




Cite this: *RSC Adv.*, 2020, 10, 4554

# The synthesis of monodispersed M-CeO<sub>2</sub>/SiO<sub>2</sub> nanoparticles and formation of UV absorption coatings with them†

Su Xunwen,<sup>a</sup> Zhu Liquan,<sup>a</sup> Li Weiping,<sup>a</sup> <sup>a</sup> Liu Huicong <sup>\*,a</sup> and Ye Hui<sup>b</sup>

CeO<sub>2</sub>/polymer nanoparticles have drawn considerable attention for their excellent UV absorption properties. However, many challenges still exist in the successful incorporation of ceria into the polymer matrix for the easy agglomeration and photocatalytic activity of CeO<sub>2</sub> nanoparticles. Herein, we address these issues by constructing three-layer structured nanoparticles (M-CeO<sub>2</sub>@SiO<sub>2</sub>) and incorporating them into a polymer matrix through a mini-emulsion polymerization process. During this process, small-sized nano-ceria became uniformly anchored on the surfaces of monodisperse silica particles first, and then the particles were coated with an MPS/SiO<sub>2</sub> shield. The morphology and dispersion of the nanoparticles were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The performance of the hybrid films was characterized using UV-vis absorption spectroscopy (UV-vis) and water contact angle (WCA) measurements. Results showed that the M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles exhibited a three-layer structure with a mean diameter of 360 nm, and they possess good compatibility with acrylic monomers. After the addition of M-CeO<sub>2</sub>@SiO<sub>2</sub>, hybrid films exhibited enhanced UV absorption capacity as expected, accompanied by an obvious improvement in hydrophobicity (the water contact angle increased from 84.2° to 98.2°). The results showed that the hybrid films containing M-CeO<sub>2</sub>@SiO<sub>2</sub> particles possess better global performance as compared with those containing no particles.

Received 31st October 2019  
Accepted 10th January 2020

DOI: 10.1039/c9ra08975f

rsc.li/rsc-advances

## 1. Introduction

Fluorinated acrylics, which generally contain perfluoroalkyl segments, are typical low surface energy materials with outstanding water/oil repellence characteristics, antifouling properties and satisfactory adhesion on different substrates.<sup>1–5</sup> These unique properties make them ideal candidates for outdoor coatings, which has attracted widespread attention from researchers.<sup>6–8</sup> The purpose of outdoor coatings is to protect the substrates from harsh environments, such as sunlight, rain, and air pollution. Therefore, it is important for fluorine-containing acrylate copolymers to maintain greater protective abilities than simple physical isolation.

Among various harsh environmental factors, ultraviolet rays, which may cause the degradation of organic matrices, leading to the failure of protective coatings, is a major source of damage. Although the polymers themselves are durable in

outdoor environments, it is necessary to incorporate some UV absorbers to improve the lifetime and improve the properties of these coatings.<sup>9</sup> Compared with organic UV absorbers that may release environmental pollutants, such as volatile organic compounds (VOC), inorganic nanoparticles such as TiO<sub>2</sub>, ZnO and CeO<sub>2</sub> seem to be better choices.<sup>10–14</sup> Among the numerous UV absorbers, ceria nanoparticles are ideal candidates due to their excellent UV absorption ability, visible light transparency and lower light refractive index.<sup>15–18</sup> Several studies have been published on the incorporation of CeO<sub>2</sub> nanoparticles into polymer latex to shield UV light.<sup>19–21</sup> Most of these studies achieved good dispersion of cerium oxide *via* physical blending or modification with ligands or hydrogen bonds, such as citric acid, polyethylene glycol and poly(acrylic acid).<sup>22–25</sup> For hybrid latex obtained using these methods, the interaction between ceria nanoparticles and the organic matrix are weak, making the long-term stability of the system open to question. To the best of our knowledge, although several approaches have been reported for the preparation of CeO<sub>2</sub>/polyacrylate hybrid latex, the use of ceria in fluorinated polyacrylate coatings has been seldom reported.

