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Peashell-like nanostructure—a new kind of one-dimensional nanostructure: the case of magnesium oxide†

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A novel type of 1D nanostructure with characteristics between those of a solid nanowire and a hollow nanotube, *i.e.* a peashell-like nanostructure comprising a 1D wire with periodically embedded hollow nanobubbles, is presented for the first time; as an example, MgO peashell-like nanostructures exhibit extraordinary dielectric and magnetization properties.

Since carbon nanotubes were discovered,¹ a large number of traditional bulk materials have been found to form one-dimensional (1D) nanostructures (such as solid nanowires and hollow nanotubes), and to exhibit interesting 1D-nanostructure-induced properties which have led to 1D nanostructures with a wide range of applications in nanoelectronics, optoelectronics, plasmonics, medical diagnostics, catalysis, drug delivery, therapeutics, separation, and chemical sensing.^{2–5} However, most of these 1D nanostructures are solid nanowires or hollow nanotubes. Therefore, it is still necessary to seek new kinds of 1D nanostructures and explore new unique properties and applications. Herein, we present a novel type of 1D nanostructure that is different from solid nanowires and hollow nanotubes, *i.e.* a peashell-like nanostructure, which is a 1D wire with periodically embedded hollow nanobubbles. The combination of such ultra-fine hollow nanobubbles and the 1D nanowire may impart some novel properties to the peashell-like nanostructure.

In this communication, an important dielectric material, magnesium oxide (MgO),⁶ has been selected as an example to synthesize a peashell-like nanostructure and show some intriguing properties of such a novel nanostructure. The synthesis strategy involves a self-catalysis vapor–liquid–solid (VLS) process in conjunction with the Kirkendall process. Due to their ultra-fine diameters and periodically embedded hollow nanobubbles, the largely synthesized 1D peashell-like MgO nanostructures show greatly enhanced dielectric function, 30 times higher than that of MgO micropowders in the low-frequency range. Moreover, such ultra-fine, embedded, hollow nanobubbles also give the peashell-like MgO nanostructures a 9 times stronger saturation magnetization than that of MgO nanoparticles (22 nm). Therefore, we believe that this new type of 1D peashell-like nanostructure not only confers the

capabilities of a multi-functional nanomaterial on MgO, but can also affect the properties (and may introduce novel properties) of other materials, such as transition metal oxides.

The X-ray diffraction (XRD) pattern of as-synthesized products can be well indexed to a face-centered cubic cell with $a = 4.2102 \text{ \AA}$, in good agreement with the standard data (ICDD-PDF 65-0476), confirming that this product is MgO with a face-centered cubic structure, as shown in a Supporting Information (SI) Figure (Fig. SI-1†). Fig. 1 demonstrates that the product contains a large amount of uniform ultra-fine 1D nanostructures. Each nanostructure has a big white tip with a rectangular shape (Fig. SI-2†). The transmission electron microscope (TEM) image in Fig. SI-3(a)† indicates that these ultra-fine 1D nanostructures are 10–30 nm in diameter. Each nanostructure has periodical bright spots when imaged under bright field TEM conditions [Fig. SI-3(b)†]. The bright spots invert contrast and appear dark when imaged under dark field TEM conditions [Fig. SI-3(c)†]. The TEM was configured to collect all of the diffracted electron intensity for dark field imaging, as shown by all of the MgO nanowires appearing white. The dark field image shows that the bright spots from the bright field image appear dark, meaning that they do not generate any diffracted electrons intensity. This confirms that the bright spots are due to absorption contrast and an increase in transmitted electron intensity. The increase in transmitted electron intensity can be due to a material impurity lighter in atomic number than MgO, or reduced thickness of the MgO nanowire. Considering the absence of impurities in the XRD pattern, it is proposed that the bright points are due to reduced thickness. To determine whether the reduced thickness is due to surface depressions or internal pores (nanobubbles), a TEM image clearly showing the nanowire structure and a high resolution TEM (HRTEM) are shown in Fig. 2(a) and (b), respectively. It can be seen that the atom array in the bright points is the same as the atom array in the darker surrounding areas. No sunken layer steps can be seen around the white points, which indicates that these white points are not umbilications on surfaces of the nanowires but are nanobubbles in the nanowires. Such nanobubbles increase the transmitted electron intensity and appear as bright points under bright field imaging conditions.

