Solid-phase sintering and vapor–liquid–solid growth of BP@MgO quantum dot crystals with a high piezoelectric response

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Abstract: Low-dimensional piezoelectric and quantum piezotronics are two important branches of low-dimensional materials, playing a significant role in the advancement of low-dimensional devices, circuits, and systems. Here, we firstly propose a solid-phase sintering and vapor–liquid–solid growth (SS–VLS-like) method of preparing a quantum-sized oxide material, i.e., black phosphorus (BP)@MgO quantum dot (QD) crystal with a strong piezoelectric response. Quantum-sized MgO was obtained by Mg slowly released from MgB\textsubscript{2} within the confinement of a nanoflake BP matrix. Since the slow release of Mg only grows nanometer-sized MgO to hinder the further growth of MgO, we added a heterostructure matrix constraint: nanoflake BP. With the BP as the matrix confinement, MgO QDs embedded in the BP@MgO QD crystals were formed. These crystals have a layered two-dimensional (2D) structure with a thickness of 11 nm and are stable in the air. In addition, piezoresponse force microscopy (PFM) images show that they have extremely strong polarity. The strong polarity can also be proved by polarization reversal and a simple pressure sensor.

Keywords: quantum dots (QDs); piezoelectric; black phosphorus (BP); MgO

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1 Introduction

Quantum dots (QDs) are the basis of quantum technology [1–3]. The QDs are nanoparticles that exhibit three-dimensional quantum confinement with sizes below tens of nanometers. They are regarded as artificial atoms with zero dimension [4–10]. To date, semiconducting QDs [1], including CdS, ZnSe, CuInS, AgS, and InP, have been the most studied. Due to their unique optical and electrical properties, they are mainly used in optoelectronic devices, such as light-emitting diodes, transistors, and solar cells, as well as in bioimaging and biosensing applications [11,12]. Zhou et al. [13] proposed that resistive switching (RS) states were discovered in the Ag|TiO\textsubscript{x} nanobelt|Ti device under different moisture levels. Strong interplay with ions, electron transfer, and migration of OH\textsuperscript{-} ions push the device into the RS memory state. Zhou et al. [14] also prepared a memristor with the structure of Ag|graphene QDs|TiO\textsubscript{2}|F-doped SnO\textsubscript{2} that exhibited typical bipolar RS memory behavior. Negative photoconductivity (NPC) effect (increase in resistance exposed to illumination) has been observed in the RS memory, which has great potential for the application in photovoltaic devices. The semiconducting QDs can be made by molecular-beam epitaxy (MBE) or chemical vapor deposition (CVD), both of which are epitaxy methods [1,2]. More specifically, during the epitaxial growth of one semiconducting material from a substrate crystal of another semiconducting material (these two methods can also make non-semiconducting materials), crystals deposit as nano-islands near the heterojunction interface, which become the QDs under the appropriate conditions. This type of QD is formed by self-assembly, and thus is called a self-assembled QD [11]. For two-dimensional (2D) materials that are susceptible to exfoliation [15], such as graphene [16] and black phosphorous (BP) [17], the QDs are often obtained with mechanical or chemical exfoliation methods. Metal oxide QDs also show wide applications such as photocatalysis (TiO\textsubscript{2}), ultraviolet protection films (ZnO), gas sensing (SnO\textsubscript{2}), and high-temperature superconductors (CuO) [18]. However, due to their high surface energy, they have heightened mechanical, thermal, and chemical instability. It is therefore relatively difficult to achieve viable large-scale production. Embedding them in amorphous matrices [18] has been reported to be an effective way to obtain stable metal oxide QDs. Analogously, embedding them in a crystal matrix would be worth trying.

