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Solid-state thermolysis of [MnO]₁₂ containing molecular clusters into novel MnO nano- and microparticles

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ABSTRACT

Novel MnO nano- and microparticles including spherical nanoparticles and various micropolyhedra of pyramid-like, truncated rectangular pyramid-like, cubic, and rhombic dodecahedral particles, were controllably synthesized via solid-state thermolysis of inorganic core containing molecular clusters $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ ($R = C_6H_5$, CH₃, and $C_6H_5OCH_2$) in a conventional horizontal tube furnace. Among them, pyramid-like, truncated rectangular pyramid-like, cubic, and rhombic dodecahedral MnO submicroscale particles were reported for the first time. The products were characterized by XRD, XPS, Raman spectrum, SEM, EDX, TEM and HRTEM. During the reaction process, thermolysis temperature, reaction time, and different molecular clusters {Mn12} precursors with different organic ligands as well play important roles in determining the sizes and shapes of the final products. The formed MnO nanospheres from $[Mn_{12}O_{12}(O_2CC_6H_5)_{16}(H_2O)_4]$ at 400 °C for 10 h exhibited weak ferromagnetic behavior at low temperature which may be due to the size-effect of nanomaterials. Furthermore, the possible formation mechanism was also discussed.

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1. Introduction

Recent years have witnessed the rapid development of nanomaterials especially semiconductors, metals, and metal oxides because they exhibit unique physical and chemical properties that differ greatly from their bulk counterparts, which depend on the sizes and shapes of them. [1-4] Until now, exploration of well-controlled synthetic methods for them is of higher challenge and interest. In the past few years, thermolysis of complexes has been applied to the generation of diverse nanoand micromaterials such as metal oxides and semiconductors as well as films and hybrid carboneous materials [5-15]. From the crystallographic viewpoint and growth mechanism, it may be a reasonable and in situ method. But the choice of right precursors becomes crucial. Meanwhile, molecular clusters have been intensively investigated because of their intrinsic beauty and interesting properties, such as metalloid molecular clusters and metal-sulfur (selenium, tellurium) molecular clusters as semiconductor, metal-oxo clusters as single molecular magnet (SMM) [16-21]. Moreover, some molecular clusters contain special

Manganese oxide (MnO) has attracted considerable interest because of its unique properties and applications in different areas such as catalysis, battery technologies and electrode, energy storage, ion exchange, and magnetic resonance imaging [23–27]. In the past few years, extensive studies have been devoted to fabrication of MnO nanostructures based mainly on the means of solution or template synthesis [28–36]. Different oxides of manganese such as MnO₂, Mn₂O₃, and Mn₃O₄, could be formed along with MnO. Up to now, exploring of selective and convenient methods for the fabrication of high quality MnO particles with novel structures from nano- to microscale is still of challenge.

Herein, we present a convenient molecular cluster precursor approach for the synthesis of various MnO nano- and microparticles. Through controlled thermolysis of nanoscale molecular clusters $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ ($R = C_6H_5$, CH₃, and $C_6H_5OCH_2$) in a one-end closed horizontal tube furnace, we successfully realized the solid-state transformation of inorganic core containing molecular clusters {Mn12} into novel MnO nano- and microscale particles in situ without using any reductive or template. Most interestingly, the phase, size, and morphology of the final products can be simply controlled by altering the precursor clusters, reaction temperature and time as well and

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inorganic cores. However, such work of utilization of molecular clusters especially nanoscale molecular clusters [22] for the fabrication of nano- and microscale metal oxide through solid-state thermal decomposition routes has never been reported.

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novel single-crystalline MnO nano- and microscale particles were obtained including spherical nano- and submicroscale particles and various submicroscale polyhedra including pyramid-like, truncated rectangular pyramid-like, cubic, and rhombic dodecahedral particles. Among them, pyramid-like, truncated rectangular pyramid-like, cubic, and rhombic dodecahedral MnO submicroscale particles were discovered for the first time.

