерода. Сделан вывод о существовании, кроме алмазных и графитовых, множества других кристаллических форм углерода — регулярных полимеров карбинонового или переходного типов.

Библиография — 297 ссылок.

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CUMULENE AND POLYYNE ARE SEMICONDUCTORS

The band gap predicted for infinite chains:

- Cumulene \((=\text{C}=\text{C}=)_n\) - 0.41\,eV (under high pressure)
- Polyyne \((-\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=-)_n\) - 1\,eV (atmospheric pressure)

ACS-NANO, 7(11), 10075 (2013); Synthetic Metals, 17, 557(1987);
Nat. Commun. 6, 6636 (2015)
The problem:

Freestanding linear chains of over 6 atoms are theoretically unstable to bending and folding. They need to be stabilized!

Our method of the carbyne synthesis

Graphene decomposition into the polyyne chains
LASER HEATING OF CARBON TARGET

Stabilization of linear carbon chains by metal nanoparticles in a solution
First step: laser-ablation in water

Second step: laser-induced fragmentation of carbon flakes
THE EVOLUTION OF A COLLOIDAL SYSTEM AT DIFFERENT STEPS OF THE EXPERIMENT

shungite  Au NPs  mixed  irradiated
RAMAN SPECTRA OF A COLLOIDAL SYSTEMS

Carbyne stretched between Me NPs

C-C

D+G

Carbyne

C-C stress

D G

Initial shungite system

2100-2300 cm\(^{-1}\) – polyyne chains \((-\text{C≡C-})_n\)

1900-2100 cm\(^{-1}\) – commulene chains \((=\text{C=C=} )_n\)
Initial amorphous flakes
Polycrystalline structures

Graphite

Diamond

Carbyne
HR TEM vs X-ray data
Carbon “onion”-structures
Carbyne based metasurfaces
OPTICAL SPECTRA OF IRRADIATION COLLOIDAL SYSTEM

Optical absorption

Photoluminescence spectra
The deposition of monoatomic carbon chains end-capped with Au NPs in the presence of a static electric field
Deposited carbynes on a Au/Pt grid
The X-ray diffraction pattern shows the fragments of a one-dimensional crystal structure. The positions of the maxima of the diffraction pattern correspond to the carbyne crystal with a lattice constant $a = 5.35\,\text{Å}$ of the space group $P6_3/mmc$ zone axis $[001]$. 
The photoluminescence spectrum of a carbyne film deposited on a fused quartz glass substrate (red line) and its fit by a distribution of Gaussian functions corresponding to individual carbon chains of fixed lengths.

The approximated length distribution of linear parts of the deposited carbon chains extracted from the photoluminescence measurements.
Luminescence vs Absorption

The luminescence mechanism of a white carbon

Jun Xiao et al Molecular Luminescence of White Carbon
Small 2017, 1603495

Carbyne with finite length: The one-dimensional sp carbon
The temperature dependence of PL spectra

The fine structure is visible on the top of wide peaks associated with chains of different lengths.

The sharp triplet structure repeats itself for chains of different lengths.
Excitons are artificial hydrogen atoms formed in semiconductor crystals.
To compare with the Excitons in CNTs

The CNT exciton binding energies on the order of 300–400 meV for the tubes with diameters between 6.8 and 9 Å

The time-resolved photoluminescence data

The extracted decay times of the TRPL signal:
- the non-radiative decay time from $T_{\text{room}}$
- the radiative decay time from $T_{\text{room}}$
- the radiative decay time from $T_{4K}$

The exciton radiative life-time decreases with the decrease of the length of the chain
Ab-initio calculation

Molecular orbitals for polyyne C14 - Au13₂ fragments.
Molecular orbitals for polyyne C14 H-terminated. Red and blue lobes correspond to positive and negative values.

HOMO and LUMO electron densities are spread over the whole chain in the absence of gold anchors at the ends!
The scheme of excitonic transitions in monoatomic polyyne chains

The neutral exciton (X) is formed by even and odd edge states that originate from the HOMO-LUMO pair.

