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TEMPLATE-FREE HYDROTHERMAL SYNTHESIS, PHOTOLUMINESCENCE AND SUPERHYDROPHOBICITY OF Cd(MoO_4) POLYHEDRAL STRUCTURE

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The hydrothermal synthesis of Cd(MoO_4) polyhedral structure has been realized in a large scale by a facile precipitation reaction between $CdCl_2$•2.5H_2O and Na_2MoO_4•2H_2O in the absence of any templates or additives. By adjusting the time and temperature of reactive system, Cd(MoO_4) polyhedral structure could be obtained. The growth mechanism was investigated on the basis of the results of time-dependent experiments. The wettability of the as-synthesized Cd(MoO_4) polyhedral structure films is studied by measuring water contact angle (CA). The static CA for water over 150^o is observed, which is closely related to both the concentration of the as-modified glass films and chemical modification. The structures, compositions, morphologies and properties of the as-prepared products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), photoluminescence spectra (PL) and UV–Vis spectroscopy.

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1. Introduction

Micro-nanoarchitectures with polyhedral structure have received tremendous interest in chemistry and material science because of their novel structure-related properties, such as low effective density, high specific surface area, efficient catalysts.[1, 2] Metal molybdates have been a recent focus. This is not only because of their diverse structural architectures but also as a result of potential applications such as photoluminescence, scintillator materials, and catalysis[3–5]. Cd(MoO_4) is one of the families of metal molybdates. It is well known owning to its excellent optical and chemical properties and electronic structure [6–8]. In the past few years, many efforts were focused on the development of new synthetic routes for preparing 1D, 2D, and 3D nanostructures, such as nanowires[9], nanotube[10], nanobelts[11], nanorods[12], nanodiscs[13], nanodendrites[14], and more complex shapes. But recently, a variety of synthetic methods have been developed for the synthesis of polyhedral nano- or microparticles. As anisotropic micro-nanocrystals, the growth habit of crystals always plays an important role in determining their final polyhedral shape. During the non-template synthesis, the large structural anisotropy of an inorganic compound and its high chemical potential in solution are two main driving forces for the formation of polyhedral micro-nanocrystals[15-17].

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To date, methods to manipulate these polyhedral structures usually include the use of various hard templates [18] or soft templates [19], which involve the adsorption of nanoparticles or polymerization on modified polymeric, or inorganic template surface and subsequent removal of the templates by calcinations or dissolution with solvents. These methods often bring difficulties related to materials compatibility, high cost and complex synthetic procedures, which may prevent them from potential applications. A number of template-free approaches employing different mechanisms, such as the Kirkendall effect [20] and Ostwald ripening [21], have been developed for the synthesis of polyhedral structure. However, the organization of micro-nanocrystals with polyhedral structures by a facile, template-free, one step solution route remains a significant challenge.

Usually, the solid surfaces with contact angles over 150 ^{o}C are attributed to superhydrophobicity[22]. In nature, many surfaces such as various plant leaves, water strider’s legs, desert beetle’s backs, and butterfly’s wings, exhibit amazing superhydrophobicity, which has been called the“self-cleaning” property. Water droplets can form nearly perfect spheres and readily roll off to pick up and remove the contaminants on the surface. It has been revealed that the superhydrophobicity is attributable to the combination of surface chemistry and rough structures of the surface. With the development of science, superhydrophobic materials are expected to apply in self-cleaning surfaces and completely water impermeable textiles. Among the metal oxides, $Cd(MoO_4)$ attracts much attention for the excellent optical and chemical properties and electronic structure. To the best of our knowledge, the simple fabrication of polyhedral structure $Cd(MoO_4)$ with superhydrophobic property has not been reported so far. Furthermore, it was observed that the obtained $Cd(MoO_4)$ showed a strong photoluminescence peak at 484 nm with the excitation wavelength 328 nm.

