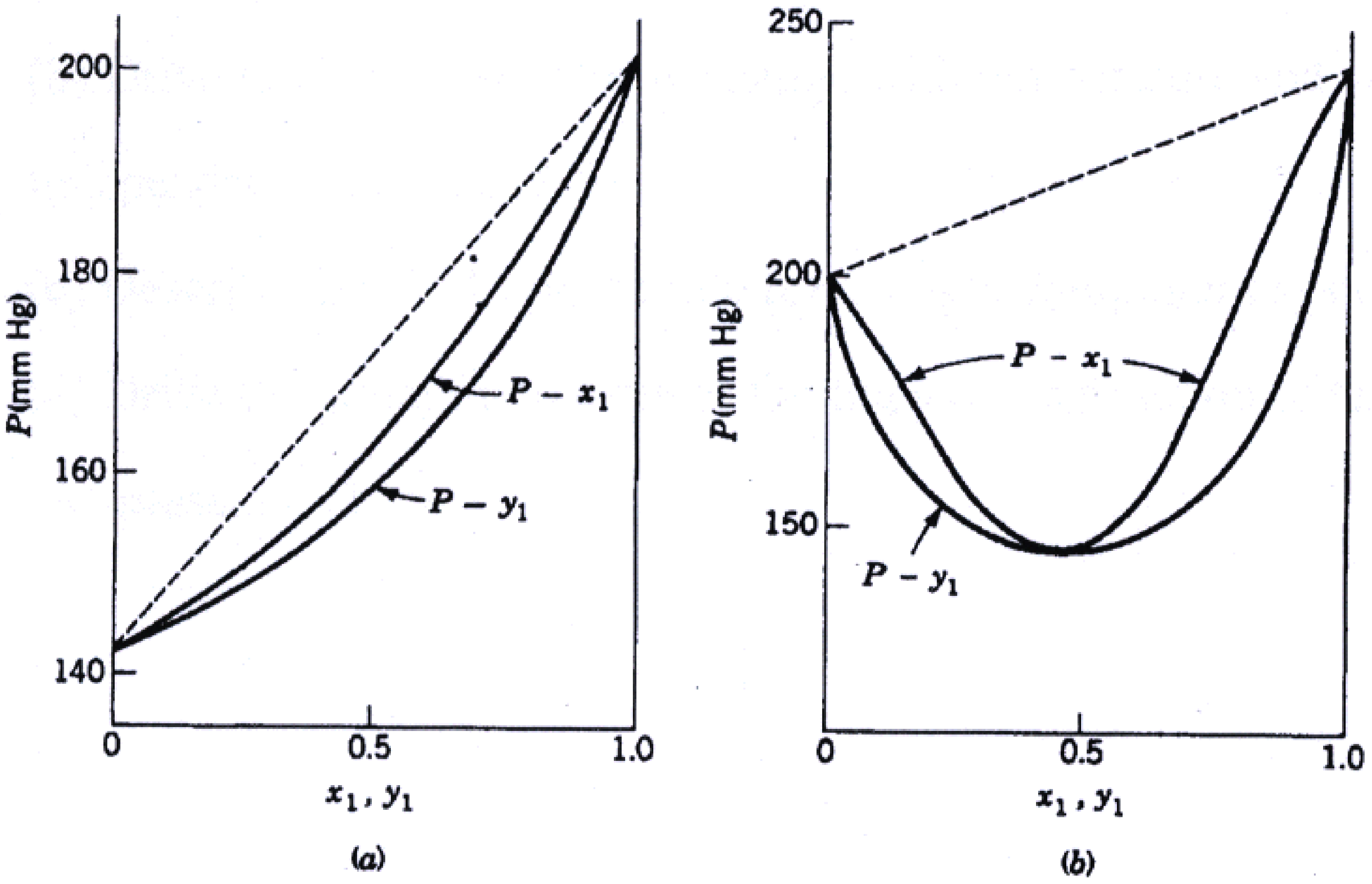
