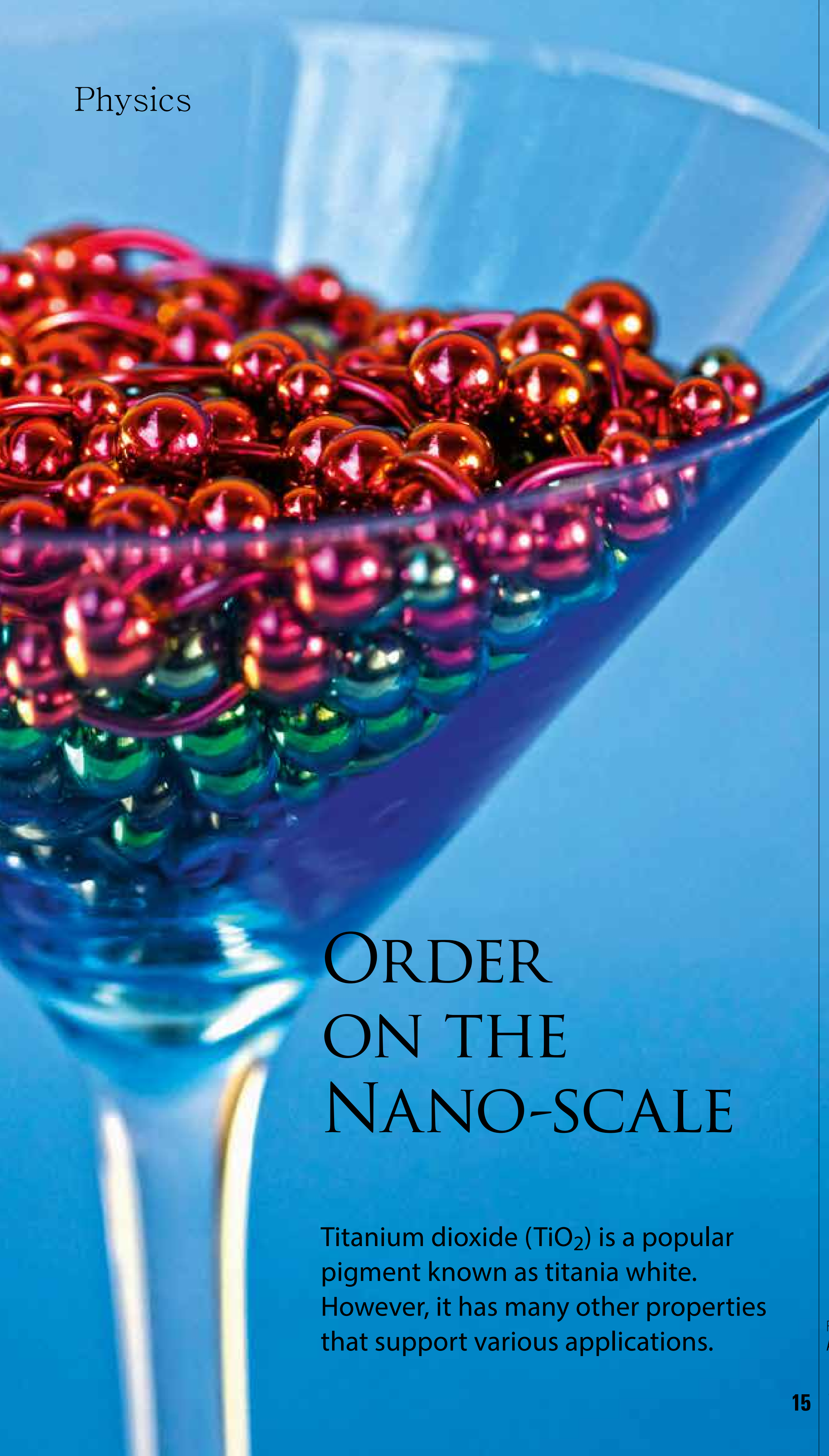

Order on the Nano-scale

Titanium dioxide (TiO_2) is a popular pigment known as titania white. However, it has many other properties that support various applications.

Fig. 1
Anodized titanium jewelry

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Currently, materials engineering is a world of myriad chemical compounds with fascinating shapes, structures and properties all of which are revolutionizing the machinery and products used by millions of people every single day. We hear about miracle paints resistant to fungi and bacteria, self-cleaning surfaces, windows which change tint or devices which can be charged in seconds and which can release this energy equally fast.