In the past decade, the VLS technique has been widely applied to synthesize 1D nanowires and nanotubes, in which liquid metallic nanodroplets act as catalysts to adsorb and dissolve reactant species to induce the nucleation and growth of nanostructures.^{7,8} The VLS mechanism has an obvious feature, *i.e.* each as-prepared 1D nanostructure has a big tip. Due to the big tips observed in the TEM images of the as-prepared 1D peashell-like nanostructures and the absence

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† Electronic supplementary information (ESI) available: XRD pattern, TEM images of the tip morphology, bright field and dark field TEM images of ultra-fine 1D peashell-like MgO nanostructures, and field-cooled and zero-field-cooled hysteresis loops of 1D peashell-like MgO nanostructures. See DOI: 10.1039/c0cc00167h

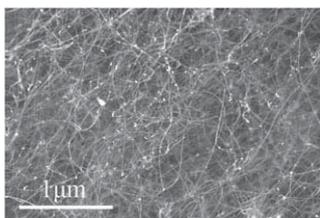


Fig. 1 SEM of peashell-like MgO nanostructures.

of other metallic droplets, it is likely that Mg droplets have functioned as a catalyst, inducing the formation of 1D MgO nanostructures during our experiment. In the first step, Mg powder is heated to generate Mg vapors at 950 °C under argon atmosphere, and some Mg vapors are condensed to form liquid Mg droplets in the low-temperature region. Then, oxygen gas is introduced to react with the Mg vapors, so that the reactant MgO, and the unreacted Mg vapors and O₂ gas can be adsorbed and dissolved in the Mg droplets, as is shown in Scheme 1(A). Upon supersaturation in the liquid Mg droplets, MgO will precipitate from the edge of the Mg droplets (Scheme 1(B)). Due to the fast oxidation rate, the growth of MgO is relatively fast, so that part of the Mg droplet deforms into a cylindrical shape. Once this cylinder exceeds a certain length, it becomes unstable, and the Mg droplets pinch off periodically while the oxygen supply is maintained, until the Mg vapor sources are consumed (Scheme 1(C)–(E)). It is worth mentioning that not all nanowires have periodically embedded droplets due to temperature fluctuation in the growth process. When the Mg vapor sources are consumed, the Mg droplet tips will be oxidized into MgO tips with a rectangular shape. After that, 1D MgO nanostructures with periodically embedded Mg droplets, Mg-in-MgO peapods, are formed (Scheme 1(F)). This is similar to cases of other 1D metal oxide nanowires, such as Au-in-SiO₂,⁹ Au-in-Ga₂O₃,¹⁰ and Au-in-MgO¹¹ peapods with periodically embedded gold catalyst particles, which have also been synthesized by the VLS process. Instead of using gold droplets as catalyst, here we used Mg droplets as catalyst in our experiment.

In the second step, the inner periodically embedded Mg droplets will out-diffuse through the MgO wall to react with the oxygen gas in the tube furnace (Scheme 1(G)). Because the diffusion rate of the Mg atoms is faster than that of O atoms, vacancy-inward diffusion will occur to compensate for the unequal material flow and eventually results in the formation of hollow nanobubbles (Scheme 1(H)). This process is the so

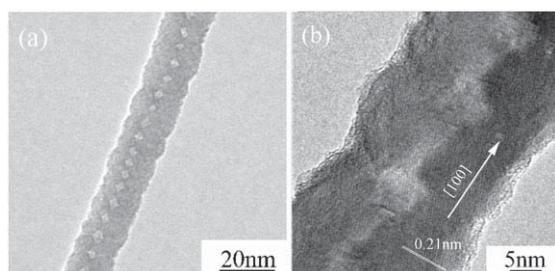
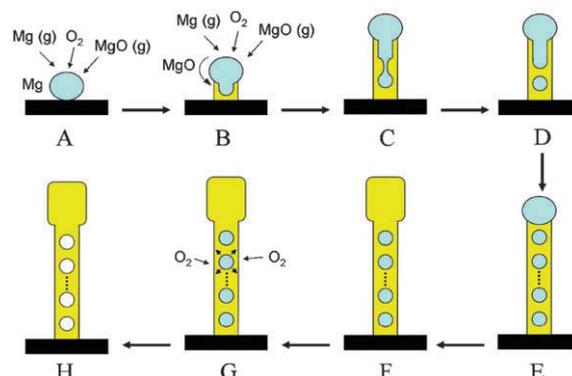


Fig. 2 TEM image (a) of peashell-like MgO nanostructures and (b) HRTEM image of single nanostructure.



Scheme 1 Schematic illustration of the formation of peashell-like MgO nanostructures by self-catalysis vapor–liquid–solid (VLS) process and Kirkendall diffusion process.

called Kirkendall diffusion process,^{12,13} which is a classical phenomenon in metallurgy. Coming to the nanoscale, since the synthesis of hollow nanocrystals was first reported by Alivisatos *et al.*,¹⁴ extensions to hollow nanostructures, such as hollow nanospheres^{15,16} and nanotubes,¹⁷ have recently been reported for this effective strategy.