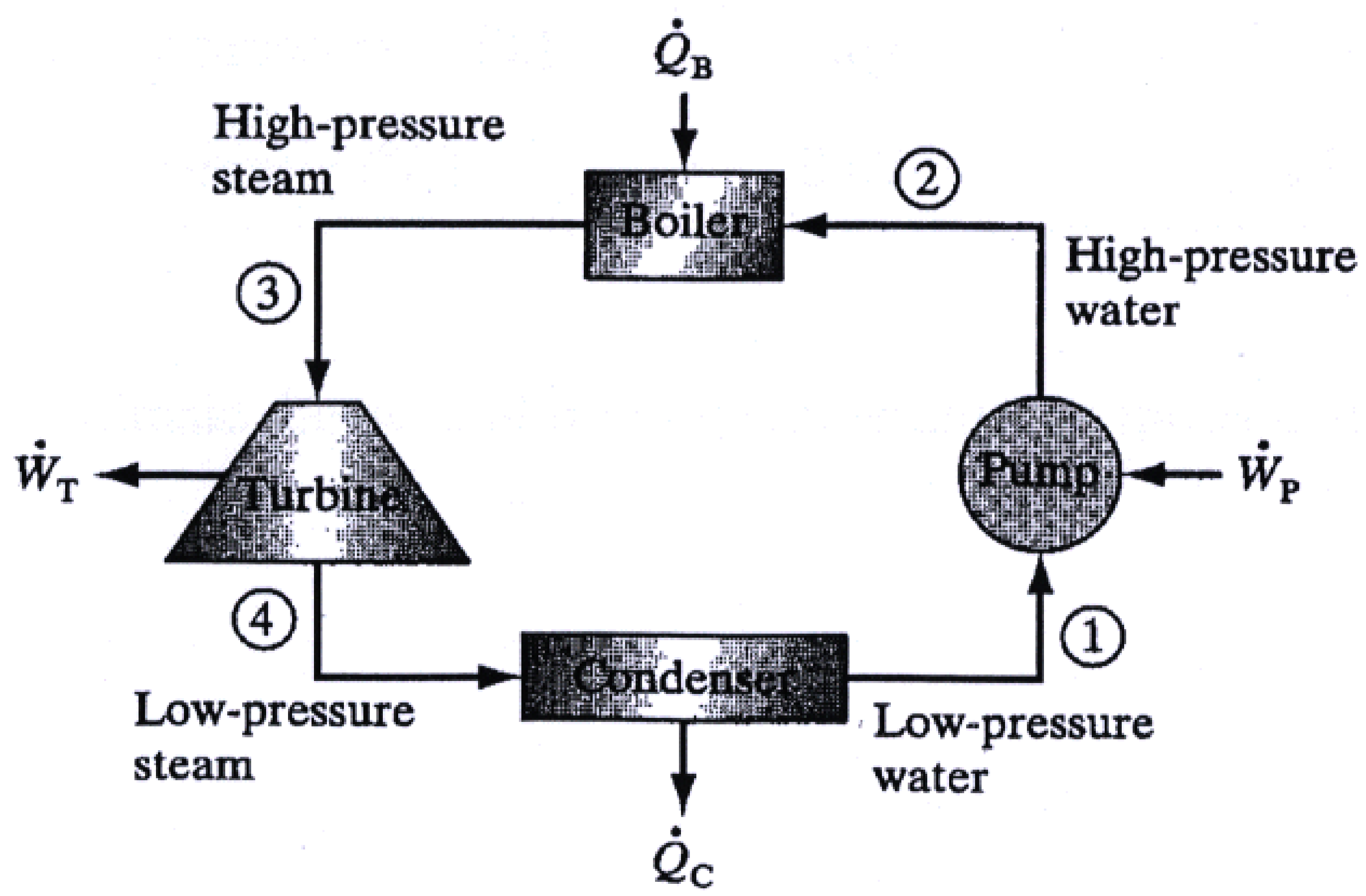
國立雲林科技大學
94 學年度博士班招生入學考試試題

