Uniform $\text{M}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ ($\text{M} = \text{NH}_4^+, \text{K}^+, \text{Cs}^+$) rhombic dodecahedral nanocrystals for effective antibacterial agents†

Junzhi He, a Huan Pang,* a,b Weiqiang Wang, a Yue Zhang, a Bo Yan, a Xinran Li, a Sujuan Li a and Jing Chen a

Uniform $\text{M}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ ($\text{M} = \text{NH}_4^+, \text{K}^+, \text{Cs}^+$) rhombic dodecahedral nanocrystals are successfully obtained using mild hydrothermal conditions or room temperature chemical precipitation method for their self-organization. The reaction temperatures and times play important roles in the possible growth proceeding of these nanostructures. Interestingly, from antibacterial testing, the nanostructured products show more effective antibacterial activity than that of the corresponding commercial products. Among these antibacterial nanomaterials, $(\text{NH}_4)_3[\text{PMo}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ rhombic dodecahedral nanocrystals show strong inhibition of the proliferation of $\text{E. coli}$ during the whole 48 h culture period, which makes it a promising antibacterial material for practical applications.

1. Introduction

The conspicuous physical–chemical properties of nanostructures, as we all know, are sensitively correlated to their surface morphology. It is very important to control the synthesis of nanomaterials to provide different shapes for morphology–property investigations.1–5 Over the past two decades, the development of a solution-based chemical control synthesis of micro/nanostructured materials has been expanded from monodispersed particles to nanowires/nanorods, cables, tubes, and polygons.6–9 The self-organization of micro/nanostructured building blocks resembles many natural dynamic processes where formation and organization take place simultaneously and has become an attractive research field in materials science.10,11 Naturally or artificially grown materials can exhibit rich morphologies and structures, such as cables, cubes, prisms, triangles, and disks,12–15 however, the challenge of developing a general technique to synthetically control the shapes and structures of building blocks has received limited success.

Polyoxometalates (POMs) are well-defined inorganic metal–oxygen anionic clusters, and the complexation of POMs with appropriate counter cations forms solid compounds exhibiting unique properties in broad fields of sciences such as catalysis, electrochemistry, photochemistry, magnetism, and medicine.16–20 Self-organized aggregates of POM and nanostructural POMs have attracted increasing attention owing to their remarkable properties reported.21–31 Among the solid POM compounds, $\text{A}_3[\text{PM}_{12}\text{O}_{40}]$, which is composed of inorganic monovalent cations ($\text{A}^+ = \text{NH}_4^+, \text{K}^+, \text{Cs}^+, \text{Ag}^+$, etc.) and Keggin-type $[\text{PM}_{12}\text{O}_{40}]^{-}$ anions ($\text{M} = \text{W, Mo}$), is one of most intensively studied systems. Muller et al. have reported the self-organization of $\text{M}_3\text{PW}_{12}\text{O}_{40}$ particles by changes in the synthetic conditions.27 Recently, they have successfully obtained cubic cesium hydrogen silicododecatungstate with rhombic bipyramidal morphology.32 However, developing a general technique to synthetically control the shape and structure of POMs has obtained limited development.

In the past years, inorganic nanomaterials have been emerging as a new kind of antimicrobial material to fulfill the increasing general demands for hygiene in daily life because of their large specific surface area and the persistence of high bioactivities. The predominant antimicrobial activity of inorganic nanomaterials can be attributed to the strong cytotoxicity to various bacterial cells, i.e. they can interact with the functional groups on the bacterial cell surface and inactivate bacteria.33–36 Nano/micromaterials generally show many size and shape-dependent properties, which is interesting for device applications. Several classes of POMs are known to have a broad spectrum of antiviral and antitumoral properties.37–41 Despite these promising factors, the development of POMs as antiviral or antitumoral agents has been limited as many derivatives have little or no hydrolytic stability.

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Herein, we have successfully synthesized uniform \( M_2\text{PMO}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O} \) (\( M = \text{NH}_4^+, \text{K}^+, \text{Cs}^+ \)) rhombic dodecahedral nanocrystals without any template agents or surfactants. The as-prepared nanomaterials show more effective antibacterial activity than that of the corresponding commercial product. Especially for \((\text{NH}_4)_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}\) rhombic dodecahedral nanocrystals, which have good antimicrobial activities and can effectively prevent bacteria from proliferating.