2. Experimental

2.1. Materials

All of the reagents were of analytical grade and used without any further purification. Deionized water was used throughout the experiments. Manganese acetate ($Mn(O_2CH_3)_2 \cdot 4H_2O$), potassium permanganate ($KMnO_4$), sodium perchlorate ($NaClO_4$), and phenylformic acid (C_6H_5COOH) were purchased from Shanghai Chemical Co., China; tetra-butylammonium bromide (N-n-Bu₄Br) was purchased from Shanghai Lingfeng Chemical Co., Ltd., China; phenoxyacetic acid ($C_6H_5OCH_2COOH$) was purchased from Alfa Aesar; acetic acid (CH_3COOH), pyridine (C_5H_5), ethanol (C_2H_5OH), methylene dichloride (CH_2C1_2) and hexanes (C_6H_6) were purchased from Nanjing Chemical Co., China.

2.2. Synthesis of molecular clusters {Mn12}

Molecular clusters {Mn12} of [Mn₁₂O₁₂(O₂CC₆H₅)₁₆(H₂O)₄] (**1**) and [Mn₁₂O₁₂(O₂CCH₃)₁₆(H₂O)₄] (**2**) were synthesized by the reported method [37,38]. The synthetic method of [Mn₁₂O₁₂(O₂CH₂OCC₆H₅)₁₆(H₂O)₄] (**3**) is similar to that of 1 and only C₆H₅OCH₂COOH replaces C₆H₅COOH. All the synthesized black molecular clusters {Mn12} were recrystallized from CH₂C1₂/hexanes for two times.

2.3. Synthesis of nano- and microscale structured products

Thermolysis was carried out in a conventional horizontal tube furnace reactor (see Scheme 1). First, powder of molecular cluster 1 (0.2 g) was layed flat on the bottom of a ceramic boat (with the length of 4.0 cm and width of 1.0 cm) and then the boat was inserted into the center of the quartz tube (inside diameter (i.d.) of 3.5 cm and length of 50 cm) mounted inside the tube furnace with two-end closed using stainless steel walves and sealed with Teflon cushions between the two ends of the reaction tube and the walves. Then the furnace was heated for hours at different temperatures in a heating rate of 10 °C min⁻¹. After every reaction was completed, the furnace was shut off and cooled to room temperature naturally.

Similarly, thermolysis of molecular clusters 2 and 3 also followed the same process above.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns were collected in a Shimadzu XRD-6000 (operating at 40 kV and 30 mA) with



Scheme 1. The sketch map of the conventional tube furnace used for thermolysis.

graphite-monochromatized Cu Ka radiation (wavelength $\lambda = 1.5147$ Å). X-ray photoelectron spectroscopy (XPS) was displayed on a VG MICROLB-MKII XPS spectrometer with a monochromatic Al $K\alpha$ source and a charge neutralizer. Field emission scanning electron microscopy (FESEM) studies were conducted with a well-aligned LEO1530VP SEM (Carl Zeiss INC.) operating at 200 kV and with an Oxford INCA energy dispersive X-ray analysis (EDX) to fulfill element microanalysis. Transmission electron microscopy (TEM) studies were operated on a JEOL 2100 TEM using at an accelerating voltage of 200 kV. Magnetic property analysis was performed on a superconducting quantum interference device (SOUID) magnetometer (MPMS XL-VII SOUID). Zero field cooling (ZFC) and field cooling (FC) curves were recorded under a 100 Oe applied field from 1.8 to 350 K. Thermogravimetric analysis (TGA) were carried out using a PerKinElmer Pyris 1 TGA (USA) with a heating rate of $10 \,^{\circ}\text{Cmin}^{-1}$ in a flowing N₂ atmosphere.

3. Results and discussion

3.1. Structure and phase characterization of the products

According to the TGA curves (see Fig. S1) of {Mn12} molecular clusters $[Mn_{12}O_{12}(O_2CC_6H_5)_{16}(H_2O)_4]$ (1), $[Mn_{12}O_{12}(O_2CCH_3)_{16}$ $(H_2O)_4$ (2), and $[Mn_{12}O_{12}(O_2CCH_2OC_6H_5)_{16}(H_2O)_4]$ (3), almost all organic ligands decompose from 400 °C, so we chose 400 °C as the initial thermolysis temperature and thermolysis at the following temperatures of 400, 500, and 600 °C for different reaction time produced different products. The crystalline structures and phase purity of as-synthesized products from 1, 2, and 3 were first investigated by XRD in Fig. 1. The crystal structure of these as-products is confirmed to be the MnO phase (sys: cubic; lattice: face-centered; S. G.: Fm3m [225]; cell parameters: a = 4.445 Å; Joint Committee on Powder Diffraction Standards (JCPDS) card no. 07-0230) and the six diffraction peaks are wellmatched to (111), (200), (220), (311), (222), and (400) crystal faces of pure solid MnO phase. The (200) peak is very strong, which may be due to the perfect crystalline of the samples. No characteristic peaks from other crystalline impurities were detected, indicating that MnO products which could be usually obtained by solution