所別：化學工程系
科目：化工熱力學

1. (25%) The following figures are *P*-*x*-*y* diagrams at constant temperature of two liquid solutions composed of two organic compounds. Please explain the significance in thermodynamics in each case.



2. (25%) Please explain thermodynamic meanings for the cylinder-piston device in the figure below, and show a full calculation to obtain work done on and heat transfer added to the fluid in each path.



國立雲林科技大學
94學年度博士班招生入學考試試題
所別：化學工程系
科目：化工熱力學

3. (a) Describe the Clausius statement of the thermaldynamic second law. (5%)

   (b) Drive the ideal gas entropy change with temperature and volume as independent variables (5%)

   (c) Describe the Gibbs phase rule for a single component system. (5%)

   (d) Drive the equation to express the fugacity as function of temperature and pressure. (10%)

4. The triple point of iodine I_2 occurs at 112.9 ^{o}C and 11.57 kPa. The heat of fusion at the triple point is 15.27 kJ/mol, and the following vapor pressure data are available for solid iodine:

Vapor pressure (kPa)	2.67	5.33	8.00
Temperature (^{o}C)	84.7	97.5	105.4

Estimate the normal boiling temperature of molecular iodine. (25%)

國 立 雲 林 科 技 大 學
94 學年度博士班招生入學考試試題

所別：化學工程系
科目：化學工程文獻

本試題共兩大題，每題 50 分。

一、附件一之文獻，篇名是 “Spinning Continuous Carbon Nanotube Yarns”，共有 6 段落。請針對「附件一」內容，回答以下問題。

1. 以中文製作本文的摘要。
2. 請將本文第 2 段內容翻譯成中文。
3. 本文如何將奈米碳管紡成連續絲？
4. 本文所紡之奈米碳管連續絲之機械性質與光電性質為何？

二、針對「附件二」內容，請回答以下問題。

1. 請將文章第一及第四段內容翻譯成中文。
2. 本文中敘述的圖書碰到什麼問題？為何會出現這種讓人困擾的問題?
3. 文中如何解決此問題?

(附件一)

Spinning continuous carbon nanotube yarns

Carbon nanotubes weave their way into a range of imaginative macroscopic applications.

The creation of continuous yarns made out of carbon nanotubes would enable macroscopic nanotube devices and structures to be constructed[1,2]. Here we show that carbon nanotubes can be self-assembled into yarns of up to 30 cm in length simply by being drawn out from superaligned arrays of carbon nanotubes, and that the strength and conductivity of these yarns can be enhanced by heating them at high temperatures. Our findings should help to translate the remarkable mechanical, electrical and thermal properties of carbon nanotubes to a macroscopic scale.

While attempting to pull out a bundle of carbon nanotubes (CNTs) from a CNT array several hundred micrometres high and grown on a silicon substrate, we obtained instead a continuous yarn of pure CNTs (Fig. 1a). This process is very similar to drawing a thread from a silk cocoon, corresponding here to the CNT array. Figure 1b shows a 100-μm-high, free-standing CNT array held by adhesive tape: the indentation at the top of the array marks the region that is being turned into a yarn 30 cm long and 200 μm wide. We estimate that an array area of roughly 1 cm^2 can generate about 10 m of yarn.

Although several methods can be used to prepare CNT arrays on different substrates[3-6], we find that continuous yarns can only be drawn out from superaligned arrays in which the CNTs are aligned parallel to one another and are held together by van der Waals interactions to form bundles (Fig. 1c). The yarns usually appear as thin ribbons composed of parallel threads that have diameters in the range of several hundreds of nanometres (Fig. 1d), with the width of the yarn roughly depending on the number of threads in the yarn. In principle, the size of the yarn can be controlled by the tip size of the tool that is used to pick up the yarn — the smaller the tip, the thinner the yarn.

To demonstrate the properties of these yarns, we constructed a light-bulb filament by winding a CNT yarn between two metal leads. The filament emits incandescent light when a DC voltage is applied in a vacuum of 5×10^{-3} Pa (Fig. 1e). After emitting light for 3 h at 70 V, the conductivity of the filament increases by 13% and the tensile strength changes from 1 mN to 6.4 mN. These results indicate that some welding effect may be occurring at the weak connection points of the CNTs during light emission, because these points have a higher resistivity and, as a result, a higher temperature when a current is applied.