## 2. Experimental section

### Materials

Rhombic dodecahedral \((\text{NH}_4)_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}\) nanocrystals (named NH-3): in a typical synthesis, ammonium hydrogen carbonate (0.100 g) and phosphomolybdic acid hydrate (0.700 g) were added into 20.0 mL of \( \text{H}_2\text{O} \). Then, the solution was transferred into a 50 mL stainless-steel autoclave lined with poly(tetrafluoroethylene) (PTFE, Teflon), which was sealed and maintained at 100 °C for 12 h in an oven. The resultant sample was purified by centrifugation and washing with water and ethanol to remove excess reagents.

For NH-1: hydrothermal condition 100 °C, 6 h, for NH-2: hydrothermal condition, 100 °C, 16 h, the other reaction conditions are the same as NH-3.

Rhombic dodecahedral \( K_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O} \) nanocrystals (named K-3): in a typical synthesis, potassium chloride (0.100 g) and phosphomolybdic acid hydrate (0.500 g) were mixed with 4.0 mL of ethylene glycol and 11 mL of deionized water, and then stirred for 4.0 h. The resultant sample was purified by centrifugation and washing with water and ethanol to remove excess reagents.

K-1: room temperature, stirred for 1 h, K-2: hydrothermal condition, 100 °C, 1 h, the other reaction conditions are the same as K-3.

Rhombic dodecahedral \( \text{Cs}_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O} \) nanocrystals (named Cs-3): in a typical synthesis, cesium carbonate (0.100 g) and phosphomolybdic acid hydrate (0.500 g) were added into 15.0 mL of \( \text{H}_2\text{O} \). Then, the solution was transferred into a 50.0 mL stainless-steel autoclave lined with poly(tetrafluoroethylene) (PTFE, Teflon), which was sealed and maintained at 100 °C for 12.0 h in an oven. The resultant sample was purified by centrifugation and washing with water and ethanol to remove excess reagents.

Cs-1: hydrothermal condition 100 °C, 6 h, Cs-2: hydrothermal condition, 100 °C, 8 h, the other reaction conditions are the same as Cs-3.

### Bacterial culture and bacterial kinetic test

Samples bacterial culture: *Escherichia coli* (E. coli) was selected as a model bacteria. Bacteria cells were grown overnight in LB medium (Luria–Bertani broth, Lennox modification) at 37 °C and then harvested at the exponential growth phase via centrifugation. *E. coli* cells were washed twice to remove residual macromolecules and other growth medium constituents and re-suspended in sterile saline solution (0.9% NaCl). The bacterial suspensions employed for the tests contained from 10^6 to 10^7 colony forming units (CFU).

Bacterial kinetic test: for the kinetic test, 25 μg mL\(^{-1}\) nanomaterials \((\text{NH}_4)_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}, K_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O} \) and \( \text{Cs}_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O} \) rhombic dodecahedral nanocrystals were prepared in each sterilized flask and inoculated with an equivalent volume of *E. coli* suspension. The initial time of adding the nanomaterials to the LB bacteria suspension was taken as zero, and 1.5 mL aliquots were withdrawn from the flasks at set time intervals. Immediately, these aliquots were maintained at 4 °C to inhibit further bacterial cell division. After 48 hours, all of the solution was diluted to an appropriate concentration, read OD\(_{600}\) to count bacterial colonies (U-3010 spectrophotometer, Shimadzu, Kyoto, Japan).

Modified Kirby–Bauer technique: the nanomaterials were mixed with molten LB-agar at 25 μg mL\(^{-1}\) of late log phase bacteria (OD\(_{600}\) \( \frac{1}{2} \) 2.0) was then plated onto solidified nanomaterials agar plates and incubated at 37 °C for 24 h. The test was carried out in triplicate to ensure reproducibility.

### Characterization

The morphology of the as-prepared samples was observed on a Hitachi S-4800 field-emission scanning electron microscope (FESEM) at an acceleration voltage of 10.0 kV. The phase analyses of the samples were performed by X-ray diffraction (XRD) on a Rigaku-Ultima III with Cu Ka radiation (\( \lambda = 1.5418 \) Å).

Transmission electron microscopy (TEM) images and HRTEM images were captured on a JEM-2100 instrument microscope at an acceleration voltage of 200 kV.