The trion transitions in charged chains, where the left-right symmetry is broken so that the optical transition (X) is between either the original HOMO state localised at one of the edges (X-) or between the hole state localised at one of the edges and the original LUMO state (X+).
1. The laser induced fragmentation of colloidal carbon systems leads to the formation of monoatomic linear carbon chains.
2. We fabricate monoatomic carbon chains attached to the golden nanoparticles that may serve as electrical contacts. This paves the way to the development of integrated nano-electronics.
3. We deposit carbynes on a substrate and demonstrate the HR TEM images of the chains containing over 50 atoms, that is an absolute length record. The diffraction pattern of carbynes confirms their one-dimensional crystal structure that is expected to possess a variety of unique physical properties.
Thank you for kind attention !!!
LASER HEATING OF CARBON PARTICLES IN A LIQUID MEDIA

Maximal temperature

\[ T_{max} = \frac{I_p k_a d}{8 \chi}, \]

\( I_p \) – peak power 10\(^9\) \( \text{W/cm}^2 \)
\( \chi \) – liquid thermal conductivity
\( d = 100 \text{ nm (initial diameter)} \)

Mie-parameter for spherical particles

\[ k_a = e^{-0.2[\sqrt{n^2+k^2}]-1}] \left( 1 - e^{-\frac{4\pi kd}{\lambda}} \right) \]

\[ T_{max} < 5000\text{K} \]

\( T_{max} \) doesn’t reach to the sublimation temperature for carbon

The second stage - fragmentation of carbon particles
Formation of π-electron delocalization in carbyne. (A) Process of atomic orbital sp-hybridization. (B) Existence of extensive π-electron delocalization in carbyne.
Scheme 1. Energy Level Diagram for J-Type Aggregates and H-Type Aggregates

J-type aggregates formed by head-to-tail arrangement of adjacent NCD particles, resulting in splitting of excited energy levels into two. The electronic transition to lower excited level is allowed. In contrast, H-type aggregates are formed via side-by-side arrangement of adjacent NCD particles, which result in splitting of excited energy levels into two. The electronic transition to higher level is allowed. Absorption (Abs) of photon and subsequent fluorescence emission (Fl) are represented by upward arrow and downward arrow, respectively. Internal conversion (IC) is indicated as dotted downward arrow.

E. Mostaani et al Quasiparticle and excitonic gaps of one-dimensional carbon chains //Phys. Chem. Chem. Phys., 2016, 18, 14810--14821

\[ \text{BLA} = \left| L_1 - L_2 \right| \]

- \( L_1 \) – is single bond length
- \( L_2 \) – is triple bond length
Figure 1. Carbyne under tension. (a) DFT calculations of stretching energy per unit cell (two atoms) as a function of strain $\varepsilon$. The bond length alternation (b) and electronic density of carbyne (c) without strain and (d) under tension, showing a more pronounced bond alternation in stretched carbyne. (e) GW band gap increase as a function of strain for structures obtained with pure (LDA) and hybrid (HSE) density functionals, the latter predicting a stronger BLA (b). (f) Dependence of GW correction to LDA band gap as a function of bond length alternation.

FIG. 3. Electron energy spectrum of a (1,1) CNT in the presence of a transverse electric field $E = \gamma_0/(ea_{c-c})$ with $\phi = 0$ (solid lines) and without the electric field (dashed lines). The inner pair of vertical dotted lines indicates the first Brillouin zone boundary in the presence of the field, whereas the outer pair corresponds to the first Brillouin zone boundary without the field. $\Delta \varepsilon$ is the Bragg gap opened by the electric field.
Figure 1. Electronic properties of carbyne under strain. (a) Bond length alternation (BLA), band gap ($E_g$), and Peierls barrier ($E_p$, inset) as a function of strain in the static case. Points, DFT calculation results. Lines, fitting based on the analytical model. The fitting is performed in the [-5%, 5%] strain range assuming that the lattice stiffness decreases linearly with strain, and is done independently for BLA and $E_g$. The $E_p$ line in the inset is computed based on the BLA fit. (b) Carrier effective masses (dashed) and mobilities (solid) of polyene as a function of strain: filled, electrons; hollow, holes.

Figure 2. Zero-point vibrations under strain. (left) Evolution of the vibrational structure of carbyne with strain. The ω-shaped lines show the potential energy as a function of BLA. Horizontal lines show the vibrational levels, and the shaded region is below the ZPV level. All quantities are normalized per 2-atom cell. (right) Real-space atomic density distributions based on ZPV wave functions (three one-atom unit cells shown, color indicates which part of the BLA wave function the density comes from).

Figure 4. Effect of end groups on carbyne BLA. Termination of the chain with sp3 groups (methyl CH3 and phenyl C6H5) increases the BLA, whereas the sp2 methylene group (CH2) decreases it, as compared to an unterminated infinite chain (black dashed line). The data for 12- and 100-atom chains show a weak decrease of BLA with chain length away from the ends with methylene termination.
Theresa Eder et al Switching between H- and J-type electronic coupling in single conjugated polymer aggregates//NATURE COMMUNICATIONS 8: 1641