Fig. 1. XRD patterns of as-synthesized products by thermolysis of {Mn12} molecular clusters in the one-end closed horizontal tube furnace: (a) from 1 at 400 °C for 10 h, (b) from 1 at 500 °C for 10 h, (c) from 1 at 600 °C for 10 h, (d) from 1 at 600 °C for 20 h, (e) from 2 at 500 °C for 10 h, (f) from 3 at 500 °C for 10 h, and (g) from 3 at 600 °C for 10 h.

methods were synthesized under current synthetic process with high crystallinity.

3.2. From molecular cluster $[Mn_{12}O_{12}(O_2CC_6H_5)_{16}(H_2O)_4](1)$ to MnO nano- and microparticles

Thermolysis of metal complexes has been used for the synthesis of many metal oxide nano- and microstructures. [39,40] In the present work, we chose nano-sized {Mn12} molecular clusters as precursors and successfully realized the transformation from {Mn12} to MnO nano- and microparticles. During the thermolysis process, reaction temperature plays an important role in the formation of the final products. From molecular cluster 1, MnO spherical nanoparticles and pyramidand truncated rectangular pyramid-like sub-microscale particles with different size were synthesized for the same reaction time of 10 h at different thermolysis temperature altering from 400 to 500 and 600 °C, respectively. Typical MnO nanospheres with a diameter of about 70 nm by thermolysis of **1** at 400 °C for 10 h are shown in Fig. 2(a) and (b). Thermolysis at 500 °C for 10 h gave pyramid-like MnO sub-microscale particles. As shown in Fig. 2c of the low-magnification SEM images, the synthesized products exhibit pyramid-like shapes with the average diameter of about $0.12\,\mu m$ and there are abundant pyramids in the samples, which are tightly stacked together and some of obvious spacing was found between them. From the high-magnification SEM images in Fig. 2(d), we can clearly see the trigonal faces of a single sub-microscale pyramid and different directional faces are shown in the samples. The fabrication of pyramid-like materials has been

studied for various metals, semiconductors, and metal oxides including metals such as Fe, Co, Ni, Cu, Ag and Au, semiconductors such as CdS, CdSe, and GaN, and metal oxides such as Fe₃O₄, ZnO, In₂O₃, and BaTiO₃. [41–49] To our knowledge, this is the first example of pyramid-like MnO sub-microstructures. Most interestingly, truncated rectangular pyramid-like MnO sub-micro-structures with the average diameter of 0.3 μ m (shown in Fig. 2(e) and (f)) were synthesized at 600 °C for 10 h.

The phase purity of as-synthesized MnO products from molecular cluster **1** was further identified by XPS in Fig. S3. In XPS, the binding energies are standardized for specimen charging using C 1 s as the reference at 284.6 eV. We can see that all the samples possess the $Mn2p_{3/2}$, $Mn2p_{1/2}$, and O1s binding energy of 641.2, 656.0, and 532.0 eV, which match well with the standard data of MnO in the literature [50–52]. And no obvious impurities could be detected in the samples, indicating that the level of impurities is lower than the magnification limit of XPS (1 atom%). From the Raman spectra in Fig. 3(a'), the products did not show obvious peaks at 1320 and 1590 cm⁻¹ which originate from disordered and ordered graphitic carbon, [53] respectively, indicating that they were only pure MnO.

The as-synthesized MnO nanospheres from molecular cluster **1** were further characterized by TEM and high magnification TEM (HRTEM). Fig. 3(a) and (b) shows typical low magnification TEM images of as-synthesized products, confirming that the synthesized nanospheres have an average diameter of about 70 nm, which is in accordance with the SEM results in Fig. 2(a) and (b). HRTEM image in Fig. 3(c) was taken from a single nanosphere, which provided further insight into the structure of as-synthesized MnO nanospheres. The spacing of the clear lattice fringes in



Fig. 2. Different magnification FE-SEM images of as-synthesized MnO by thermolysis of 1 in the one-end closed horizontal tube furnace (a) and (b) at 400 °C for 10 h, (c) and (d) at 500 °C for 10 h, and (e) and (f) at 600 °C for 10 h.



