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Ultrasonics and Carbon Nanotubes

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Ultrasonics and Carbon Nanotubes

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Subjects:

- sonochemical filling of CNTs with semiconducting ferroelectrics of SbSI - type (antimony sulfoiodide - type),

- ultrasonic welding of CNTs to metal electrodes.
1991 - Discovery of carbon nanotubes by Sumio Iijima

1998 - Encapsulated atoms from Group 17 in CNTs

(e.g. I₂, BaI₂, LaI₃ molten with CNTs at high temperatures for long time)
1991 - Discovery of carbon nanotubes by Sumio Iijima

1998 - Encapsulated atoms from Group 17 in CNTs
  (e.g. \( \text{I}_2, \text{BaI}_2, \text{LaI}_3 \))

2008 – **sonochemical** preparation of SbSI nanowires

2009 – CNTs filled with SbSI **sonochemically**
Properties of SbSI

- semiconductor ($E_{glf} = 1.83(3)$ eV)

- ferroelectric ($T_c = 292(1)$ K)
  (in case of 0.1% substitution I atoms by Cl atoms $T_c = 334$ K)

- high spontaneous polarization $P_s=0.30$ C/m²

- low coercive field $E_c=10^4$ V/m ($T=0^\circ C$, 50 Hz)
Properties of SbSI

- strong anisotropy

After [6]
Properties of SbSI

- high piezoelectric modulus
  \(d_{333}=7(2) \cdot 10^{-9} \text{ m/V}\)

- high electrostriction coefficient
  \(Q_{3333}=4.6(1) \cdot 10^{-13} \text{ m}^2/\text{V}^2\)

- high electromechanical coupling coefficient
  \(k_{33}=0.9\)
Properties of SbSI

- pyroelectric (60 mC/(m²K))
- very high pyro-optical coefficient along c axis
- strong electro-optical properties
- optically doubly refracting
- optically nonlinear
SONOCHEMISTRY

application of ultrasounds in chemistry
by Richards and Loomis in 1927:
SONOCHEMISTRY

application of ultrasounds in chemistry
(20 kHz – 100 kHz)

Advantages:
• short reaction time,
SONOCHEMISTRY
application of ultrasounds in chemistry

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• decrease quantity or total elimination of catalyst from reaction
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 Advantages:
• short reaction time,
• change of conditions necessary for chemical reactions,
  e.g., decreasing of temperature of the process,
• increase of reacting substances chemical activity,
• ability of decrease quantity or total elimination of catalyst from reaction,
• effective mixing,
Advantages:
• short reaction time,
• change of conditions necessary for chemical reactions, e.g., decreasing of temperature of the process,
• increase of reacting substances chemical activity,
• ability of decrease quantity or total elimination of catalyst from reaction,
• effective mixing,
• higher productivity.
Sound motion in a medium = energy is transferred by molecular motion

Main event: Creation, growth, collapse of a bubble that is formed in the liquid.
ACOUSTIC CAVITATION

IN THE CAVITY

extreme conditions on collapse
5000°C and 2000 atmospheres
with rapid change $10^{11}$ K/s

IN THE BULK MEDIA

intense shear forces
Expermental data (Xe (4 torr) in sulfuric acid and in water (pointed curve); 20 °C, T=0.25 μs) after Hopkins et al. (2005)
Sonoluminescence after [Suslick Group Website]
Sonochemical preparation of SbSI – bottom up technology

Before and after sonochemical synthesis of SbSI

\[
\begin{align*}
S &= 0.486g \\
Sb &= 1.847g \\
I &= 1.928g
\end{align*}
\]
Responses of mass spectrometer on the switch-on and switch-off of ultrasonic irradiation of ethanol with Sb, S, and I$_2$
Change of color and consistence during the sonication of Sb, S and I$_2$ in ethanol (a-i) and the obtained SbSI (j) as well as SbSeI (k) xerogels (a- dry elements before the process; b- test-tube with the elements in ethanol at the beginning of the process; c- after 20 sec. of sonication, T=323 K; d- 3 min.; e- 6 min.; f- 26 min.; g- 48 min.; h- 75 min.; i- SbSI ethanogel solidified after 110 min.)
Diffusive reflectance controls sonochemical process

\[ \text{C}_2\text{H}_5\text{OH} + \text{SbI}_3 + \text{Sb}_2\text{S}_3 \]