Novel low-dimensional piezoelectric [19] materials and quantum piezotronics are important branches of low-dimensional material research, as they play a significant role in the advances of low-dimensional devices, circuits, and systems [20,21]. Piezoelectric materials, which can convert mechanical and electrical energy, offer a wide range of applications, and have been utilized in a variety of smart devices [22] with both active functions (emitting sound waves, moving objects, etc.) and passive functions (such as sensing), are the key materials in the age of intelligence. The most widely known nano-piezoelectric material is ZnO [23–25]. Zinc oxides that have a wurtzite crystal structure or a cubic β-ZnS structure exhibit piezoelectric effects with single layers, which preserve the bulk materials’ piezoelectricity in 2D. In contrast, although the bulk material of MgO is not piezoelectric, we observed strong piezoelectricity in our synthesized BP@MgO QD crystal. This phenomenon has been described by Lin et al. [20], who demonstrated that from the perspective of crystallography, 2D morphologies represent spontaneous breakdowns of three-dimensional symmetries; therefore, the nonpiezoelectric bulk materials can exhibit their intrinsic piezoelectricity in 2D. Therefore, it may be possible to combine the piezoelectric nature of the 2D materials with other intriguing properties (e.g., quantum tunneling effect, semiconducting, or spintronic properties) in the QD crystals. Microscopically, the piezoelectric effect occurs when dipoles are aligned asymmetrically. Our MgO QD dipoles embedded in the 2D BP layers, similar to the tips of a needle, stand up on a flat surface without symmetry, but they are all aligned. They have the smallest size but the strongest piezoelectric effect. MgO QD can control the piezoelectric effect on the nanoscale and improve the compatibility between the piezoelectric materials and the nanodevices. The coupling between the piezoelectricity and the semiconducting properties in the BP@MgO QD crystals may be useful in powering the nanodevices, even the optoelectronic devices with only a few atomic layers thick.

To obtain small crystals, the reaction must be segmented and confined to a small area; thus, the product is unable to grow further. Mg slowly released by MgB\textsubscript{2} during heating can only produce nanometer-sized MgO, as shown in the Electronic Supplementary Material (ESM). Thus, confined conditions must be considered, and we added a heterojunction matrix: nanoflake BP.
The vaporization temperature of P is lower than the liquefaction temperature of Mg, so liquid Mg can preserve gaseous P very well. More importantly, the gaseous P provides good confinement for the growth of MgO. As the temperature decreases, P crystalizes to become the BP [26–30], while MgB2 decomposes completely and reacts with oxygen to form MgO and amorphous B2O3. With the BP as the vapor core, MgO QD-embedded BP@MgO QD crystals formed. These crystals are stable in the air; in other words, the MgO QDs and nano-BP are air-stable. The BP is easy to decompose in the air [31]. Most efforts have been made to make the BP stable [32–35]. With a stable crystal structure and high piezoelectric response, these powerful BP@MgO QD crystals are self-supporting freestanding, and compatible with any device. We also believe that by careful choosing of the segment and confine condition, the invented solid-phase sintering and vapor–liquid–solid growth (SS–VLS-like) method [36] in this work can be used to prepare other metal oxide QDs.

2 Materials and methods

High-purity MgB2 and red phosphorus (RP) powders (> 99.9%) as starting materials with a ratio between 4 : 1 and 5 : 1 were put into a vacuum ball mill and milled under N2 protection for 48 h. The same results were obtained with both dry and wet ball milling. The mixed powders were placed in a sealed crucible without vacuum for heat treatment at 670 °C for 12 h.

The BP@MgO QD crystals were thoroughly ground and dispersed in ethanol, and then dropped on the sticky side of a copper foil strip. It would dry naturally in about 2 min. By using a small iron ring with an inner diameter of 9 mm and an outer diameter of 12 mm as a mask, the upper electrode was sputtered on the side coated with BP@MgO QD crystal film by a magnetron sputtering apparatus. Finally, it was wrapped with a polyimide tape.

The morphology of the as-prepared samples was characterized by a scanning electron microscope (SEM; S4800, Hitachi, Japan; 5 kV). Transmission electron microscopy (TEM) observations were conducted with a JEM-2011 microscope (JEOL, Japan) operated at 200 kV and a JEM-ARM200F microscope (JEOL, Japan) equipped with an energy-dispersive X-ray spectrometer. X-ray diffraction (XRD) patterns were obtained by an X-ray diffractometer (D8 Advance,Bruker, Germany) with a Cu Kα radiation source (λ = 0.15418 nm). Raman spectra were collected with a spectrophotometer (InVia, Renishaw, Germany) using a laser of 514 nm. Fourier transform infrared (FTIR) spectra were recorded on a spectrometric analyzer (6700 FTIR, Nicolet, USA). Thermal gravimetric (TG) analysis was carried out with a Q600 SDT instrument (TA Instruments, USA) under an N2 atmosphere. The N2 adsorption–desorption isotherms were obtained by using a 3Flex analyzer (Micromeritics, USA) at a testing temperature of 77 K. Before the measurements, each sample was degassed under vacuum at 200 °C for at least 8 h.

Piezoresponse force microscopy (PFM) results were conducted with a piezoresponse force microscope (NT-MDT Spectrum Instruments, Ntegra Prima, Russia). The output voltages of BP@MgO QD crystal pressure sensor were tested by a high-precision digit multimeter (DMM7510, Keithley, USA).