### 3. Results and discussion

We demonstrated the successful control of the self-organization of ammonium oxonium molybdenum oxide phosphate rhombic dodecahedral nanocrystals by a mild hydrothermal condition at 100 °C without any seeds, surfactants or templates. The synthetic times and temperatures were also further measured for exploring the possible formation and growth mechanism of ammonium oxonium molybdenum oxide phosphate nanostructures.

The XRD pattern of a typical product is shown in Fig. 1, and in the left inset there is the optical photo of the as-prepared products. The position and relative intensity of diffraction peaks are in accordance with those of pure \((\text{NH}_4)_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O} \) (JCPDS no. 70-0129). In the right inset of Fig. 1, the crystal structure of ammonium oxonium molybdenum oxide phosphate is projected from Inorganic Crystal Structure Data (ICSD) 59380. We can see that polyhedrons show the MoO\(_6^{-}\) unit of \( \text{PMO}_{12}\text{O}_{40}\) (marked with an orange color hexagon ring), and such a symmetric molecular structure might drive the self-organization of ammonium oxonium molybdenum oxide phosphate particles at a molecular level and the \([\text{PMO}_{12}\text{O}_{40}]^{-}\) anions (Keggin-type), which it is easy to see self-organize the rhombic dodecahedral particle.\(^{28}\)
Representative scanning electron microscopy (SEM) images of the as-prepared samples are shown in Fig. 2a and b. The products mainly contain rhombic dodecahedrons with an average size of 200 nm in Fig. 2a and b. From the TEM image of sample NH-3, the size and morphology are further proved in Fig. 2c. The corresponding SAED patterns recorded along the mark shown in Fig. 2c are shown in Fig. 2d. These results indicate that the rhombic dodecahedral ammonium oxonium molybdenum oxide phosphate nanocrystals are single-crystal line structures.

To understand the growth mechanism of the rhombic dodecahedral ammonium oxonium molybdenum oxide phosphate nanocrystals accurately, it is necessary to investigate the morphology of the intermediates involved in the formation. Herein, samples were collected at different stages for the observation, shown in ESI Fig. S1a and b.† Clearly, small formless nanoparticles (6 h) have transformed to uniform rhombic dodecahedral morphology with the increasing time (12 h). When further prolonging the reaction time to 16 h or increasing the temperature to 160 °C, the size of the particle has changed from nanometers to several micrometers, and the uniform nanorhombic dodecahedral morphology has become a micropolyhedron in ESI Fig. S1c and d.† However, we also find some microrhombic dodecahedral crystals among these micropolyhedrons.

Besides the temperature and time of reactions, different amounts of the reactants would also affect the final morphology of the product. The SEM images of the products obtained using different amounts of the reactants are shown in Fig. 3. The morphology is near to the nanosphere when using 0.4 g of phosphomolybdic acid hydrate and keeping the other reaction conditions the same as in the Experiment section for ammonium oxonium molybdenum oxide phosphate. When increasing the amount of phosphomolybdic acid hydrate to 0.6 g, there are some nanorhombic dodecahedral particles. It is obvious that uniform nanorhombic dodecahedral particles have formed completely when increasing the amount of phosphomolybdic acid hydrate to 0.7 g. However, several nanorhombic dodecahedral particles have further grown to larger sized particles when increasing the amount of phosphomolybdic acid hydrate to 0.8 g. The above aggregations of particles are the same as N. Mizuno et al. reported.28 It is probable that the formation and aggregation of particle proceeds by ‘nucleation–formation–growth’.

NH₄⁺, K⁺, and Cs⁺ are inorganic monovalent cations, so, it is not surprising that potassium oxonium molybdenum oxide phosphate (K₃[PMo₁₂O₄₀]·nH₂O) and caesium oxonium molybdenum oxide phosphate (Cs₃[PMo₁₂O₄₀]·nH₂O) uniform nanorhombic dodecahedral particles would be obtained under similar conditions. As was expected, we have successfully obtained K₃[PMo₁₂O₄₀]·nH₂O uniform nanorhombic dodecahedral particles by room temperature chemical precipitation method in a mixed ethylene glycol–deionized water solvent.