Titanium dioxide plays an important role in all these applications. Known as titania white, it is a common component in pigments for its concealing, supporting and brightening properties. The discovery that adding the compound results in the decomposition of organic contamination when exposed to light has resulted in extensive research into its other properties. We have learned that titanium dioxide exhibits a high chemical stability and catalytic and electrochemical activity when illuminated. It is also non-toxic and widely available; selecting the appropriate method and conditions of synthesis makes it possible to obtain a range of shapes (rods, tubes, particles) which determine the material's specific properties such as light absorbance and acting as a moisture barrier. The different properties and controlled morphology mean that titanium dioxide is used as a component of paints, creams and pastes as well as in the construction of third-generation photovoltaic cells, electrochromic devices and batteries. This roused my interest in studying TiO_2 and attempting to control its shape on a nanoscopic scale.

From tangled yarn to a well-kept lawn

Since the discovery of carbon nanotubes by Samui Ijima in 1991, their specific molecular geometry and the properties it gives rise to have inspired the world of nanotechnology and fueled extensive efforts in physics, chemistry and material engineering to master the synthesis and discover the properties of such structures. The tubes have unique electrical properties including high electron mobility, developed active surface and mechanical resistance. Although carbon nanotubes are still a widely used and studied material, high numbers of other chemical compounds such as metal oxides or sulfides with a one-dimensional geometry – such that one dimension is greater than the other two – are being synthesized and shown to exhibit fascinating properties. While carbon nanotubes tangle readily into jumbled bundles (visible in Fig. 2a), certain chemical synthesis methods make it possible to obtain ordered oxide structures (seen in Fig. 2b, c) directly on a surface.

The German saying *Ordnung muss sein* ("there must be order") is often regarded as expressing a principle of the highest virtue in day-to-day life. In fact, the importance of order extends down into the invisible world of nanomaterials. You would be forgiven for thinking that achieving such ordered spatial organization of a material requires advanced equipment and expensive reagents, and that synthesis would take a long time, yet this couldn't be further from the truth. Structures of titanium dioxide like those shown in Fig. 2b, c, remarkably reminiscent of a well-groomed bed of grass, can be obtained through electrochemical anodizing in a two-electrode arrangement. Such a research setup comprises an anode on which the material builds up in layers and a cathode, both immersed in an electrolyte with a precisely balanced composition. The method is widely known and used on an industrial scale for surface processing of metals, and it results in the formation of oxides. Anodizing is mainly used for aluminum and its alloys as well as certain steels and titanium and magnesium alloys; it provides anti-corrosive protection of metal surfaces or an isolating layer on aluminum foil used in condensers. The technology is also used in decorative jewelry, since anodized aluminum alloys have a distinctive texture and color if tints are added to the electrolyte bath (see Fig. 1).

Just immerse a metal plate?

Titanium dioxide nanotubes can be obtained using the same process; the key part is selecting the correct components of the electrolyte and electrical parameters of the process. It is especially important that the electrolyte should contain a compound which serves as a source of fluoride ions (for example ammonium

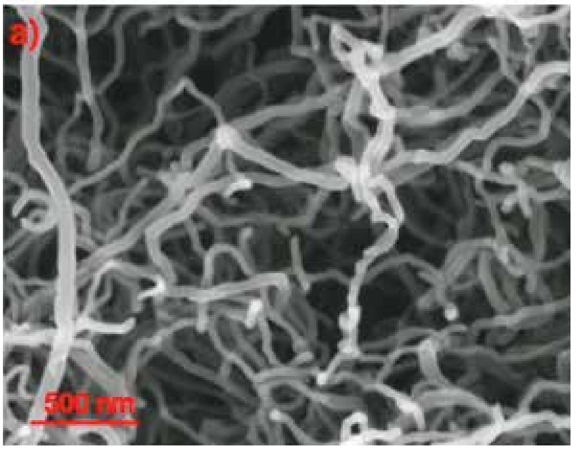


Fig. 2
Carbon nanotubes (a), TiO_2 nanotubes viewed from the side and from above (b, c) – electron microscopy image.