Constructing core-shell structures is commonly used in nano-modification. In this way, the surfaces of nanoparticles are covered with a layer of other materials for protection or modification.<sup>26–30</sup>

<sup>a</sup>Key Laboratory of Aerospace Materials and Performance (Ministry of Education), School of Materials Science and Engineering, Beihang University, Beijing 100191, China. E-mail: liuhc@buaa.edu.cn; Fax: +861082317113; Tel: +861082317113

<sup>b</sup>Aerospace Research Institute of Materials and Processing Technology, No. 1 South Dahongmen Road, Beijing, 100076, China. E-mail: yehui@buaa.edu.cn

† Electronic supplementary information (ESI) available: Details of SEM images. See DOI: 10.1039/c9ra08975f



In this paper, we constructed a core-shell-shell structure to solve the above-mentioned problems. In this structure, silica has been used as the core and shell material due to its well-known characteristics of easy dispersion and high stability.<sup>31</sup> Firstly, small-sized ceria particles were uniformly deposited on the surface of monodispersed silica nano-spheres. Then, a layer of SiO<sub>2</sub>/MPS (3-methacryloxypropyltrimethoxysilane) shell was introduced to isolate the ceria from the external environment, which provides the active site for the subsequent mini-emulsion reaction. The resulting nanoparticles were used to prepare a polyacrylate/M-CeO<sub>2</sub>@SiO<sub>2</sub> latex *via* a mini-emulsion polymerization process for outdoor functional coatings. In addition to the original advantages of the fluorine-containing acrylic resin, the latex coating exhibits excellent UV absorption capabilities. Furthermore, due to the increase in surface roughness and the enrichment of the fluorine component on the surface, the hydrophobicity of the coating is also improved.

## 2. Experimental

### 2.1 Materials

Cerium nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, ≥99.95%) and commercial ceria (CeO<sub>2</sub>, 99.5%) were obtained from Aladdin Industrial Corporation. Tetraethoxysilane (TEOS, AP), hexamethylenetetramine (HMT, ≥99%), *N*-hexadecane (HD, ≥98%), sodium dodecyl sulfate (SDS, CP), and acrylic acid (AA) were bought from Xilong Chemical Co., Ltd (Guangzhou, China). Sodium bicarbonate (≥99.5%), ammonia (25 wt%), hydrogen peroxide (≥30%), and absolute ethanol were obtained from Beijing Chemical Works. 3-Methacryloxypropyltrimethoxysilane (MPS) and dodecafluoroheptyl methacrylate (DFMA) were purchased from Nanjing Xiangqian Chemical Co., Ltd and Harbin Xeogia Fluorine-Silicon Chemical Co., Ltd, respectively. All the above reagents were used as received.

Methyl methacrylate (MMA) and butyl acrylate (BA) were used as monomers which were purified using a neutral alumina column to eliminate inhibitors before use. Ammonium persulfate (APS) was obtained from Tianjin Bodi Chemical Co., Ltd, and was recrystallized before use. SiO<sub>2</sub> with a mean diameter of 310 nm was synthesized in our lab using the Störber method.<sup>32</sup> Deionized water and absolute ethanol were used in all processes.

### 2.2 Characterization techniques

The morphologies and sizes of all the prepared particles (SiO<sub>2</sub>, CeO<sub>2</sub>@SiO<sub>2</sub>, and M-CeO<sub>2</sub>@SiO<sub>2</sub>) were characterized using field emission scanning electron microscopy (FESEM, JSM-7500F, Japan) and transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). The TEM samples were prepared by dispersing the particles into ethanol followed by dropping the suspension onto a carbon-coated Cu grid. Particle sizes were measured directly, taking about 50 particles in the SEM pictures into account using software named Nano measurer. An X-ray diffractometer (XRD, D/MAX-2500RB, Japan) was used to identify the crystal structure using Cu K $\alpha$  radiation with a scan speed of 6° min<sup>-1</sup> in the 2 $\theta$  range from 10° to 100°. Fourier