3 Results and discussion

A schematic illustration of the formation mechanism of the BP@MgO QD crystals is shown in Fig. 1. MgB2, with the properties of slow Mg release and a low melting point (650 °C), was the source of quantum-sized Mg. The RP with a low vaporization temperature (580 °C) and 2D crystal phase BP were the source of the vapor core (later the nano-BP). How can the vapor be the core? Because only the vapor core, which is preserved by liquid Mg, remains. Therefore, the amount of the Mg source is 4 times that of the P source. The mixture of MgB2 powders and RP was ball milled for 12 h under nitrogen gas inside an uninsulated crucible. The temperature of this setup was gradually increased to 670 °C and then maintained for 12 h, followed by cooling to room temperature. The resulting powders were a mixture of the BP@MgO QD crystals and amorphous B2O3. The micromorphology of the BP@MgO QD crystals was 2D layers, and the matrix was 2D nano-BP crystals. More details are shown in the ESM. The slowly released Mg, which initially existed in the solid state, was the precursor of the MgO QDs. When the temperature increased to 580 °C, phosphorous became a gas. When the temperature reached 650 °C, elemental Mg turned into liquid. After all of MgB2 had decomposed into Mg and B, the whole system consisted of gaseous phosphorous, liquid Mg,
and amorphous $B_2O_3$, with $B_2O_3$ preserving P and Mg to be similar to paraffin. Once the temperature decreased, the BP@MgO QD crystals grew and deposited analogously to the VLS model in CVD [36–38]. The whole process can be summarized as the method of SS–VLS-like growth, which contains two stages. At the first stage, i.e., solid-phase sintering, as the temperature increased, Mg was slowly released from MgB$_2$ and became liquid, with P turning into its vapor phase. B reacted with O$_2$ and produced amorphous solid phase $B_2O_3$. The amorphous $B_2O_3$ preserved liquid Mg and vapor P like paraffin wax. The second stage is the VLS-like growth. At this stage, the temperature decreased, and the volume of the system shrank. With $O_2$ getting involved in the reaction, P crystalized and became BP. Simultaneously, QD liquid Mg reacted with $O_2$ to become MgO QD, and a lot of MgO QDs were formed at the surface of layered BP. As shown in Table 1, according to the state of raw materials in the preparation process, the preparation methods of the QDs are divided into three categories: solid phase method, solution method, and gas phase method. The SS–VLS-like method uses the solid-phase sintering and undergoes a vapor–liquid–solid state transition during the whole reaction process. Therefore, this method has the advantages of the solid phase, solution, and gas phase methods. By carefully choosing the segment and confine condition, the application scope of the SS–VLS-like method can be expanded. In particular, the obtained QD crystals are self-supporting, freestanding, and compatible with any device.

![Schematic illustration of formation mechanism of BP@MgO QD crystals.](image)

**Fig. 1**  Schematic illustration of formation mechanism of BP@MgO QD crystals. Mixture of MgB$_2$ powders and RP are starting materials. With temperature increasing, MgB$_2$ continues to decompose into Mg, MgB$_4$, and MgB$_7$ until all of MgB$_2$ is disassembled [35], and whole system consists of liquid Mg, P vapor, and amorphous solid $B_2O_3$. As temperature decreases, P vapor crystallizes into layered BP; simultaneously, segmented liquid Mg reacts with $O_2$ to produce MgO QDs on surface of layered BP, and MgO and BP grow together by atomic connection of Mg$_2$P$_2$O$_7$. Thus, BP@MgO QD crystals form by SS–VLS-like growth.