2. Experimental Section

2.1 Preparation of $Cd(MoO_4)$

$Cd(MoO_4)$ products were prepared by hydrothermal method in the absence of any template or additive. All reagents were analytical grade pure and used as received without further purification. In a typical procedure, 0.002 mol $CdCl_2$•$2.5H_2O$ and 0.002 mol Na_2MoO_4•$2H_2O$ were dissolved into 10 mL distilled water, respectively. After $CdCl_2$•$2.5H_2O$ powder was dissolved, the solution of Na_2MoO_4 was added, white precipitation formed immediately, continue stirring for 10 min. Subsequently, the resulting mixed solution was transferred into 30 mL Teflon-lined stainless steel autoclave and sealed tightly. Hydrothermal synthesis was carried out at 140~180 °C for 24 h in an electric oven without shaking or stirring. After cooling to room temperature naturally, the precipitation was collected, washed with distilled water and absolute ethanol for several times, and then dried in a vacuum oven at about 60 °C for 10 h.

2.2 Preparation of superhydrophobic surfaces

The surface of a glass substrate was cleaned with acetone to remove any pollutants, and then etched with a 30% hydrochloric acid aqueous solution. The superhydrophobic surface was prepared via a facile dip-coating method: firstly, a glass surface was modified by slow evaporation of a dilute Cd(MoO_4) ethanol dispersion, followed by drying at room temperature. In the second step, the films on glass substrates were modified by adding a methanol solution of 2% (v/v) 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane(PFOTS), followed by drying at 120 °C for 1 h.

2.3 Characterization of Cd(MoO_4)

The phase purity and crystal structure of the obtained products were examined by X-ray diffraction(XRD) using a MiniFlex2 goniometer , employing a scanning rate of 0.02°s^{-1} in the 2θ range from 10° to 80°, the operation voltage and current were maintained at 30 kV and 15 mA, respectively. The size distribution and morphology of the products were analyzed by scanning electron microscopy(SEM), the SEM morphology were observed by on a Scaning Electron Microscope (JSM-6610LV). The UV-vis spectra of the as-synthesized Cd(MoO_4) were recorded on a Lambda 25 spectrometer. Fourier transform infrared spectroscopic (FTIR) analysis was carried out using pressed KBr disks in the region of 4000-400 cm^{-1} by using a Perkine Elmer spectrometer instrument. Room-temperature photoluminescence(PL) spectra were recorded by a Hitachi 850 fluorescence spectrometer with a Xe lamp as the excitation source at 25 °C.

2.4 Wetting Behavior Test of the surfaces modified with Cd(MoO_4)

Water contact angle (CA) measurement was carried out on water droplet (drop volume 10 μL) by using an optical contact angle meter (Data Physics Inc., OCA 20) at room temperature.

3. Results and discussions

3.1 Structural analysis

The phase and composition of the products, which were prepared with different reaction conditions, were characterized by XRD (Figure 1). Figure 1(A) shows the XRD patterns of the products synthesized at 160 °C for 5 h, 9 h, 19 h, and 24 h, respectively. The lattice constants of Cd(MoO_4) are a=b=5.156 Å and c=11.196 Å, which are in good agreement with the standard values of the tetragonal phase Cd(MoO_4) (JCPDS Card Number 88-0182). No other peaks of impurities were detected, indicating that the products are pure tetragonal structure of Cd(MoO_4) crystals. From Figure 1(A), we also observed that the crystallinity of obtained products increased with the increasing of reaction time. Obviously, the reaction time plays an important role in the preparation of the Cd(MoO_4). Figure 1(B) shows the XRD patterns of the products heating at different temperatures, when the reaction time keeps 24h. . As shown in Figure 1(B), the crystallinity of products increases with the reaction temperature getting higher. Therefore, the temperature and time play important roles in determining the crystallinity of the Cd(MoO_4) crystals.