transformed infrared (FT-IR) absorption spectra were recorded on a NEXUS-470 FTIR analyzer (Nicolet, USA) from 4000 cm<sup>-1</sup> to 500 cm<sup>-1</sup> at a resolution of 8 cm<sup>-1</sup>. A UV-3600 ultraviolet transmittance analyzer (Shimadzu, Japan) was used to record the UV-vis absorption spectra of the latex films in the wavelength range of 250–700 nm. The static contact angle of water was measured on the surface of films using a DSA 20 (KRÜSS, Germany) at room temperature. Inorganic nanoparticle films were prepared using the compression method with a powder compressing machine (769YP-15A, Tianjin Keqi High & New Technology Corporation), which pressed nano-powder into round flakes under high pressure. Atom force microscopy (AFM) was used to investigate the surface topography of the latex films. 4  $\mu$ l water droplets were used and five measurements were done for each example. The films were prepared by dropping 1 ml of emulsion onto each slide and then drying at 60 °C for 3 h. All optical photographs were obtained using a digital camera (Olympus E-PL1, Japan).

### 2.3 Synthesis of CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles

The deposition of CeO<sub>2</sub> onto SiO<sub>2</sub> is affected by electrostatic attraction in a weak alkaline environment. In a typical experiment, 1 g of the prepared SiO<sub>2</sub> and various amounts of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were added into 60 ml of ethanol in a three-necked flask followed by sonicating for 30 min to make it dispersed. Afterward, 3.23 g HMT and 20 g H<sub>2</sub>O were added into the flask with agitation. The solution was stirred for 2 h at a temperature of 75 °C, and then 400  $\mu$ l H<sub>2</sub>O<sub>2</sub> was added to oxidize Ce<sub>2</sub>O<sub>3</sub> to CeO<sub>2</sub>. The precipitates were centrifuged and washed with absolute ethanol three times before drying at 60 °C overnight in an oven.

### 2.4 Synthesis of M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles

Subsequently, the CeO<sub>2</sub>@SiO<sub>2</sub> particles were covered with a mixture of MPS and TEOS, so as to separate CeO<sub>2</sub> from the atmosphere, to prevent the catalytic decomposition of CeO<sub>2</sub>. Specifically, 0.2 g CeO<sub>2</sub>@SiO<sub>2</sub> was dispersed in a solution of 1.2 g water and 16 g ethanol under constant ultra-sonication for 30 min. After that, 0.3 g TEOS and 0.72 g ammonia were added in sequence. After 5 min, 0.2 g MPS (this amount is based on our previous work<sup>33</sup>) dissolved in 10 ml ethanol was added into the flask. The reaction was carried out at room temperature and aged for 8 h. The resulting M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles were centrifuged and then washed three times with ethanol, after which the M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles were obtained by drying overnight in an oven at 60 °C.

### 2.5 Preparation of PFA/M-CeO<sub>2</sub>@SiO<sub>2</sub> latex and film

The PFA/M-CeO<sub>2</sub>@SiO<sub>2</sub> latex was prepared using a typical mini-emulsion polymerization procedure. As shown in Table 1, the oil phase was prepared by mixing all the monomers, the co-stabilizer (HD) and a certain amount of M-CeO<sub>2</sub>@SiO<sub>2</sub> (the amount of M-CeO<sub>2</sub>@SiO<sub>2</sub> varied from 0 g to 0.12 g, and the latex was denoted as FPA-0 to FPA-12 accordingly). The mixture was sonicated and stirred by a mechanical agitator for 30 min to disperse the nanoparticles evenly. Then the water phase was



Table 1 Recipes used in the mini-emulsion polymerization

|             | Component                            | Weight/g            |
|-------------|--------------------------------------|---------------------|
| Oil phase   | MMA                                  | 4.5                 |
|             | BA                                   | 4.5                 |
|             | MAA                                  | 0.2                 |
|             | DFMA                                 | 0.8                 |
|             | M-CeO <sub>2</sub> @SiO <sub>2</sub> | 0–0.12 <sup>a</sup> |
|             | HD                                   | 0.4                 |
| Water phase | SDS                                  | 0.08                |
|             | NaHCO <sub>3</sub>                   | 0.02                |
|             | Deionized water                      | 40                  |

<sup>a</sup> According to the EDS results which are shown in Table S1 (see ESI), 1 g of M-CeO<sub>2</sub>@SiO<sub>2</sub> contains approximately 0.395 g of CeO<sub>2</sub>.

added into the oil phase and sonicated in an ice bath for 30 min. Afterward, a high-speed shearing machine was used at a speed of 8000 rpm for 30 min to generate a homogeneous mini-emulsion. Finally, the resultant mini-emulsion was transferred into a 100 ml three-necked flask equipped with a thermometer, a reflux condenser, a mechanical agitator and a nitrogen inlet. 10 ml of 1 wt% APS aqueous solution was used as an initiator and the reaction was kept at 75 °C for 6 h.