Fig. 3. (a) and (b) TEM and (c) HRTEM images of as-synthesized MnO by thermolysis of 1 at 400 °C for 10 h in the one-end closed horizontal tube furnace.



Fig. 4. (a) and (b) Low- and (c)-(e) high magnification FE-SEM images, and (f)-(h)TEM images of as-synthesized MnO by thermolysis of 2 at 500 °C for 10 h in the one-end closed horizontal tube furnace.

Fig. 4f was found to be about 0.256 nm, which was coincident with the (100) *d*-value of MnO. Furthermore, the EDX analytic results in Fig. S2 show that only Mn and O elements were detected with atom ratio of about 1:1, indicating that pure phase MnO was obtained from **1**.

To visualize the detailed shape and orientation of the formed pyramid- and truncated rectangular pyramid-like MnO submicroparticles from molecular cluster **1** more clearly, high magnification FE-SEM images of the synthesized single MnO polyhedron were obtained in Fig. S4. All the images in Fig. 4(a) give live structures of as-synthesized sub-microtruncated rectangular pyramids: clear arris, two parallel faces with the anterior small and back big, and trapeziform side faces. EDX analysis has been taken for as-synthesized pyramids and truncated rectangular pyramids. Only Mn and O were detected with the element molar ratio of Mn and O of almost 1:1, indicating that the products were pure MnO.

3.3. The effect of different precursors on the final products

Under the same reaction condition, thermolysis of the other two [Mn12] molecular clusters of **2** and **3** resulted in three kinds of MnO microparticles including sub-microspheres from **2** and sub-microcubes and rhombic dodecahedral sub-microparticles from **3**.

Fig. 5 shows different magnification FE-SEM and TEM images of the formed MnO sub-microspheres by thermolysis of 2 at 500 °C for 10 h. As shown in Fig. 4(a) and (b) of low magnification FE-SEM images, large-scale of uniform products were obtained.

From high magnification FE-SEM images in Fig. 4(c)–(e), the synthesized products show surface-smooth spherical with the average diameter of about 0.5 μ m. For their solid stack in Fig. 4(c), during examining process, some of the spheres desquamated and hollow shell structures were remained in the samples. Furthermore, TEM images in Fig. 4(f)–(h) further show that the synthesized particles have a diameter of about 0.5 μ m, which agrees with the SEM results. XRD patterns in Fig. S5 by thermolysis of **2** at 500 °C for different reaction time indicate that all the formed products were MnO phase.

Thermolysis of molecular cluster **3** at different temperatures resulted in different MnO sub-microscale polyhedra including cubic and rhombic dodecahedral sub-microparticles with different sizes. First, thermolysis of 3 at 500 °C for 10 h resulted in MnO sub-microcubes. As shown in Fig. 5(a)–(e) of the FE-SEM images, the formed MnO sub-microcubes have the average diameter of about 0.3 μ m. Fig. 5f shows the geometrical models of the cubic MnO sub-microscale particles, which lively exhibits the structures of the cubic samples. Furthermore, TEM images in Fig. 6(g and h and HRTEM image in Fig. 5(i) show that the synthesized MnO



Fig. 5. (a) and (b) Low- and (c)–(e) high magnification FE-SEM images, (f) geometrical models, (g) and (h) TEM images, and (i) HRTEM image of as-synthesized MnO by thermolysis of 3 at 500 °C for 10 h in the one-end closed horizontal tube furnace.