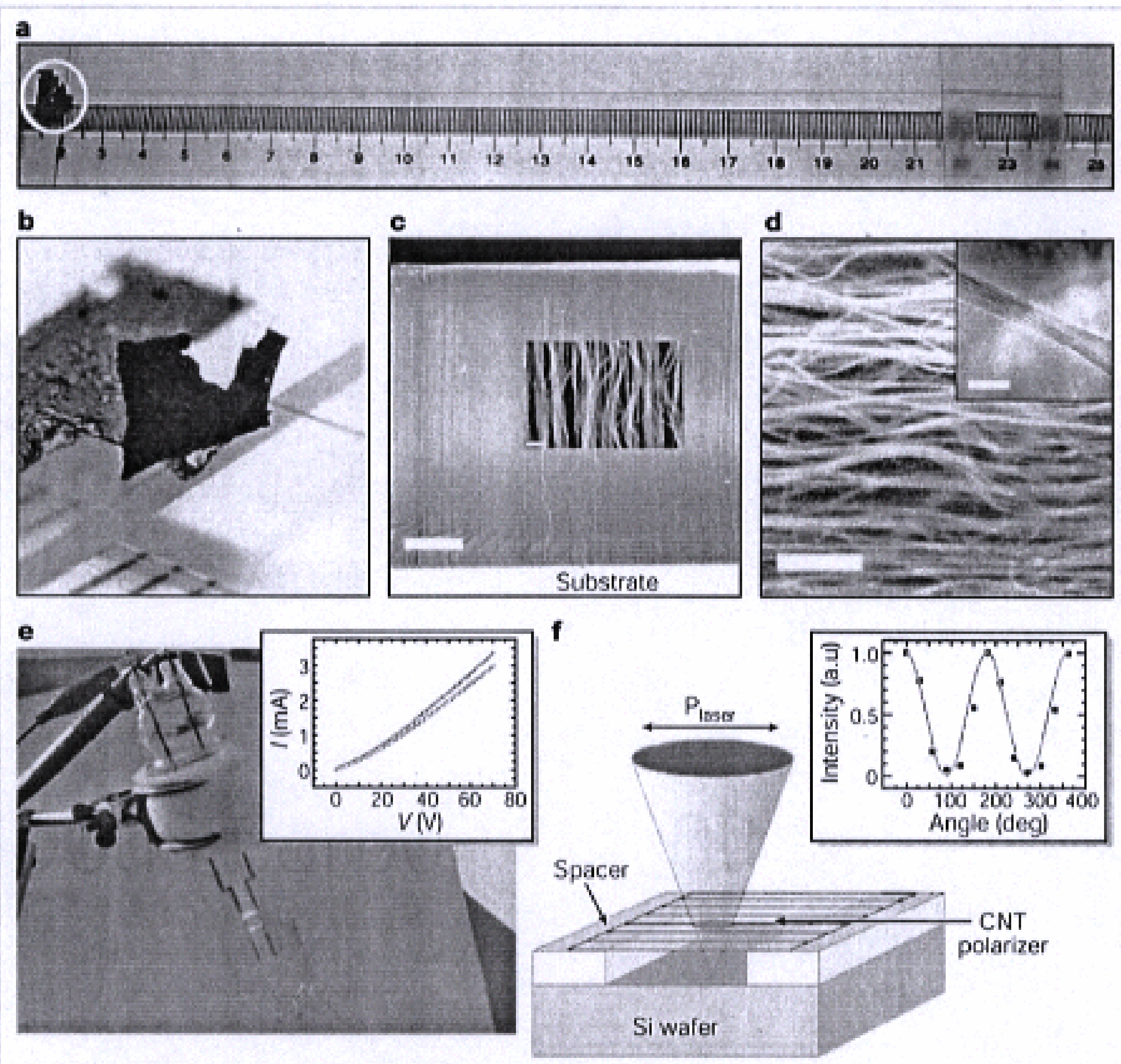


Figure 1 Carbon nanotube yarns. **a, b,** A carbon nanotube yarn being continuously pulled out from a free-standing carbon nanotube array (**a**), which is shown enlarged in **b** (roughly ×8 magnification). **c,** Scanning electron microscope (SEM) images of a carbon nanotube array grown on a silicon substrate, showing the superalignment of carbon nanotubes (scale bars: 100 μm; inset, 200 nm). **d,** SEM image of the yarn in a; inset, transmission electron microscope (TEM) image of a single thread of the yarn (scale bars: 500 nm; inset, 100 nm). **e,** Carbon nanotube filaments emitting incandescent light. Inset, *I*–*V* curve measured before (green) and after (red) light emission for 3 h at 70 V. **f,** A carbon nanotube polarizer. Polarized laser light (P_{laser}) is focused on the surface of a silicon wafer and reflected back, passing the carbon nanotube polarizer twice before being collected by a CCD detector. Inset, normalized intensity (squares, ratio of the current I to I_{max}; a.u., arbitrary units) plotted against the angle between the polarization direction of the laser light and the carbon nanotube polarizer, compared with values calculated from Malus's law ($I = I_0 \cos^2\theta$; red line).