| Synthesis method | Advantage | Disadvantage |
|------------------|-----------|--------------|
| Solid phase method | Solid-phase sintering and mechanical grinding | Simple operation, high yield, good repeatability, and fine and stable product particles | Non-uniform particle size distribution, irregular morphology, and easy oxidation |
| Solution method | Microemulsion method, co-precipitation method, and hydrothermal method | Simple operation, low toxicity of raw materials, and controllable particle size | Low fluorescence yield and large size distribution |
| Gas phase method | CVD and MBE | Easy to combine with semiconductors and high charge transfer efficiency | High cost |
| SS–VLS-like method | Solid-phase sintering and vapor–liquid–solid growth | Simple operation, good repeatability, low toxicity of raw materials, and high charge transfer efficiency | Application scope to be expanded |
The TG–differential thermal analysis (TG–DTA) (Fig. 2) shows that the system was in an exothermic state beginning at a temperature of 700 °C, indicating that no chemical underwent phase change. At approximately 345 °C, the mass of the system started to increase, which was likely related to the burning of elemental Mg; additionally, the oxides in the system, including B$_2$O$_3$, MgO, and Mg$_2$P$_2$O$_7$, began to form. The period after the system reached 650 °C was where the vapor, liquid, and solid phases coexisted. Figure 2(b) shows the XRD pattern of the BP@MgO QD crystals. These crystals are composed of BP (PDF Card No. 76-1957), MgO (PDF Card No. 78-0430), and the heterojunction oxide Mg$_2$P$_2$O$_7$ (PDF Card No. 08-0038). Throughout the sintering process, as shown in Fig. 2(c), the solid B$_2$O$_3$ preserved the liquid QD Mg and P vapor to be similar to paraffin. When the temperature decreased, the P vapor crystalized into layered BP, the volume of the vapor–liquid–solid system shrunk, and Mg reacted with O$_2$ to produce MgO QDs on the surface of the layered BP. MgO and BP grew together by the atomic connection of Mg$_2$P$_2$O$_7$. Figure 2(c) also shows the detailed atomic connection of the heterojunction. In Fig. 2(d), the amorphous B$_2$O$_3$ looked like the paraffin wax, and the BP@MgO QD crystals arose from the sea of B$_2$O$_3$. Zooming in the BP@MgO QD crystals (Fig. 2(e)), it can be seen that their micromorphology was like 2D layers; this was due to their vapor core being layered by the BP crystals.

From the TEM images of the (200) plane of the
**BP@MgO QD crystals** (Figs. 3(a) and 3(b)), the size of the MgO QDs was determined to be approximately 2 nm. Note that crystal planes of (200), (020), and (002) are equivalent, as MgO is cubic. Figure 3(c) is the TEM image of the heterojunction between the BP and Mg$_2$P$_2$O$_7$ at the (040) plane of the BP and the (020) plane of Mg$_2$P$_2$O$_7$. Figures 3(d) and 3(e) illustrate the connection between the three phases in the BP@MgO QD crystals, where Fig. 3(e) shows the atomic construction in the plane, as shown in Fig. 3(c). P atoms circled with the dashed lines show the connection relationship between the P atoms in the heterojunction on the same plane. In the BP crystal structure in Fig. 3(d), the three neighboring P atoms, circled with solid lines, were replaced by Mg and O, thereby forming the heterojunction in Mg$_2$P$_2$O$_7$. These three positions form a triangle, where the distances between them were 4.380, 5.434, and 6.036 Å. It can be seen from the relative positions of the three P atoms (Fig. 3(e)), circled with solid lines, that the relative positions of the P atoms in Mg$_2$P$_2$O$_7$ depended on their positions in the BP, as the distances between them were 4.552, 5.381, and 6.630 Å. Figures 3(f)–3(i) display energy-dispersive X-ray spectroscopy (EDS) analysis of the mixture of the BP@MgO QD crystals and B$_2$O$_3$. The images show that the P and Mg atoms mainly existed in the crystal area circled with the white dashed lines, while the B atoms were present across the whole field of view. This further suggested that the BP and MgO form the BP@MgO QD crystals, and that the B atoms existed as amorphous B$_2$O$_3$.

The piezoelectric properties of the BP@MgO QD crystals were characterized by the PFM, Raman spectroscopy, and infrared spectroscopy. Compared to traditional piezoelectric materials such as BaTiO$_3$, zero-dimensional MgO displayed a simpler piezoresponse. In theory, because zero-dimensional MgO is a uniaxial crystal (Fig. 4(o)), its vibration is primarily along its axial axis, from the stretching and bending vibrations of Mg–O bonds, while the vibration perpendicular to the axial direction is trivial. In addition, the vibration amplitudes under the same voltage should be the same. The PFM results showed that the signals from the out-of-plane amplitude and out-of-plane phase were fairly

![Fig. 3](https://www.springer.com/journal/40145)