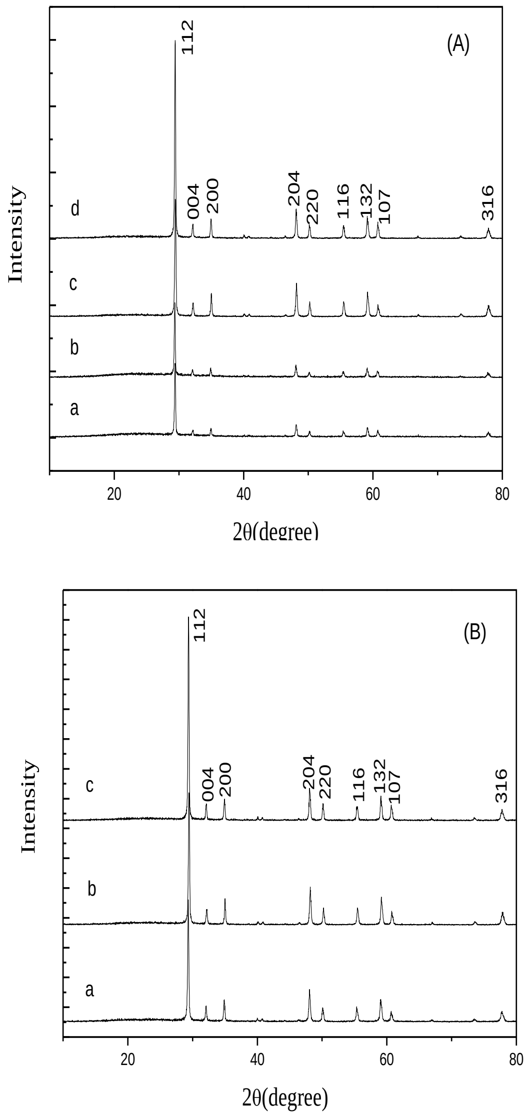

Fig. 1. X-ray diffraction patterns of Cd(MoO$_4$) obtained (A) under 160 °C, with different time: (a) t=5h (b) t=9h (c) t=19h (d) t=24h ; (B) under the same time at t=24h, with different temperatures: (a) T=140 °C (b) T=160 °C (c) T=180 °C

To confirm the formation of the Cd(MoO$_4$) crystal structure, Fourier transform infrared (FT-IR) spectroscopy was performed (Figure 2). The strongest absorption peak at 1016 cm^{-1} is assigned as ν_3 antisymmetric stretching, which is caused by the Mo-O vibration in [MoO$_4$]$^{2-}$ tetrahedrons [23]. It implies that the crystalline Cd(MoO$_4$) has formed in the as-prepared product.

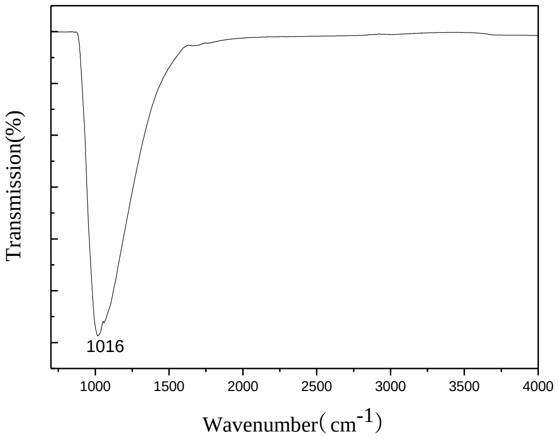

Fig. 2. The FT-IR spectrum of Cd(MoO$_4$) synthesized under 180°C, t=24h

3.2 Morphology Control

Fig. 3 shows the SEM images of the Cd(MoO$_4$) nanocrystals obtained at 160 °C with different reaction time. When the reaction time is 5 h, the morphology of the products is inhomogenous microspheres, which are composed of nanoparticles (Figure 3a). When the reaction time was 9 h, Cd(MoO$_4$) with irregular polyhedron morphology appeared, and the number of microspheres decreased (Figure 3b). With the reaction time increasing, the number of Cd(MoO$_4$) crystals with regular polyhedron morphology increased, and the number of microspheres decreased (Figure 3c~d). These results indicate that the reaction time is a key factor in the formation of Cd(MoO$_4$) crystals with regular polyhedron morphology.