Fig. 1 Switching and tuning between different types of electronic coupling. a) Mechanisms of H-type and J-type coupling and the suppression of interactions and their expected relationship with aggregate morphology. b) Switching between H-type and J-type coupling by drying (green box) and swelling (blue box) the aggregate embedded inside a polymer matrix by solvent vapor annealing. c) Structures of samples used to tune between H-type (PPEB-1), J-type (PPEB-2), and suppressed coupling (PPEB-3) by changing the side chains.
Curves on the plane

Topologies

Peano-curves (1D-structures)

Fractal-curves (1D-structures)

Stabilities

Articles

Figure 1: Direct observation of LLC@DWNTs. a, HRTEM image of an LLC@DWNT with bending. The LLC inside a DWNT is longer than 20 nm, which means that it consists of more than 200 contiguous carbon atoms. Inset: an enlarged part of the HRTEM image (top), a simulated HRTEM of an LLC@DWNT (middle), and a molecular model of an LLC@DWNT (bottom). The corresponding line profiles of the experimental and simulated LLC@DWNT are shown, respectively. b, A DWNT with partial LLC filling. c, The line profiles at positions along the blue and red lines shown in b represent the empty DWNT and LLC@DWNT, respectively. d, STEM image of an LLC@DWNT. Inset: a simulated STEM image of an LLC@DWNT. a, The line profiles at positions along the blue, red, and green lines shown in b represent an empty DWNT, an LLC@DWNT, and a thin inner-tube LLC@DWNT, respectively. Scale bars, 2 nm.
**STABILITY OF LINEAR CARBON CHAINS**

Tersoff potential

**multivariable function interaction of neighboring atoms**

\[ \Phi_n(r_n) = \sum_{m \neq n} f_c(r_{nm})(f_r(r_{nm}) - a_{nm}f_a(r_{nm})) \]

**attraction**

\[ f_r(r_{nm}) = \varepsilon^{(1)} \exp(-\alpha r_{nm}) \]

**repulsion**

\[ f_a(r_{nm}) = \varepsilon^{(2)} \exp(-\beta r_{nm}) \]

**structural function**

\[ f_c = \begin{cases} 
1, & r_{nm} < r^{(1)} \\
\frac{1}{2} + \frac{1}{2} \cos \left( \frac{\pi(r_{nm} + r^{(1)})}{(r^{(2)} + r^{(1)})} \right), & r^{(1)} < r_{nm} < r^{(2)} \\
0, & r_{nm} > r^{(2)} 
\end{cases} \]

\[ a_{nm} = 1 + b_n^\gamma_n \left( \sum_{k \neq n,m} f_c(r_{nk})\omega_{nk}g(\varphi_{nmk}) \right) \gamma_n \]

\[ g(\varphi_{nmk}) = 1 + \left( \frac{c_n}{d_n} \right)^2 - \frac{c_n^2}{d_n^2 + (e - \cos(\varphi_{nmk}))^2} \]

\[ \varphi_{nm,k} - \text{angle between atoms n, m, and n, k} \]

\[ \alpha, \beta, \varepsilon^{(1)}, \varepsilon^{(2)}, r^{(1)}, r^{(2)}, b, \gamma, c, d, e \]

- constants

\[ \Phi(r) \sim 3 \times 10^{-16} - 26 \times 10^{-16} V \text{ for linear chains} \]

\[ \text{для форм 3 till 20 atoms} \]

\[ \Rightarrow F(r) = -\frac{d\Phi(r)}{dr} \]

\[ F(r) \sim 10^{-4} - 10^{-6} N \]
STM measurements on carbyne samples
(collaboration with Prof. Manuela Scarselli, Tor Vergata, Rome, Italy)

Scan size 400 nm x 400 nm
(file name: m56)
Summary of STM measurements on the sample (grid) A7

(a) Tunneling current (nA) vs. Applied Voltage (Volt)

(b) Tunneling current (nA) vs. Applied Voltage (Volt)

(c) Density of states (nA/Volt) vs. Applied Voltage (Volt)

Scan size 8nm x 8 nm (from file m15)

Theoretical calculation
(Prof. Olivia Pulci)

This is a semiconductor!
2-probe spectroscopic measurements at atomic level

- Lateral electrical transport measurements with atomically precisely positioned probes
- Can the transconductance component experimentally be extracted?

The future Carbyne laboratory

The International Center of Polaritonics invests in 1D crystals

Why?

• Very interesting new physics
• Applications in nano-electronics
• Applications in lasing and photonics
• Applications in quantum technologies
• SERS possibilities for biosensing and medicine

We do not want to repeat what Cambridge, Stanford and Tokyo do: we want to develop a new field and be the world leaders
Ultimate Nanoprobing at Low Temperatures

The Low Temperature NANOPROBE defines a new class of analytical instrumentation that merges SEM-navigated local transport measurements with atomic scale precision, high performance STM imaging, spectroscopy, and manipulation at LHe temperatures.