The dielectric properties of the ultra-fine 1D peashell-like MgO nanostructures were measured in the frequency range from 40 Hz to 10 MHz at room temperature. Fig. 3 shows the room-temperature frequency spectra of the relative dielectric constant, ϵ_r , for samples of ultra-fine peashell-like MgO nanostructures and MgO micropowders. It can be seen that ϵ_r of the peashell-like MgO sample increases with decreasing measurement frequency, which is similar to previous reports for other nanomaterials.^{18,19} Amazingly, the ϵ_r of the ultra-fine peashell-like MgO nanostructures is enhanced by 30 times over that of the MgO micropowders, especially at low frequencies. Fang *et al.* also reported that the ϵ_r of MgO nanoflowers is 4 times higher than that of MgO micropowders at low frequencies.²⁰ According to the theory of dielectric polarization,²¹ it is the space charge polarization that mainly contributes to the enhanced dielectric behavior of ultra-fine peashell-like MgO nanostructures. In nanomaterials, the smaller size, larger interface area, and higher density of defects can induce more positive and negative space charges. When the charges are trapped by these defects, space charge polarization will occur. That is to say, nanostructured materials with small sizes and large interface areas can benefit in terms of the space charge polarization, and an abundance of defects, such as vacancies, dislocations, and dangling bonds in nanostructured materials, can also result in enhancement of the space charge polarization. Therefore, it is not difficult to understand that our ultra-fine peashell-like MgO nanostructures, which are only 10–30 nm in diameter with periodically embedded hollow nanobubbles, have great enhancement of ϵ_r compared to the bulk MgO micropowders. The ϵ_r enhancement of the MgO nanostructures occurs at low frequencies due to the space charge polarization appearing in the low-frequency range.

Fig SI-4 (a)† shows the results of magnetization measurements performed at 305 K on the peashell-like MgO nanostructures. It can be seen that these MgO nanostructures show a much

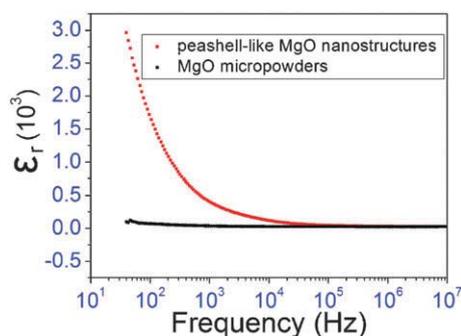


Fig. 3 Dielectric properties of the peashell-like MgO nanostructures and micropowders at room temperature.

stronger saturation magnetization (0.01817 emu/g), 9 times higher than that of the 22 nm MgO nanoparticles (0.00204 emu/g) which were reported by Kumar.²² It is well known that magnetism can arise from surface defects, which decrease with increasing particle size due to the decrease in the surface to volume ratio. Mg vacancies have also been reported to result in ferromagnetism of MgO nanoparticles.²³ However, our peashell-like MgO nanostructures are 10–30 nm in diameter with a similar or lower surface to volume ratio compared to that of the MgO nanoparticles reported by Kumar (22 nm), and they show no obvious enhancement of Mg vacancies due to the richer Mg vapor during synthesis. This suggests that the strong magnetic moments of the peashell-like MgO nanostructures may not originate from the surface of the nanostructures or from Mg vacancies, but originate from the periodically embedded hollow nanobubbles, which include nanobubbles with regular shapes: rhombohedral, cubic, and spherical (Fig. SI-2†). It has also been reported that the corners of such regular shapes can impart strong magnetic moments to otherwise non-magnetic materials.²⁴ On the other hand, field-cooled (FC) and zero-field-cooled (ZFC) hysteresis loops were measured at 5 K, respectively (Fig. SI-4 (a) and (b)†). There is no obvious shift of the hysteresis loop toward negative magnetic fields and no obvious enhanced coercivity, the so-called exchange bias, indicating that the strong magnetic moments mostly originate from inner nanostructures, *i.e.* hollow bubbles which include regular shapes, not from the surface. The two phenomena indicate that the periodically embedded hollow nanobubbles are likely to be mainly responsible for the strong magnetic moments.

In conclusion, a novel type of 1D nanostructure combining features of a solid nanowire and a hollow nanotube, a peashell-like nanostructure that consists of a 1D wire with periodically embedded hollow nanobubbles, is reported for the first time. Taking an important dielectric material as an example, large amounts of ultra-fine 1D MgO peashell-like nanostructures have been successfully synthesized by a self-catalysis VLS process in conjunction with the Kirkendall process. The ultra-fine 1D nanostructure and the periodically embedded hollow nanobubbles impart greatly enhanced dielectric responses, 30 times higher than that of MgO

micropowders, to these peashell-like MgO nanostructures. Moreover, the periodically embedded hollow nanobubbles also give these peashell-like MgO nanostructures a 9 times stronger saturation magnetization than that of MgO nanoparticles. We believe that such a new kind of 1D nanostructure, the peashell-like nanostructure, not only confers the properties of a multi-functional nanomaterial on MgO, but could also impart some novel properties to other materials. Therefore, these novel peashell-like nanostructures are likely to inspire a large amount of future work that will be important for the development of modern science and technology.

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