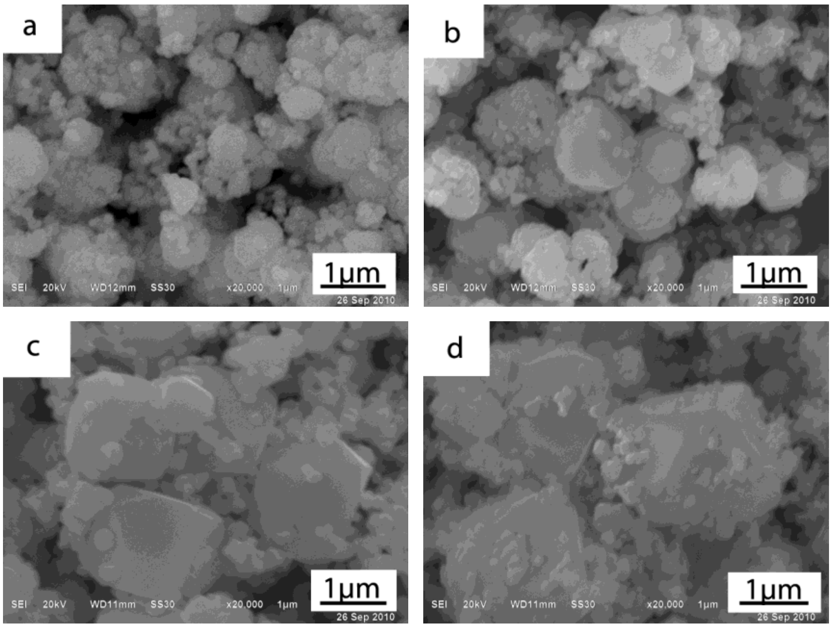

Fig. 3. SEM images of Cd(MoO$_4$) synthesized under 160 °C, with different reactive time:
(a) t=5h (b) t=9h (c) t=19h (d) t=24h

Fig. 4 exhibited the surface topography of the Cd(MoO$_4$) crystals, which were produced at different reaction temperature 140°C, 160°C and 180°C for 24h, respectively. It is clearly shown that the as-synthesized product presents irregular polyhedron morphology accompanying with nanoparticles (Figure 4a). When the reaction temperature was 160 °C, minority of Cd(MoO_4) crystals with regular polyhedron morphology were formed, and the number of nanoparticles reduced (Figure 4b). Increasing the reaction temperature to 180 °C, the quantity of Cd(MoO_4) crystals with regular polyhedron morphology was larger, and the number of nanoparticles became less (Figure 4c). These results indicate that the reaction temperature plays an important role in the formation of Cd(MoO_4) crystals with regular polyhedron morphology.