Fig. 6. (a)-(c) FE-SEM images, (d) geometrical models, (e) and (e) TEM images, and (f) HRTEM images of as-synthesized MnO by thermolysis of 3 at 600 °C for 10 h in the one-end closed horizontal tube furnace.

sub-microcubes have a diameter of about 0.3 µm. XRD patterns in Fig. S5 indicate that thermolysis of **3** at 500 °C for different reaction time of 5, 15, 20, and 30 h all gave MnO. Then thermolysis of **3** at 600 °C gave rhombic dodecahedral MnO sub-microparticles. As shown in Fig. 5 of FE-SEM, TEM and HRTEM images by thermolysis of **3** at 600 °C for 10 h, the synthesized MnO rhombic dodecahedral sub-microparticles were uniform with average diameter of about $0.4 \,\mu\text{m}$. Fig. 5(d) shows the lively geometrical models of the rhombic dodecahedral MnO sub-microparticles. XRD patterns in Fig. S6 of the products synthesized by thermolysis of 3 at 600 °C for different reaction time show MnO phase. With the increase of reaction time to 5 h, typical rhombic dodecahedral MnO appeared with FE-SEM images in Fig. 7(a). It is interesting to note that the formed rhombic dodecahedra have uniform diameter of about $0.3 \,\mu\text{m}$, as indicated in Fig. 7(b). With the reaction time rising to 15 h, MnO rhombic dodecahedra also appeared. At 600 °C for 20 and 30 h (see Fig. 7(c) and (d)), MnO rhombic dodecahedra with surface deformed were obtained. EDX analysis showed that there were only two elements of Mn and O in the particles and with the element ration of about 1:1 and this indicated that the as-formed products were also MnO phase. From above analysis, too longer reaction time is not good for the growth of the final products.

3.4. Reaction conditions on the final products

Comparison with different products generated from three {Mn12} molecular clusters **1**, **2**, and **3** indicates that the organic ligands play important roles in determining the sizes and shapes of the final products. The possible reason for the formation of different products may be due to that different organic ligands might provide different environments of the nucleation and growth of the final products and finally significantly affect the sizes and shapes of the final products. Reaction time has a

significant effect on the sizes of the final products. With the increase of reaction time, obvious changes in the relative intensities of the XRD peaks can be observed in Fig. S5, S6, and S7 and the peaks become higher and narrower. For instance, with the increase of reaction time, (200) diffraction peak becomes stronger and stronger. Such changes may be due to that the diameter of the produced particles is getting larger with the increase of time. FE-SEM images at different reaction time also proved that.

When direct thermolysis of **1** in the air, another kind of MnO Mn_3O_4 with XRD patterns in Fig. S8 of the products show that they are consistent with tetragonal Mn_3O_4 with JCPDS Card no. 24-0734 for abundant oxygen in the air participated in the process of decomposition of the precursor clusters and nucleation of the final products, but we could not obtained uniform products (see FE-SEM images in Fig. S9).

3.5. Magnetic properties of the as-synthesized MnO nanoparticles from $\{Mn12\}(1)$

Magnetism in small oxide particles is a universal feature. Standard ZFC and FC temperature-dependent magnetization (M(T)) curves of the synthesized MnO nanospheres from 1 at 400 °C for 10 h at 100 Oe in Fig. S10(a) show that these nanospheres reveal ferromagnetic behaviors at low temperature and the field-dependent magnetization (M(H)) of them at low temperature display hysteresis typical of a ferromagnet. The peak structure in the ZFC curve is the blocking temperature, $T_{\rm B} = 44.5$ K. Fig. S10(b) shows the *M* versus *H* data measured at 1.8 K; the magnetization shows no sign of saturation in the applied field of 0.1 T. The coercivity determined from the hysteresis loop is about 0.32 kOe. Recent studies have shown weak ferromagnetic behavior in nanosized MnO particles at low temperatures. The possible reason may be ascribed to the size and shape anisotropy effects and the purity of MnO nanoparticles and the exchange



Fig. 7. Different magnification FE-SEM images of as-synthesized MnO by thermolysis of 3 at 600 °C in the one-end closed horizontal tube furnace for different reaction time, (a) and (a') 5 h, (b) and (b') 15 h, (c) and (c') 20 h, and (d) and (d') 30 h.



Scheme 2. Proposed formation mechanism from the molecular clusters {Mn12} to MnO nano- and microstructures. See text for details (pink: Mn, red: O, and black: C). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

interactions between unpaired electron spins arising from oxygen vacancies at the surfaces of the nanoparticles [54,55].