\[ T = 323 \text{ K} \]
$F_{K-M}$ spectra recorded during sonochemical preparation of SbSI
$F_{K-M}$ spectra recorded at different times of sonochemical preparation of SbSI (1508 mg Sb, 397 mg S, 1573 g I$_2$, 8 ml C$_2$H$_5$OH; T = 323 K)
1 – t = 0 min, 2 - 0.5 min, 3 - 3 min, 4 - 8 min, 5 - 16 min, 6 - 29 min, 7 - 53 min, 8 - 110 min
Shift of absorption edge during sonochemical preparation of SbSI in methanol
Change of the energy gap (for isoabsorption at $G_{K-M}=0.1$) of SbSI nanoparticles during sonochemical preparation in methanol
Quantum dot of SbSI
SbSI nanowires
HRTEM image of an individual nanowire of SbSI
HRTEM image of an individual nanowire of SbSI (JEM 3010)
High resolution image of SbSI nanowire with inserted filtered part (a), the FFT image of the filtered part (b) and its indexed diagram (c)
Comparison of the part of filtered high resolution image of SbSI nanowires (A) with calculated distribution of atoms (B- view comparable with the experiment; C- view along the c axis of the SbSI nanowires; black, gray and green colors represent the Sb, S and I atoms, respectively; the vertical line shows the (210) plane; red rectangle presents cell in the SbSI crystal).
Typical SEM micrograph of SbSn xerogel.
AFM image of individual nanowire of SbSI: semiconductor, ferroelectric and piezoelectric ($k_{33}=0.9$).
Nanoproducts of the author’s group

- quantum dots: \( \text{SbSI, BiI, Sb}_3\text{I} \)
- nanowires: \( \text{SbSI, SbSeI, BiSI} \)
  \( \text{Bi}_x\text{Sb}_{1-x}\text{SI} \)
  \( \text{SbS}_{1-x}\text{Se}_x\text{I} \)
  \( \text{SbS}_{1-x}\text{O}_x\text{I} \)
  \( \text{SbSCl}_{x}\text{I}_{1-x} \)
  \( \text{Bi}_x\text{Sb}_{1-x}\text{Se}_y\text{S}_{1-y}\text{Cl}_z\text{I}_{1-z} \)
- films of aligned nanowires: \( \text{SbSI} \)
- nanowires in carbon nanotubes: \( \text{SbSI, SbSeI} \)
Typical HRTEM images of individual nanowires from sonochemically prepared SbSI (a), SbS$_{0.75}$Se$_{0.25}$I (b) and SbSeI (c) ethanogel. The 0.654(8) nm fringe spacings in image (a) correspond to the interplanar distances between the (110) planes of SbSI crystal (0.65294 nm [36]). The fringe spacings in image (b) are 0.641(5) nm. The 0.661(7) nm fringe spacings in image (c) correspond to the interplanar distances between the (110) planes of SbSeI crystal (0.66648 nm [28,29], 0.66752 nm [26,27]). The surfaces of the nanowires show amorphous layers.
Comparison of the diffuse reflectance spectra and Kubelka-Munk functions of SbS$_{1-x}$Se$_x$I nanowires with different molar compositions

- SbSI
- SbS$_{0.8}$Se$_{0.2}$I
- SbS$_{0.6}$Se$_{0.4}$I
- SbS$_{0.4}$Se$_{0.6}$I
- SbS$_{0.2}$Se$_{0.8}$I
- SbSeI
Energy gap of SbS$_{1-x}$Se$_x$I vs. molar composition (■ - this paper; □ - [14]; ○-[51]; △, ▽ - for plane polarized light with electric field perpendicular and parallel to the c-axis, respectively [12], ◇-[19]; line represents the least square fitted linear dependence).
Nanoproducts of the author’s group

- **quantum dots:** SbSI, BiI, Sb$_3$I

- **nanowires:** SbSI, SbSeI, BiSI
  Bi$_x$Sb$_{1-x}$SI
  SbS$_{1-x}$Se$_x$I
  SbS$_{1-x}$O$_x$I
  SbSCl$_{1-x}$I$_{1-x}$
  Bi$_x$Sb$_{1-x}$Se$_y$S$_{1-y}$Cl$_z$I$_{1-z}$

- **films of alligned nanowires:** SbSI

- **nanowires in carbon nanotubes:** SbSI, SbSeI
Dried multiwalled CNTs filled with SbSI ultrasonically in methanol.

The typical SEM micrograph of dried multiwalled CNTs filled with SbSI ultrasonically in methanol.
TEM image of the end of multiwalled CNT filled with SbSI.
Typical HRTEM image of an individual multiwalled CNT filled with SbSI ultrasonically in methanol. The fringe spacings of 0.319(2) nm (1) and 0.209(2) nm (2) correspond to the interplanar distances between the (220) planes of SbSI crystal and (101) planes of carbon nanotube, respectively.
Powder XRD pattern of dried multiwalled CNTs filled with SbSI ultrasonically in methanol.
TEM image of ferroelectric domains in SbSI nanowire in CNT.
Fig. The SbSI nanowire before (a) and after heating (b,c) in the microscope with the focused electron beam
Ferroelectric domains in SbSI single crystal (T=293.89 K)
$T = 294.92 \text{ K}$
T = 293.97 K
T = 293.96 K
T = 293.89 K
$T = 293.87 \, \text{K}$
$T = 292.99 \text{ K}$
The energy dispersive X-ray (EDS) spectra of dried multiwalled CNTs filled with SbSI ultrasonically in methanol.
Table. Atomic concentration of components of the dried multiwalled CNTs filled with SbSI ultrasonically in methanol determined by EDX.