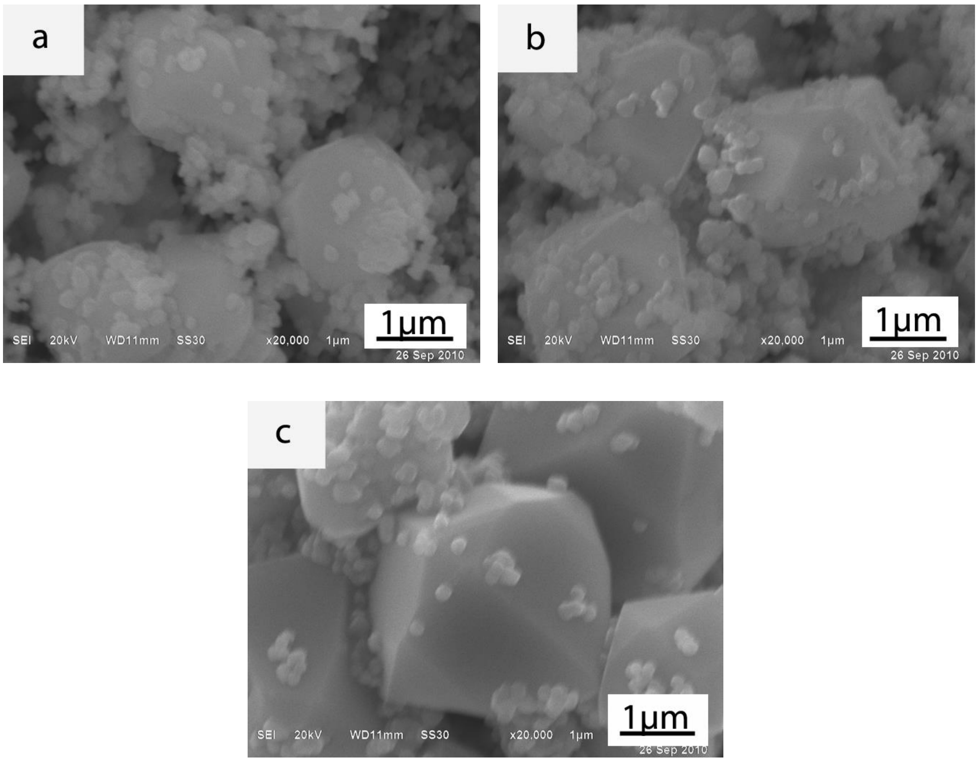

Fig. 4. SEM images of Cd(MoO_4) synthesized under t=24h, with different reactive temperatures: (a) 140 °C (b) 160 °C (c) 180°C

3.3 Formation mechanism

From Figure 3, we can probe the growth mechanism of the Cd(MoO_4) with polyhedron morphology. When the reaction time was 5 h, the morphology of the product was microsphere, which was composed of a great deal of small nanoparticles. When the reaction time increased to 9 h, the subunits (nanoparticles) grew larger and showed clear edges. When the reaction time was 19 h, some Cd(MoO_4) with irregular polyhedron morphology were observed, indicating that irregular polyhedron morphology began to form for the nanoparticles aggregating. Finally, Cd(MoO_4) crystals with regular polyhedron morphology formed heating for 24 h. It reveals that there are two growth stages during the whole process. One is the aggregation and growth of the nanoparticles, and the other is the formation of the regular polyhedron-shaped structure. According to our experimental results, it is reasonable to presume that the formation of Cd(MoO_4)

with polyhedron morphology is based on the Ostwald ripening mechanism, and the evolution process can be viewed in Figure 3. At the first stage, tiny Cd(MoO_4) nanoparticles were quickly produced, when the MoO_4^{2-} was added into the solution containing Cd^{2+}. Then, tiny nanoparticles aggregated spontaneously to form large microspheres to minimize their surface energy:

$$CdCl_2 + Na_2MoO_4 \rightarrow CdMoO_4\downarrow + 2NaCl$$

During the continuous heating process, these nanoparticles grew larger gradually. At the second stage, the kernels reached to the balance of dissolving and merging to form regular polyhedron morphology ultimately.

3.4 UV–Vis spectroscopy and Photoluminescence Properties of Cd(MoO_4)

UV–Vis spectroscopy has been used for characterizing the optical property of the Cd(MoO_4). Products for the UV/vis absorption spectra experiments were prepared by dispersing the as-prepared Cd(MoO_4) with ethanol in a sonication bath for 30 min to form clear solutions. Figure 5 gives the UV–Vis absorption spectra of the Cd(MoO_4) obtained under 180 °C, with different reactive time. As seen from Figure. 5, the spectra do not have much difference among the Cd(MoO_4) products prepared at different reactive time. All the absorption peaks of the products at about 326 nm, which is due to the charge-transfer transition between molybdenum and oxygen in MoO_4^{2-}. In addition, the steep absorption edge indicates that the band gap is due to the intrinsic transition of the micro-nanomaterials but not due to the transition from impurity level.