Latex was spin-coated onto the slides and dried at 60 °C for 3 h to form a film for follow-up tests.

### 3. Results and discussion

#### 3.1 Preparation of M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles

In order to avoid the agglomeration of cerium oxide, improve its dispersion within the coatings, and allow it to play the role in the UV absorption, a three layer structure was designed. In the structure, monodispersed SiO<sub>2</sub> particles were used as cores to ensure the even distribution of cerium oxide, and MPS/SiO<sub>2</sub> was used as the shell material to improve the compatibility with the polymer system and prevent the catalytic performance. The particle synthesis diagram is illustrated schematically in Fig. 1a.

SEM/TEM photos in Fig. 1b–f show an intuitive view of the three-layer structure. In Fig. 1b and e, uniform and monodispersed SiO<sub>2</sub> with a diameter of ca. 300–320 nm can be clearly observed. When CeO<sub>2</sub> was deposited (Fig. 1c and f), particle sizes increased to 335–350 nm, and a distinctive layer of CeO<sub>2</sub> (the dark layer) can be clearly observed. As for M-CeO<sub>2</sub>@SiO<sub>2</sub> (Fig. 1d and g), the particle sizes are further increased to 355–365 nm, with an MPS/SiO<sub>2</sub> layer (the semi-transparent layer) completely covering the surface of CeO<sub>2</sub> to separate CeO<sub>2</sub> from the environment. As is well known, silica particles prepared by the Stöber method usually have smooth surfaces because of the relatively complete hydrolysis and condensation of TEOS in water/ethanol solution.<sup>34</sup> They are negatively charged in neutral or alkaline dispersion. When Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O is added into SiO<sub>2</sub> dispersion, the positively charged Ce<sup>3+</sup> ions are attracted to the vicinity of SiO<sub>2</sub> through electrostatic interaction and become deposited on the SiO<sub>2</sub> surface in a weakly alkaline environment. Then the deposited Ce<sub>2</sub>O<sub>3</sub> is oxidized to CeO<sub>2</sub> by the addition of H<sub>2</sub>O<sub>2</sub>. For the purpose of optimizing the cerium loading, the Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O to SiO<sub>2</sub> mass ratio was varied as follows:

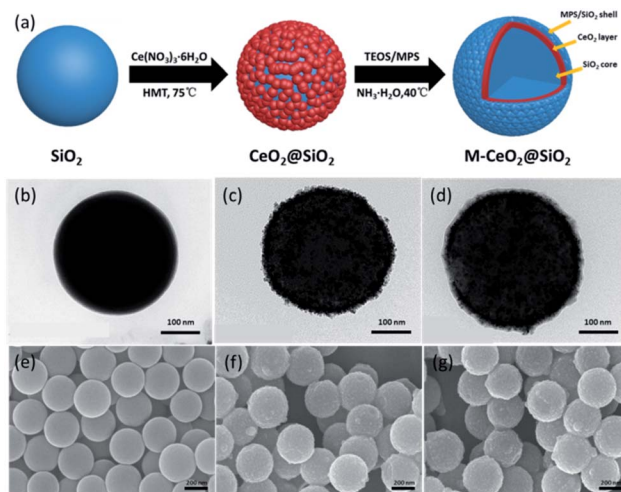


Fig. 1 (a) A schematic drawing of the preparation process of M-CeO<sub>2</sub>@SiO<sub>2</sub>. FESEM and TEM images of the synthesized nanoparticles: (b) SiO<sub>2</sub>-TEM, (c) CeO<sub>2</sub>@SiO<sub>2</sub>-TEM, (d) M-CeO<sub>2</sub>@SiO<sub>2</sub>-TEM, (e) SiO<sub>2</sub>-SEM, (f) CeO<sub>2</sub>@SiO<sub>2</sub>-SEM and (g) M-CeO<sub>2</sub>@SiO<sub>2</sub>-SEM.