**Fig. 3** TEM images of BP@MgO QD crystals, EDS mappings, and 2D schematics of crystal structures. (a–c) TEM images of BP@MgO QD crystals, where (b) is magnified view of MgO QDs in (a), and (c) is lattice joint of heterojunction-phase Mg$_2$P$_2$O$_7$ and BP. Numerous MgO QDs can be seen in these TEM images. (d, e) Details of atomic connection between three phases in BP@MgO QD crystals. It is clear that relative positions of P atoms in Mg$_2$P$_2$O$_7$ somehow inherit their position in BP. (f–i) Energy mapping results, where white dashed lines circle crystal fragment. P and Mg atoms mainly existed in crystal area, while B atoms were present across the whole field of view.
strong, revealing significant contrast; in comparison, the signals from the in-phase amplitude and in-plane phase were lower (Figs. 4(e) and 4(f)). This difference between the amplitudes was mostly dependent on the distribution of the MgO QDs; in other words, the areas with amplitude signals appeared where the MgO QDs were located. There were bands of equal width in both Figs. 4(b) and 4(d) (with magnification in Fig. 4(c)) that were measured to be approximately 11 nm. These bands were caused by contrast, while the lamellar BP@MgO QD crystals vibrated along with changes in thickness; therefore, the width of the bands represents the thickness of the crystals. Figures 4(g)–4(j) are the PFM images when a direct current (DC) bias of ±10 V was applied to the area indicated by the dashed lines. Because the MgO QDs are not smooth like piezoelectric nanofilms, there was a slight shift in the images during the measurement. This behavior was different from the motion of the piezoceramic domain walls and was caused by the changes in the positions of the MgO QDs. Regardless, comparing the areas after applying positive and negative voltages revealed polarization reversal [39], taking Figs. 4(h) and 4(j) as examples. When a forward bias or a reverse bias was added, substantial phase changes in the vibrations of the MgO QDs were measured, while the amplitudes became more similar. A phase–voltage loop of the BP@MgO QD crystals was that of a typical electric hysteresis.
loop, and an amplitude–voltage loop demonstrated butterfly loops. The piezoelectricity at the two lowest points in the butterfly loop (i.e., the voltages at the coercive field) were $-1.2$ and 0.55 V. Interestingly, there were no signals in the Raman spectrum, even after multiple measurements (Fig. 4(m)). Theoretically, this was because the Raman spectrum detects vibrations from nonpolar symmetric molecules [40,41], and the BP@MgO QD crystals are strongly polarized crystals with weak vibrations from symmetric molecules. In other words, different from MgO crystals [42,43], the lack of Raman signal just proved that the symmetry of the MgO QDs was broken, or even that it had no symmetry at all. In contrast, the FTIR spectrum showed ample information from polar molecules (Fig. 4(n)). The intense absorption band present in the region within approximately 900–1250 cm$^{-1}$ was due to the stretching mode of the $P-O$ bond of the pyrophosphate group $P_2O_7^{4-}$. The peak at 749 cm$^{-1}$ was attributed to the stretching mode of the $P-O-P$ bond. The IR band in the region within 500–600 cm$^{-1}$ was attributed to the bending mode of the $O-P-O$ bond [44]. Finally, the peak at 597.8 cm$^{-1}$ was caused by the stretching and bending vibrations of $Mg-O$ [45,46]. The value of $d_{33}$ was calculated as 654 pm/V (Fig. S10 in the ESM). Although this absolute value from the PFM test was not accurate, we could still see that this value was very high (the $d_{33}$ value of popular lead–zirconate–titanate piezoelectric (PZT) ceramics is about 300–500 pm/V).

To further demonstrate the strong piezoelectric effect of the BP@MgO QD crystals, we fabricated an extremely simple pressure sensor. As shown in Fig. 5(a), by using the adhesion of a copper foil bonding surface, we dispersed the finely ground BP@MgO QD crystals with ethanol, followed by dropping them onto the copper foil bonding surface and applying the BP@MgO QD crystal ethanol dispersion evenly. It would dry naturally in about 2 min. By using a small iron ring with an inner diameter of 9 mm and an outer diameter of 12 mm as a mask, the upper electrode was sputtered on the side coated with the BP@MgO QD crystal film by a magnetron sputtering apparatus. This setup could be secured by wrapping it with a polyimide tape. The thickness of the BP@MgO QD crystal film is about 7.5 μm (Fig. 5(d)). When this BP@MgO QD crystal-based pressure sensor is applied with a dynamic finger pressure of 9–11 N, its output voltage is shown in Fig. 5(f). We can see that the pressure response of the sensor has a high signal-to-noise ratio. By this sensor, we demonstrated the piezoelectric effect of the BP@MgO QD crystals and showcased their potential in the field of the sensor.
4 Conclusions

The BP@MgO QD crystals prepared in this work are self-supporting, freestanding, and compatible with any device. Their high piezoelectric response and zero dimensionality allow broad application prospects in the field of low-dimensional devices. The invented SS–VLS-like method proposed in this work can also be used to prepare other metal oxide QDs, after carefully choosing the segment and confine condition.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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