<table>
<thead>
<tr>
<th>Element</th>
<th>Results of EDS investigations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of all detected elements (at. %)</td>
</tr>
<tr>
<td>Sb</td>
<td>5.1(3)</td>
</tr>
<tr>
<td>S</td>
<td>1.7(3)</td>
</tr>
<tr>
<td>I</td>
<td>3.8(3)</td>
</tr>
<tr>
<td>C</td>
<td>89.4(13.4)</td>
</tr>
</tbody>
</table>
Comparison of the diffuse reflectance spectra of the multiwalled CNTs filled with SbSI (■) ultrasonically in methanol and of the empty multiwalled CNTs (□) in methanol.
CNT filled with SbSeI
TEM line scan EDS for SbSeI encapsulated in CNT
Comparison of the fitted spectra of the Kubelka–Munk function calculated for diffuse reflectance of the multiwalled CNTs filled with SbSeI (■) and SbSI (□). Solid curves represent the least square fitted theoretical dependences.
<table>
<thead>
<tr>
<th>Fitted parameters</th>
<th>CNTs filled with SbSeI</th>
<th>SbSeI nanowires</th>
<th>CNTs filled with SbSI</th>
<th>SbSI nanowires</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Values determined assuming</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Indirect allowed absorption</td>
<td>Indirect allowed absorption without phonon statistics – normalized for $h\nu$</td>
<td>Indirect forbidden absorption</td>
<td></td>
</tr>
<tr>
<td>$c^2$</td>
<td>0.1223</td>
<td>5.592</td>
<td>78.14</td>
<td>–</td>
</tr>
<tr>
<td>$E_{\text{gll}}$ [eV]</td>
<td>–</td>
<td>–</td>
<td>1.6(1)</td>
<td>1.63</td>
</tr>
<tr>
<td>$E_{\text{gla}}$ [eV]</td>
<td>1.61(6)</td>
<td>1.72(4)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$E_{\text{ph}}$ [eV]</td>
<td>0.099(6)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$A_{60}$ [1/eV$^3$m]</td>
<td>–</td>
<td>–</td>
<td>41(2)</td>
<td>94.8</td>
</tr>
<tr>
<td>$A_{125}$ [10$^{12}$m$^{-3}$]</td>
<td>11.14(1)</td>
<td>11(2)</td>
<td>11.11(1)</td>
<td>–</td>
</tr>
<tr>
<td>$A_{50}$ [1/eV$^2$m]</td>
<td>27.7(6)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$A_{41}$ [1/eV$^2$m]</td>
<td>–</td>
<td>60(1)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$A_0$ [1/m]</td>
<td>1.019(1)</td>
<td>1(1)</td>
<td>1.02(2)</td>
<td>0.01071</td>
</tr>
<tr>
<td>$E_U$ [eV]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0810</td>
</tr>
<tr>
<td>$A_U$ [1/m]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.09·10$^{-10}$</td>
</tr>
</tbody>
</table>

Note: Table entries represent values for different fitted parameters, with units specified in parentheses or as specified in the table.
The probable reaction route of SbSeI in CNTs synthesis and the mechanism of formation of its nanowires in the presence of ethanol under ultrasonic irradiation:
The probable reaction route of SbSeI in CNTs synthesis and the mechanism of formation of its nanowires in the presence of ethanol under ultrasonic irradiation:

(1) iodine, I\(_2\), dissolved in ethanol reacts with antimony and forms antimony triiodide, also dissolved in ethanol

\[
2\text{Sb} + 3\text{I}_2 \rightarrow 2\text{SbI}_3
\]
(2) dehydrogenation, dehydration as well as decomposition of ethanol in or close to the cavitation bubbles leads to the formation of hydrogen and water.

\[
\begin{align*}
C_2H_5OH & \leftrightarrow C_2H_4O + H_2 \\
C_2H_5OH & \leftrightarrow C_2H_4 + H_2O \\
C_2H_5OH & \leftrightarrow C_2H_5O + H
\end{align*}
\]
(3) the sonolysis of water yields the H\(^\bullet\) and OH\(^\bullet\) radicals
(4) ultrasonic irradiation facilitates the reduction of chalcogens to the active forms of Se$^{-2}$ that react with the in-situ generated H• radicals forming H$_2$Se

\[ \text{Se} + 2\text{H}\cdot \rightarrow \text{H}_2\text{Se} \]
(5) CNT's suck the released $\text{H}_2\text{Se}$ molecules and $\text{SbI}_3$ in ethanol. This is allowed by the capillary effect.
It is well known, that open CNTs are impregnated with excess of the precursor solutions under ultrasonic conditions to ensure that most of the tubes can be filled by the impregnating solution.