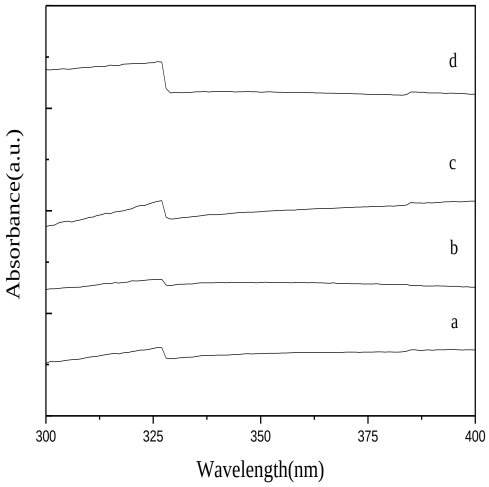

Fig. 5. UV/Vis spectra of the as-synthesized Cd(MoO_4) under 180 °C, with different reactive time: (a) t=5h, (b) t=9h, (c) t=19h, (d) t=24h

Fluorescence spectroscopy can supply valuable information about the intermolecular interactions of molecules in molecular crystals and monolayers[24]. Room temperature photoluminescence spectra of the as-synthesized Cd(MoO_4) were shown in Figure 6. All the products show a broad emission band centered at 483 nm with an excitation wavelength of 328 nm. Also, the intensity of the peaks at 483 nm increases sharply as the reactive time increases. Usually, the emission spectra of M(MoO_4) are mainly attributed to the charge-transfer transitions between the O 2p orbitals and the Mo 4*d* orbitals within the [MoO_4^{2-}] complex[25]. Previous researches have shown that the PL properties of M(MoO_4) are sensitive to synthetic conditions, morphologies, size, surface defect states, etc[23].

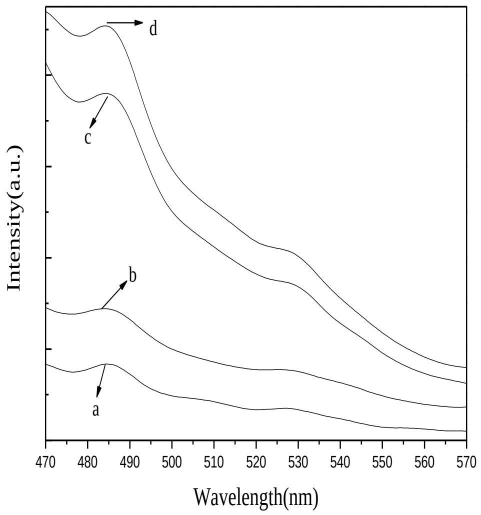

Fig. 6. Room-temperature photoluminescence spectra of Cd(MoO_4) obtained after the hydrothermal treatment under 180 °C, with different reactive time: (a) t=5h, (b) t=9h, (c) t=19h, (d) t=24h

3.5 Wetting Behavior of the as-synthesized Cd(MoO_4)

Surface wettability of the as-synthesized Cd(MoO_4) polyhedral structure films was studied by measurement of the water CA using a water droplet of 9 μL (Figure 7). Figure 7a shows the CA value of 63.9° of the glass surface without any treating. Figure 7b shows the CA value of 92.9° after the glass surface was treated by using a methanol solution of 2% (v/v) PFOTS. In contrast, the CA values of the glass treated with as-synthesized Cd(MoO_4) nanocrystals were measured. Distinct enhancement of hydrophobicity of the surface treated by using the as-synthesized Cd(MoO_4) could be observed. The different concentration of Cd(MoO_4) on the as-modified glass films varies from 0.02 to 0.04, and 0.06 $g \cdot mL^{-1}$, respectively. As shown in Figure 7c-e, the CA values are 126.1° (Figure 7c), 147.4° (Figure 7d), 154.7° (Figure 7e), corresponding to the concentration of 0.02, 0.04, and 0.06 $g \cdot mL^{-1}$, respectively. Besides, the CA value is 141.9° (Figure 7f), when the glass surface was treated only by as-synthesized Cd(MoO_4), without adding PFOTS, corresponding to the concentration of 0.06 $g \cdot mL^{-1}$. Such results confirm that the surface wettability of solid can be tuned via combining the formation of physical roughness with chemical surface treatment. Obviously, the concentration of the as-modified glass films and the use of PFOTS play important role in the surface wettability, and the reason may be as follows: when the concentration of the as-modified glass film is 0.02 $g \cdot mL^{-1}$, the CA value is considerably low. But when the concentration increases to 0.06 $g \cdot mL^{-1}$, the CA value increases to 154.71°, these results indicate that the concentration of the as-modified glass films can influence the roughness of the surface of glass, which leads to the wettability change. In addition, PFOTS can reduce surface energy, which also influences surface wettability.