The XRD pattern of the typical product is shown in Fig. 4, and in the left inset there is the optical photo of product, and the colour is dark yellow. The position and relative intensity of

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**Fig. 1** XRD patterns of the product NH-3, obtained when ammonium hydrogen carbonate (0.100 g) and phosphomolybdic acid hydrate (0.700 g) were added into 20.0 mL of H₂O, and maintained at 100 °C for 12 h under hydrothermal conditions. In the left inset there is the optical photo of the product, and in the right inset the crystal structure of (NH₄)₃[PMo₁₂O₄₀]·nH₂O projected from ICSD 59380.

**Fig. 2** (a, b) SEM images of the product NH-3, obtained when ammonium hydrogen carbonate (0.100 g) and phosphomolybdic acid hydrate (0.700 g) were added into 20.0 mL of H₂O, and maintained at 100 °C for 12 h under hydrothermal conditions. The corresponding (c) TEM image, and (d) SAED patterns, the scale is 200 nm.
the diﬀerential peaks of the samples are in accordance with those of pure K₃[PMo₁₂O₄₀]·nH₂O (JCPDS no. 09-0408). In the right inset of Fig. 1, the crystal structure of K₃[PMo₁₂O₄₀]·nH₂O projected from ICSD 209 is shown, from which polyhedrons show the MoO₆ unit of PMo₁₂O₄₀ (marked with white color hexagon ring), which might drive the self-organization of K₃[PMo₁₂O₄₀]·nH₂O particles in the molecular level. The SEM image of K₃[PMo₁₂O₄₀]·nH₂O particles is shown in Fig. 5a, from which it can be seen it is composed of uniform rhombic dodecahedral particles with sizes of ~150 nm. TEM images from different viewing directions are shown in Fig. 5b and c. As in the corresponding SEM image, uniform rhombic dodecahedral K₃[PMo₁₂O₄₀]·nH₂O nanocrystals self-arrange. The single-crystalline structure of the rhombic dodecahedral K₃[PMo₁₂O₄₀]·nH₂O nanocrystals is proved by the corresponding SAED patterns shown in Fig. 5c.

We found that the morphology of the products obtained after only stirring for 1 hour (with the other reaction conditions the same as in the Experimental section for rhombic dodecahedral K₃[PMo₁₂O₄₀]·nH₂O nanocrystals) is not as uniform as that of 4 hours, and some crystals are much smaller than in the product after 4 hours in Fig. 6a. Hydrothermal condition also affects the morphology of products. Particles have become formless and the size has increased as the prolonging hydrothermal condition time from 1 to 4 hours in Fig. 6c and d.

The kind of reactants play an important role in the nano-structural formations of K₃[PMo₁₂O₄₀]·nH₂O particles. SEM images of samples obtained from the same amount of different potassium ions (K₂CO₃, K₃PO₄, K₂SO₄, or KCl, and phosphomolybdic acid hydrate (0.500 g) were mixed with 4.0 mL of ethylene glycol and 11.0 mL deionized water, and then stirred for 4.0 h) are shown in Fig. S2.† The morphologies of samples obtained from K₂CO₃ and K₃PO₄ show nearly no rhombic dodecahedral nanostructures, however some particles are aggregates in formless structures in Fig. S2a and b.† When using K₂SO₄, several rhombic dodecahedral particles were seen in Fig. S2c,† but some are near to nanospheres. The uniform rhombic dodecahedral K₃[PMo₁₂O₄₀]·nH₂O particles have been

![Fig. 3 XRD patterns of the sample K-3, obtained by mixing potassium chloride (0.100 g) and phosphomolybdic acid hydrate (0.500 g) with 4.0 mL of ethylene glycol and 11 mL of deionized water, and then stirring for 4.0 h. The left inset is the optical photo of the product, and right inset the crystal structure of KMoP is projected from ICSD 209.](image)

![Fig. 4 XRD patterns of samples obtained when ammonium hydrogen carbonate (0.100 g) and phosphomolybdic acid hydrate (0.500 g) with 4.0 mL of ethylene glycol and 11 mL of deionized water, and then stirring for 4.0 h.](image)