3.6. Possible growth mechanism

Using the mixture of metals or metal oxides and carbon as precursors, carbon reductive method has widely used for the synthesis of various metal oxide nano- and microstructures [56-60] such as ZnO nanowires, nanobelts, nanosheets, and nanocastles and In₂O₃ octahedrons. Our synthetic route may be similar to it. Below the complete decomposition temperatures of the precursor, molecular clusters such as 250 °C, black products were obtained with high ratio of carbon in the samples proved by XRD patterns and EDX spectra. With the increase of temperature, carbon reductive process takes place and different MnO nano- and microstructures appeared. Generally, carbon reductive method uses metals and metal oxides as precursors, which needs high reaction temperature above 500 °C of metal oxides and metals even beyond 1000 °C. However, our method needs lower temperature of the complete decomposed temperature of molecular clusters.

The formation of MnO structures may include a decomposition-reduction-assembly process, and the involved chemical reactions may be given as follows:

$$\begin{split} [Mn_{12}O_{12}(O_2CC_6H_5)_{16}(H_2O)_4] &\to [Mn_{12}O_{12}]^{16+} \\ &\quad + 4H_2O + \ 16C_6H_5CO_2^- \end{split} \tag{1'}$$

$$[Mn_{12}O_{12}]^{16+} + 16e^{-} \rightarrow [Mn_{12}O_{12}] \tag{2'}$$

$$[Mn_{12}O_{12}] \rightarrow 12\{MnO\}$$
 (3')

Recently, Lee et al. [61] reported the synthesis of sponge-like nanoporous ZnO by decomposition of solid coordination complex precursor $[Zn(tda) \cdot H_2O]$ (tda = $S(CH_2COO)_2^{2-}$) at 300 °C. Thermolysis of layered metal oxide hybrid $[WO_3(bpy)_{0.5}]_n$ (bpy = 4,4'bipyridine) precursor at 600 °C gave regular rectangular orthorhombic $(WO_3)_n$ structures. [62] Based on our experimental results and in comparison with the reported solvent thermolysis synthesis mechanism, a possible mechanism for the formation of MnO structures from {Mn12} under current reaction condition is proposed in Scheme 2. By the assumption that the conversion process includes two processes: nucleation and growth. During the first process, with the increase of thermolysis temperature. organic moieties and inorganic coordinated water, molecules are gradually lost from {Mn12} molecular clusters and finally the [MnO]₁₂ inorganic core remained which serves as a nuclei for the further reaction stages, and their distribution inherits the [MnO] core of the mother structure. Meanwhile, with the deoxidization of the decomposed organic ligands, all Mn³⁺ and Mn⁴⁺ centers were converted into Mn²⁺. Deoxidization of decomposed organic ligands came from our experimental results below. Second, the formed [MnO]₁₂ inorganic core assembly from all directions and MnO structures were formed. Meanwhile, during the assembly process, with the influence of temperature and different organic atmosphere from different precursor clusters, different MnO structures were formed as a result of different thermolysis

environments. The oxygen in as-products should originate from the MnO-lattice in the starting {Mn12} because the reaction has been conducted with rigorous exclusion of other oxygen sources. During all the synthesis process, we tried without success to obtain other phased manganese oxides such as MnO₂, Mn₂O₃, and Mn₃O₄.

4. Conclusions

In summary, by a convenient molecular cluster and solventless approach through thermolysis of molecular clusters [Mn₁₂O₁₂ $(O_2CR)_{16}(H_2O)_4$] (*R* = C₆H₅, CH₃, and C₆H₅OCH₂), novel singlecrystalline MnO nano- and microscale structures was controllably synthesized including spherical particles and various sub-microscale polyhedra of pyramid-like, truncated rectangular pyramid-like, cubic, and rhombic dodecahedral particles. For the first time, direct solid-state transformation of manganese molecular clusters {Mn12} into MnO nano- and microstructures was realized. Thermolysis temperature, reaction time and different precursor {Mn12} clusters with different organic ligands as well play important roles in determining the sizes and shapes of the final products. Our results show that the convenient molecular cluster and soventless thermolysis approach to metal oxide is initially successful and among them, pyramid-like, truncated rectangular pyramid-like, cubic, and rhombic dodecahedral MnO sub-microscale particles were reported for the first time. Compared with the known synthesis of MnO, our approach is very simple and unprecedented. It provides a simple and convenient approach for the selective fabrication of metal oxides with novel structures from nano- to microscale. Further work concerning about broadening this field, investigation of mechanism in details, and design special structures with different sizes and shapes is going on.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at 10.1016/j.jssc.2009.03.002.

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