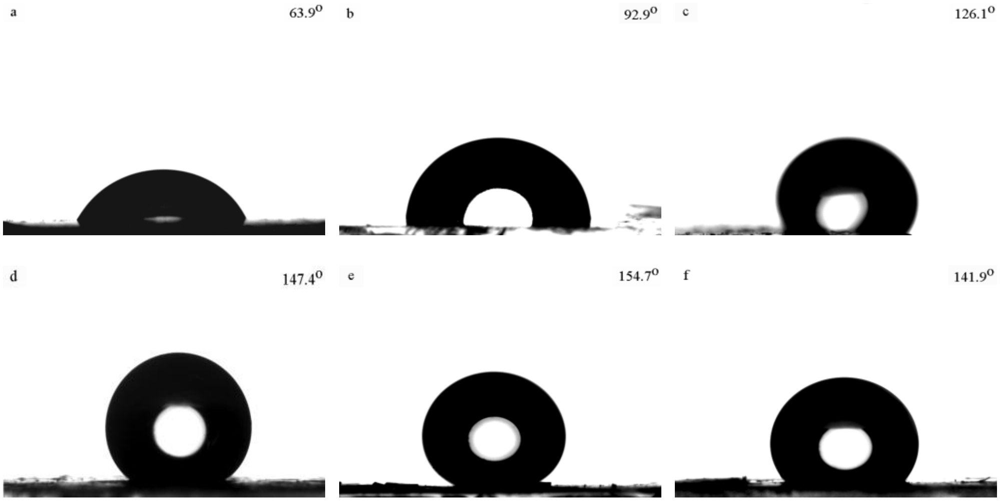

Fig. 7. Water contact angle (CA) measurements of (a) without any treating. (b) treated with PFOTS; (c, d and e) first treated with Cd(MoO$_4$) ethanol solution, corresponding to the concentration of 0.02, 0.04, and 0.06 g·mL^{-1}, respectively and a methanol solution of PFOTS; (f) only treated with Cd(MoO$_4$) ethanol solution, corresponding to the concentration of 0.06 g·mL^{-1}.

In a word, the superhydrophobicity of the glass modified by as-synthesized Cd(MoO$_4$) crystals and PFOTS can be attributed to constructing a much rougher surface texture on the glass surface and chemical treatment.

4. Conclusion

In summary, regular polyhedron-shaped structure of Cd(MoO$_4$) has been successfully prepared by a facile aqueous solution route in the absence of any templates or additives. The structural characteristics and luminescent performance of the as-prepared products were studied by XRD, SEM, FT-IR, UV–vis and PL. It was found that the reactive time and temperature of the hydrothermal solution play a key role on the morphology evolution of the products. Besides, a possible growth mechanism of Cd(MoO$_4$) with the morphology of polyhedron was briefly discussed. Additionally, superhydrophobicity of the Cd(MoO$_4$) polyhedral structure was demonstrated. The static CA for water over 150^{o} was observed, which was closely related to both the concentration of the as-modified glass films and chemical modification.

Acknowledgment

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