A major challenge in the development of novel devices in molecular and atomic scale electronics is their interconnection with larger scaled electrical circuits to control and characterize their functional properties. Local electrical probing by multiple probes with atomic precision can significantly improve efficiency in analysing electrical properties of individual structures without the need for full electrical integration. The LT NANOPROBE employs four independent, ultimate stability SPM’s with precision in the picometer-range as individual probes for electrical transport measurements, and uses a scanning electron microscope for efficient and fast navigation of the probes.

The excellent stability allows for atomic resolution in STM and nc-AFM (QPlus) and expands applications towards the creation of atomically precise structures as well as their direct analysis by electrical transport measurements and SPM-based spectroscopy methods. The system – including simultaneous SPM and SEM operation – is operated near thermal equilibrium at T< 5K and has been optimised towards extremely low thermal drift as the most important ingredient to allow for enough measurement time on atomic structures, a precision regime that is virtually inaccessible at room temperature.

References:
LT NANOPROBE
SEM Imaging and Tip Navigation at T< 5K

For the navigation of four independent STM probes, simultaneous SEM imaging is indispensable as it bridges dimensions from the mm-scale down to the nm-scale. The SEM enables a large field of view for probe coarse positioning as well as fine positioning and rapid localisation of nanometer-sized structures.

The UHV Gemini column is the ultimate tool for that purpose. It offers unsurpassed resolution under true UHV conditions and at low temperatures.

In combination with the LT NANO-PROBE, the in-lens Secondary Electron Detector (SED) represents a key advantage. Only one small access port is needed in the thermal shield compartment of the microscope stage (at T <5 K). Thus thermal impact is minimised, while still offering a suitable signal for high resolution imaging.

Alternatively, other UHV SEM columns or optical microscopes can cover the lower resolution range if sample structures do not require ultimate resolution.

STM is the key to advancing probing technology into the sub-nanometer scale. It ensures extremely accurate probe positioning and STM-based safe tip approach of fragile probe tips having diameters in the range of a few tens of nanometers. SEM ensures fast and efficient navigation of STM probes from the millimeter- to the nanometer-range. However, the STM tip shadows SEM imaging of structures smaller than the tip apex (please refer to page 10). Subsequently, STM is employed for atomically precise positioning of the tip and its point of contact.

Tip re-positioning accuracy is important as the probes are approached and positioned sequentially. During the approach process of an individual probe, the other probes need to be retracted to a safety distance of a few 100nm. When the positioning process is finished, all four probes are approached to contact. The outstanding precision of the LT Nanoprobe allows to land on the same atom again.

Electrical Transport Measurements

During STM approach the distance control is based on tunnelling current feedback and therefore requires a dedicated low noise I/V converter. When the tunnelling contact is established, the individual probe-sample distance is well controlled in the nm range.

To establish electrical contact and to control its resistance, the STM feedback is de-activated and the probe is manually approached by setting a piezo scanner z-offset. The individual contact properties are analysed by an I/V measurement between the tip and the grounded sample.

Transport measurements in various configurations such as four-point transport or three terminal measurements with one tip acting as (tunnelling) gate, require the I/V converter to be taken out of the signal line. Thus, a pA STM compatible and TTL trigger controlled switching technology is used to route signals of the four probes to external BNC connectors. Using LabVIEW, experimental workflows can be integrated with third party measurement electronics.
Nanocrystalline hexagonal diamond formed from glassy carbon
Thomas, B. Shiell, Dougal G. McCulloch, Jodie E. Bradby, Bianca Haberl, Reinhard Boehlert & David. R. McKenzie

The Nature of Metastable AA’ Graphite: Low Dimensional Nano- and Single-Crystalline Forms
Jae-Kap Lee1, Jin-Gyu Kim1, K. P. S. Hembram2, Yong-II Kim3, Bong-Ki Min1, Yesung Park4, Jeon-Kook Lee1, Dong Ja Moon1, Wooyoung Lee1, Sung-Gil Lee1 & Phillip John1

Carbyne with finite length: The one-dimensional sp carbon
Bitao Pan1, Jun Xiao1, Jiling Li1, Pu Liu, Changxin Wang, Guowei Yang2

Confined linear carbon chains as a route to bulk carbyne
Lei Shi1, Philip Rohringer1, Kazu Suenaga2, Yoshiko Nilm3, Jan Kotakoski1, Jannik C. Meyer1, Herwig Peterlik1, Markus Wanko1, Seymour Cahangirov9, Angel Rubio2,3, Zachary J. Lapin2, Lukas Novotny3, Paolo Ayala4 and Thomas Pichler8