![Fig. 5 (a) SEM image of the product K-3, obtained by mixing potassium chloride (0.100 g) and phosphomolybdic acid hydrate (0.500 g) with 4.0 mL of ethylene glycol and 11 mL of deionized water, and then stirring for 4.0 h. (b, c) The corresponding TEM images. The inset of (c) shows SAED patterns, the scale is 150 nm.](image)
perfectly obtained by using KCl, as shown in Fig. S2d.† The role of ethylene glycol is also as a kind of morphology indexing agent. We do not obtain perfect rhombic dodecahedral nanocrystalline K$_3$PMo$_{12}$O$_{40}$ without ethylene glycol (Fig. S3†). The morphology of the product is formless particles, as seen in Fig. S3†. Indeed, we found that the pH value possibly affects the formation of K$_3$PMo$_{12}$O$_{40}$ nanocrystals. There are different pH conditions in the four potassium salts (CO$_3^{2-}$, PO$_4^{3-}$, SO$_4^{2-}$, Cl$^-$), and K$_3$PMo$_{12}$O$_{40}$ rhombic dodecahedral nanocrystals formed easily under neutral conditions (K$_2$SO$_4$ and KCl). We have done some experiments to prove this supposition in Fig. S4,† and it is seen that the morphology of the K$_3$PMo$_{12}$O$_{40}$ particles has changed from rhombic dodecahedral nanocrystals to formless micropolyhedrons with the increasing amount of KOH solution.

Cs$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O uniform nanocrystalline Cs$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O nanocrystals, XRD patterns and an optical photo of the typical product are shown in Fig. S5.† The morphology of Cs$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O was observed by SEM and TEM, as shown in Fig. 7. In Fig. 7a and b, different ways of packing are seen, and the size of a single rhombic dodecahedral nanocrystal is ∼100 nm. Furthermore, the product also shows single crystal characteristics from the SAED patterns in Fig. 7d.

We also tried to explore the possible formation of the rhombic dodecahedral Cs$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O, and found the times and temperatures of reactions affected the morphology of the product. In Fig. S6,† SEM images of samples obtained from different reaction times are shown. It is obvious that the morphology is nanospheres when the reaction is maintained under hydrothermal condition for 4 h in Fig. S6a.† When the time is increased to 6 h, the nanosphere has grown to a nanopolyhedron in Fig. S6b.† Several rhombic dodecahedrons can be seen in Fig. S6c† when the reaction time has been prolonged to 8 h. Then, uniform rhombic dodecahedrons have successfully formed in Fig. S6d.†

Small nanoparticles have formed in Fig. S7a† under room temperature by a chemical precipitation method, and some nanoparticles have grown to rhombic dodecahedrons in Fig. S7b† when raising the temperature to 60 °C. When further raising the temperature to 100 °C, the uniform rhombic dodecahedrons have successfully formed in Fig. S7c† and these uniform particles have further grown together and fused into spheres in Fig. S7d† as the temperature was further raised to 120 °C.

We demonstrate the successful control of the self-organization of [NH$_4$]$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O, K$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O and Cs$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O rhombic dodecahedral nanocrystals under mild conditions without any seeds or templates. We have quantitatively evaluated the antibacterial activity of the samples by studying the E. coli growth kinetics in LB liquid media (seen in Experimental section). The bacterial proliferation was monitored by the optical density at 600 nm (OD$_{600}$) based on the turbidity of the cell suspension within 48 h. The growth curve showed a typical nanostructured dependent antibacterial effect of [NH$_4$]$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O, K$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O and Cs$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O nanostructures and the corresponding bulk commercial materials (Fig. 8). Clearly, nanostructured [NH$_4$]$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O, K$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O and Cs$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O samples show better antibacterial activities than those of corresponding bulk commercial samples. It is interesting that the uniform rhombic dodecahedral nanocrystals have more effective antibacterial activities than those of formless particles and the corresponding bulk commercial sample in each kind of M$_3$PMo$_{12}$O$_{40}$ material. Especially, [NH$_4$]$_3$[PMo$_{12}$O$_{40}$]·nH$_2$O rhombic dodecahedral nanocrystals.
have the most effective antibacterial activity of all the uniform rhombic dodecahedral $\text{M}_3\text{PMo}_{12}\text{O}_{40}$ nanocrystals. This may be caused by the weak acidic properties of $\text{NH}_4^+$, and $\text{(NH}_4\text{)}_3[\text{PMo}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ rhombic dodecahedral nanocrystals can release $\text{NH}_4^+$ easier than the bulk sample because of their defect crystal plane surfaces. $\text{(NH}_4\text{)}_3[\text{PMo}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ rhombic dodecahedral nanocrystals killed nearly all the $\text{E. coli}$ during 48 h of experiments, as shown in Fig. 8a. Remarkably, $\text{(NH}_4\text{)}_3[\text{PMo}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ rhombic dodecahedral nanocrystals (NH-3) have strongly inhibited the proliferation of $\text{E. coli}$ during the whole 48 h culture period when the concentration of $\text{(NH}_4\text{)}_3[\text{PMo}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ rhombic dodecahedral nanocrystals (NH-3) was 25 $\mu\text{g mL}^{-1}$. These data suggested the long-term antibacterial activity of the $\text{(NH}_4\text{)}_3[\text{PMo}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ rhombic dodecahedral nanocrystals toward $\text{E. coli}$ bacteria suppression, which is particularly important to practical applications.