$m(\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}) : m(\text{SiO}_2) = 1.5 : 1, 2 : 1, 2.5 : 1, 3 : 1$  and  $4 : 1$ . As shown in Fig. S1,† when  $m(\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}) : m(\text{SiO}_2)$  was below 2, CeO<sub>2</sub> was evenly distributed on the surface of SiO<sub>2</sub>. As the amount of Ce<sup>3+</sup> ions increased, they began to agglomerate. Individual cerium oxide crystals with irregular sizes and shapes are visible. When  $m(\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}) : m(\text{SiO}_2) = 2.5 : 1$ , larger cerium oxide grains can be clearly observed and randomly distributed over the surface of SiO<sub>2</sub>. When the ratio further increased to  $3 : 1$  or  $4 : 1$ , the ceria grains agglomerated, resulting in the sedimentation of the nanoparticles. Therefore, the ratio of  $m(\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}) : m(\text{SiO}_2) = 2 : 1$  was chosen as the preferred ratio.

XRD patterns are typically used to study the phase structure of various nanoparticles. As shown in Fig. 2a, a broad diffraction peak at 23° can be seen in the XRD curve of pure SiO<sub>2</sub>, which corresponds to the typical characteristics of amorphous silica. After coating with ceria, four distinct diffraction peaks (28.4°, 32.9°, 47.4°, and 56.2°) can be observed, which correspond to the reflections of the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of the CeO<sub>2</sub> crystal, respectively. This result proves the existence of CeO<sub>2</sub> in CeO<sub>2</sub>@SiO<sub>2</sub> and confirms it to have the cubic fluorite structure. The strong and sharp peaks reveal that CeO<sub>2</sub> possesses an intact crystal structure. No new diffraction

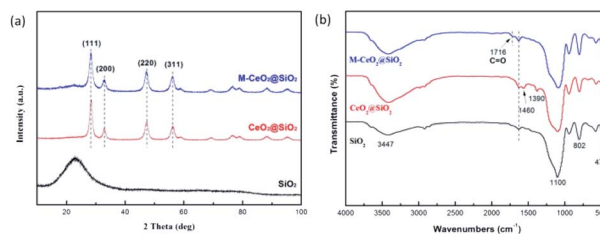


Fig. 2 (a) XRD and (b) FT-IR spectra of pure SiO<sub>2</sub>, CeO<sub>2</sub>@SiO<sub>2</sub>, and M-CeO<sub>2</sub>@SiO<sub>2</sub>.



peaks appear in  $\text{M-CeO}_2@\text{SiO}_2$ , but the relative intensities of the  $\text{CeO}_2$  diffraction peaks decrease, owing to the coverage of  $\text{MPS/SiO}_2$ . Fig. 2b shows the FT-IR curves of pure  $\text{SiO}_2$ ,  $\text{CeO}_2@\text{SiO}_2$  and  $\text{M-CeO}_2@\text{SiO}_2$ . The absorption at  $1100\text{ cm}^{-1}$  is assigned to the stretching vibration of  $\text{Si-O-Si}$ , while the peaks at  $802$  and  $470\text{ cm}^{-1}$  belong to the bending vibration of  $\text{Si-O}$ . The broad peak at around  $3447\text{ cm}^{-1}$  is ascribed to the stretching vibration of  $-\text{OH}$ . The peaks at  $1460$  and  $1390\text{ cm}^{-1}$  are attributed to the  $\text{Ce-O}$  bond. Compared with  $\text{CeO}_2@\text{SiO}_2$  and  $\text{SiO}_2$ , the absorption of the carboxyl group ( $\text{C=O}$ ) at  $1716\text{ cm}^{-1}$  in the  $\text{M-CeO}_2@\text{SiO}_2$  curve demonstrates the successful grafting of MPS on the surface of the  $\text{CeO}_2@\text{SiO}_2$  nanoparticles.

In summary, the monodispersed three-layer structure nanoparticles were synthesized as anticipated. Silica is the central core, cerium dioxide forms the middle layer and  $\text{MPS/SiO}_2$  is the outmost layer.