fluoride or hydrofluoric acid), responsible for the specific treatment of the titanium surface. The electrolyte usually contains an organic-water solution with ethylene glycol or glycerin as the organic component; this contributes to the height and shape of the nanotubes. Another important parameter of the process is the voltage between the anode and the cathode. Its value makes it possible to control the geometric size of the TiO_2 structures, including the internal diameter and wall thickness. The duration affects the required length of the nanotubes; for the most commonly used structures the fabrication process takes around two hours After anodizing, the titanium plates covered with nanotubes are processed thermally at approx. 500°C to convert the amorphous structure into a crystalline one in which the ordered arrangement of atoms determines the physicochemical properties, which in turn affects the material's future use. A major advantage of the synthesis method is that the material is formed directly on the anodized surface, which means it is ready for use without further processing to create a uniform layer.

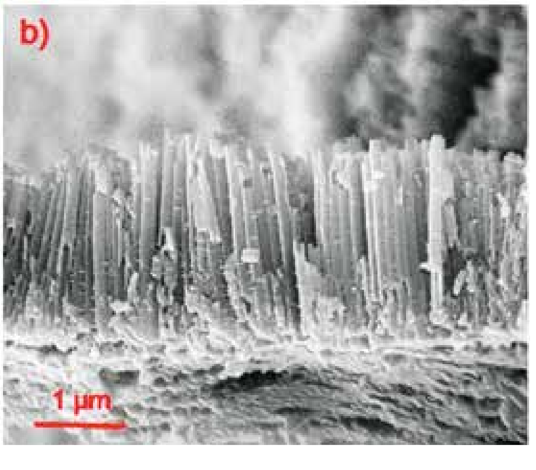
According to other publications and the results of my own research, the ordered structure has four important advantages over a disordered layer. Firstly, it absorbs light with a higher efficiency because light waves are reflected multiple times within nanotubes. Secondly, there are fewer recombination centers – locations which catch electrical charge – which lowers the value of the generated electricity. Thirdly, electrical charges move faster through ordered structures. Finally, other substances (such as drugs) can be placed inside the nanotubes and then gradually released when needed.

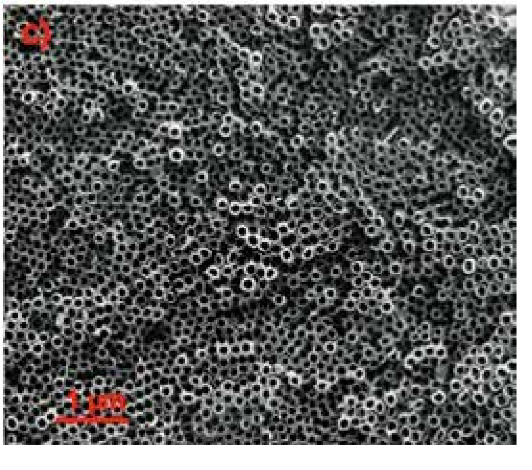
TiO_2 nanotubes in your mouth?

Thanks to their ordered morphology, TiO_2 nanotubes have been successfully used in photovoltaic cells, super condensers, photocatalytic processes involved in the degradation of contaminants by irradiating the material, in electrochromic devices in which a color change is caused by an electrical impulse, and in lithium-ion batteries. Researchers from Michigan Technological University recently announced that titanium dioxide nanotubes can also be used to coat dental implants. Although many existing implants are perfectly sufficient, some fall out or need to be removed due to problems such as infections. Research indicates that using a TiO_2 coating on titanium implants eliminates such complications. Additionally, tests on new generation implants show that a biocompatible titanium dioxide coating promotes faster growth of bone tissue and as a result improves the integration between the implant and the patient's bones. And these are not the only positive aspects: for instance, the tubular structures can be filled with anti-inflammatory drugs which are slowly released following the implant, eliminating the need for delivering the medication by mouth or as an injection. Additionally, thin layers of TiO_2 are transparent and provide a visually appealing, natural appearance of the implant.

Titanium dioxide nanotubes, invisible to the human eye, open a beautiful, brand new world in which familiar materials and device have unexpected applications. Techniques for putting the nano- and macro-scale worlds in order are certainly proving useful. ■

> When illuminated, titanium dioxide exhibits a high degree of chemical stability and catalytic and electrochemical activity. It is non-toxic and readily available, and it can be made in a variety of shapes.





Further reading:

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