Table S1† shows the BET of as-prepared different samples. Although $\text{(NH}_4\text{)}_3[\text{PMO}_{12}\text{O}_{40}]$ particles show a larger BET value than those of others, it is difficult to find the direct correlation between the specific surface area and the antibacterial activity. We also investigated the antimicrobial efficiency of the NH-3, K-3 and Cs-3 rhombic dodecahedral nanocrystals by supplementing Luria–Bertani (LB) agar media with an aqueous suspension of NH-3, K-3 and Cs-3 rhombic dodecahedral nanocrystals at a concentration of 25 $\mu\text{g mL}^{-1}$. With the suspension of the bacterial $\text{E. coli}$ but no NH-3, K-3 and Cs-3 rhombic dodecahedral nanocrystals, the LB-agar was coated by many white dots corresponding to grown bacterial colonies, as shown in Fig. 9a. But with the addition of NH-3, K-3 and Cs-3 rhombic dodecahedral nanocrystals, from Fig. 9b, it can be clearly seen that the $\text{E. coli}$ can be killed largely by NH-3 rhombic dodecahedral nanocrystals and the LB-agar is transparent. With the addition of K-3 or Cs-3 rhombic dodecahedral nanocrystals, several white dots corresponding to part $\text{E. coli}$ bacterial colonies grow on the LB-agar in Fig. 9c and d, but they are fewer than those in Fig. 9a. To compare with bulk commercial samples, $\text{(NH}_4\text{)}_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$, $\text{K}_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ and $\text{Cs}_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ bulk commercial samples were used to investigate the antimicrobial efficiency by supplementing Luria–Bertani (LB)-agar media colonies on it. Fig. S8† displays photographs of $\text{E. coli}$ growing on LB agar coated with the different bulk commercial materials ($\text{(NH}_4\text{)}_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$, $\text{K}_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ and $\text{Cs}_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$). The results show that these bulk commercial materials display poor antimicrobial activities and only partly kill the bacteria under our experiment conditions. All these data demonstrate the superior antibacterial effect of $\text{(NH}_4\text{)}_3[\text{PMO}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$ rhombic dodecahedral nanocrystals (NH-3) against the bacteria $\text{E. coli}$, which guarantees it is a...
good potential choice as a kind of external-use antimicrobial drug. This property makes this material potentially usable to prohibit bacteria from colonizing on the surface of dental machines, textiles, and ceramic materials as an effective and stable inorganic antimicrobial agent.

4. Conclusions

In conclusion, uniform M₄PMO₁₂O₄₀·nH₂O (M = NH₄⁺, K⁺, Cs⁺) rhombic dodecahedral nanocrystals without any template agents or surfactants were synthesised by mild hydrothermal conditions or room temperature chemical precipitation method. The possible formation of these nanostructures has been explored, and it was found that reaction temperatures and times play important roles in the growth proceeding. More importantly, the nanostructured products show more effective antibacterial activity than that of the corresponding commercial products. Among these antibacterial nanomaterials, (NH₄)₃[PMo₁₂O₄₀]·nH₂O rhombic dodecahedral nanocrystals show strong inhibition of the proliferation of E. coli during the whole 48 h culture period. Given these advantages, we expect the [NH₄]₃[PMo₁₂O₄₀]·nH₂O nanostructures are a promising antibacterial material for clinical and environmental applications. It is a good example to prove that the physical and chemical properties of nano/microstructured materials are related to their structures, and the precise control of the morphology of nanomaterials will allow for control of the performance.

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