We were also able to construct a CNT polarizer by parallel alignment of CNT yarns. When a beam of light passes through the CNT polarizer, photons having a polarization direction parallel to the axis of the CNTs are absorbed, whereas those that are perpendicularly polarized pass through it[7,8]. Because the CNT diameter is about 10 nm, the polarizer can work in the ultraviolet region, and could even be used for ultraviolet light of wavelengths in the region of tens of nanometres. Figure 1f shows the polarization ability of the CNT device measured at 325 nm, which is in good agreement with that predicted by Malus's law, $I = I_0 \cos^2\theta$. The degree of polarization of the CNT polarizer, $P = (I_{max} - I_{min})/(I_{max} + I_{min})$, is 0.92.

We envisage that pure CNT yarns such as these, particularly after appropriate heat treatment, should eventually be able to be woven into a variety of macroscopic objects for different applications, such as bulletproof vests and materials that block electromagnetic waves.

Kaili Jiang, Qunqing Li, Shoushan Fan
Department of Physics and Tsinghua-Foxconn Nanotechnology Research Center, Tsinghua University, Beijing 100084, China
e-mail: fss-dmp@mail.tsinghua.edu.cn

1. Vigolo, B. *et al. Science* **290**, 1331–1334 (2000).
2. Ball, P. *Nature* **414**, 142–144 (2001).
3. de Heer, W. A. *et al. Science* **268**, 845–847 (1995).
4. Li, W. Z. *et al. Science* **274**, 1701–1703 (1996).
5. Ren, Z. F. *et al. Science* **282**, 1105–1107 (1998).
6. Fan, S. S. *et al. Science* **283**, 512–514 (1999).
7. Wang, J. F., Gudiksen, M. S., Duan, X. F., Cui, Y. & Lieber, C. M. *Science* **293**, 1455–1457 (2001).
8. Li, Z. M. *et al. Phys. Rev. Lett.* **87**, 127401–1274014 (2001).

Competing financial interests: declared none.

(附件二) **Self-Destructing paper**

The New York City Public Library has 88 miles of bookshelves, and on 36 miles of these shelves the books are quietly disintegrating between their covers. In fact, an estimated 40% of the books in the major research collections in the United States will soon be too fragile to handle.

The problem results from the acidic paper widely used in printing books in the past century. Books from the eighteenth, seventeenth, sixteenth, and even fifteenth century are in much better shape. Bibles contain paper that is in remarkably good condition. In those days, paper was made by hand from linen or rags, but in the nineteenth century, the demand for cheap paper skyrocketed. Paper manufacturers found that paper could be made economically, by machine, using wood pulp. To size the paper (that is, fill in microscopic holes to lower absorption of moisture and prevent seeping or spreading of inks), alum [$Al_2(SO_4)_3$] was added in large amounts. Because the hydrated aluminum ion is an acid ($K_a \approx 10^{-5}$), paper manufactured using alum is quite acidic. Over time this acidity causes the paper fibers to disintegrate; the pages of books fall apart when they are used.

One could transfer the contents of the threatened books to microfilm, but that would be a very slow and expensive process. Can the book be chemically treated to neutralize the acid and stop the deterioration? Yes. In fact, you know enough chemistry at this point to design the treatment patented in 1936 by Otto Schierholz. He dipped individual pages in solutions of alkaline earth bicarbonate salts [$Mg(HCO_3)_2$, $Ca(HCO_3)_2$, and so on]. The HCO_3^- ion present in these solutions react with the H^+ in the paper to give CO_2 and H_2O. This treatment works well and is used today to preserve especially important works, but it is slow and labor-intensive.

It would be much more economical if large numbers of books could be treated at one time without disturbing the bindings. However, soaking entire books in an aqueous solution is out of question. A logical question then is: Are there gaseous bases that could be used to neutralize the acid?

An effective treatment involves diethylzinc [$(CH_3CH_2)_2Zn$], which boils at 117 ℃ and 1 atm. Diethylzinc (DEZ) reacts with oxygen or water to produce ZnO. The solid zinc oxide produced in these reactions is deposited among the paper fibers, and being a basic oxide, it neutralizes the acid present.