From the thermodynamic point of view, the dissolution of the impregnating solution sticking to external walls of CNTs into the washing medium necessitates the condition of the solvation energy gain smaller than zero.

On the other hand, the energy gain for the capillary filling of a CNT must be smaller than the solvation energy to ensure that the solution is stable in the internal cavity of CNTs.
(6) \( \text{H}_2\text{Se} \) reacts with \( \text{SbI}_3 \) to yield \( \text{SbSeI} \) molecules

\[
\text{SbI}_3 + \text{H}_2\text{Se} \rightarrow \text{SbSeI} + \text{H}_2 + \text{I}_2
\]
SbSeI molecules, under the microjets and shockwaves formed during collapsing of the bubbles, are pushed towards each other in CNTs and are held by chemical forces. Therefore, the nuclei of SbSeI are formed as a result of the interparticle collisions.
the freshly formed nuclei in the solution are unstable and have the tendency to grow into double chains \([(\text{SbSeI})_\infty]_2\) consisting of two chains related by a twofold screw axis and linked together by a short and strong Sb-Se bonds.

Local turbulent flow associated with cavitation and acoustic streaming greatly accelerates mass transport in the liquid phase.
(9) the SbSeI chains can be readily crystallized into a 3D lattice in the CNTs through van der Waals interactions. Induced by this structure, crystallization tends to occur along the c-axis, favoring the stronger covalent bonds over the relatively weak, inter-chain van der Waals forces.

Thus, this solid material has a tendency to form highly anisotropic, 1D structures also inside the CNTs.
Sample of SbSI xerogel for impedance spectroscopy
Surfaces of alumina substrates with interdigitated platinum lines as electrodes and the platinum temperature detector before (a) and after (b) deposition of a 5 μm thick film of aligned SbSI nanowires.
Alligned SbSI nanowires on Al$_2$O$_3$ substrate ($5 \cdot 10^5$ V/m)
Experimental data of spectral dependences of photoconductive currents in a 5 μm thick film of aligned SbSI nanowires for different illumination levels at 323 K (p=1.33 Pa). Solid curves show the spectral dependences of illumination intensities. Symbol ● presents photoconductivity current normalized for $I_0 = 5 \cdot 10^{17}$ photo/(m²s).
\[ \beta = \frac{\alpha_{PC}}{\alpha_T} \eta \]

\[ \alpha = \sum_{i=1}^{I_F} A_i \left\{ \frac{(h \nu - E_{gla} + E_{Fi})^2}{\exp\left(\frac{E_{Fi}}{k_B T}\right) - 1} + \frac{(h \nu - E_{gla} - E_{Fi})^2}{1 - \exp\left(-\frac{E_{Fi}}{k_B T}\right)} \right\} \]
Ultrasonic welding of CNTs to metal electrodes
Al₂O₃ single crystal
Carbon nanotube photovoltaic device with asymmetrical contacts


Ultrasonically welded CNTs after Chen et al. (2008)
Carbon nanotubes on Si/SiO$_2$ substrate with Au electrodes after ultrasonic welding
AFM image of carbon nanotubes on Si/SiO$_2$ substrate with Au electrodes after ultrasonic welding (CNTs produced by directly spinning from an aerogel sock [Stano et al. (2008)])
Nanowires of SbSI on Si/SiO$_2$ substrate with Au electrodes after ultrasonic welding
Nanowires of SbSI on Si/SiO$_2$ substrate with Au electrodes after ultrasonic welding.
Prototype
Conclusions:

The presented ultrasonic techniques of:

- sonochemical filling of CNTs with semiconducting ferroelectrics of SbSI type,

- ultrasonic welding of CNTs to metal electrodes,

are:
- convenient,
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Conclusions:

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- ultrasonic welding of CNTs to metal electrodes,

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- fast,
- mild,
- efficient, and
- environmentally friendly routes of production of nanostructures.

Probably they can be extended to preparation of some other nanomaterials.
References on sonochemical preparation of SbSI and SbSeI nanowires


- M. Nowak, Photoferroelectric nanowires; in „Nanowires Science and Technology”, Ed. N. Lupu, INTECH, Croatia 2010, pp. 269-308.

(Available from: www.intechopen.com/articles/show/title/photoferroelectric-nanowires)