### 3.2 Performance of $\text{M-CeO}_2@\text{SiO}_2$ nanoparticles

The  $\text{MPS/SiO}_2$  shell shielded the catalytic properties of  $\text{CeO}_2$ , and photo-degradation experiments were carried out to prove it. The results are shown in Fig. 3a. It can be clearly observed that the Rh B concentration decreased rapidly when  $\text{CeO}_2$  is not coated. After 4 h of irradiation with a Xe lamp, about 79.44% and 98.2% of Rh B was degraded by pure  $\text{CeO}_2$  and  $\text{CeO}_2@\text{SiO}_2$ , respectively. As a comparison, only 31.94% Rh B was degraded in  $\text{M-CeO}_2@\text{SiO}_2$  suspension, which is even slightly lower than that of the blank sample (35.65%). Throughout the process, the decomposition curve of the  $\text{M-CeO}_2@\text{SiO}_2$  suspension was almost parallel with that of the blank sample. The tiny gap arises from the fact that the opaque  $\text{M-CeO}_2@\text{SiO}_2$  suspension blocked part of the light. It is obvious that nanoparticles with the  $\text{MPS/SiO}_2$  layer show no catalytic properties. As a result, the synthesized  $\text{M-CeO}_2@\text{SiO}_2$  can be safely added into the organic system, avoiding the potential decomposition of the polymer matrix.

The  $\text{MPS/SiO}_2$  layer also improves the compatibility of nanoparticles with the polymer latex. It is well known that the compatibility of nanoparticles with the monomer mixture is of vital importance for the stability and global properties of the final emulsion. 1 wt% of pure  $\text{CeO}_2$ ,  $\text{CeO}_2@\text{SiO}_2$  and  $\text{M-}$

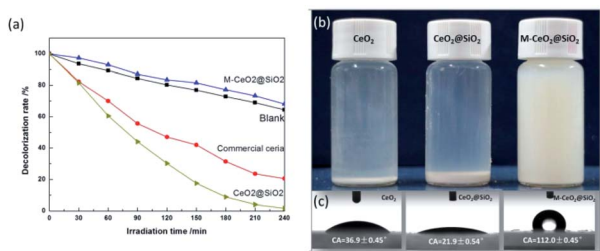


Fig. 3 Performance of the synthesized nanoparticles: (a) the photocatalytic degradation of Rh B; (b) the dispersion of  $\text{CeO}_2$ ,  $\text{CeO}_2@\text{SiO}_2$  and  $\text{M-CeO}_2@\text{SiO}_2$  (1 wt%) in monomer mixtures; and (c) the water contact angles of  $\text{CeO}_2$ ,  $\text{CeO}_2@\text{SiO}_2$  and  $\text{M-CeO}_2@\text{SiO}_2$ .

$\text{CeO}_2@\text{SiO}_2$  nanoparticles were dispersed separately into the monomer mixture which was composed of  $\text{MMA/BA} = 50/50\text{ wt\%}$ . As shown in Fig. 3b, after a 12 h sedimentation test at room temperature,  $\text{CeO}_2$  and  $\text{CeO}_2@\text{SiO}_2$  nanoparticles precipitated at the bottom of the monomer mixture; however, the  $\text{M-CeO}_2@\text{SiO}_2$  nanoparticles did not form sediment and exhibited a uniform opaque feature, presenting constant stability and compatibility. The contact angle of the nanoparticles reflected this phenomenon to some extent. As is well known, acrylic monomers are oleophilic monomers, which are incompatible with water. To be dispersed uniformly within acrylic monomers, nanoparticles should also be hydrophobic, too. That means the water contact angle (WCA) should be larger than  $90^\circ$ . Fig. 3c presents the WCAs of the nanoparticles. Obviously, pure  $\text{CeO}_2$  and  $\text{CeO}_2@\text{SiO}_2$  nanoparticles are hydrophilic, and the WCAs are  $36.9^\circ$  and  $21.9^\circ$ , respectively. After modification with MPS, however, the WCA dramatically increased to  $112^\circ$ . This may be attributed to the uniform dispersion of  $\text{M-CeO}_2@\text{SiO}_2$  nanoparticles amongst the acrylate monomers. The  $\text{M-CeO}_2@\text{SiO}_2$  nanoparticles are more likely to maintain their stability in the polymer system compared with pure  $\text{CeO}_2$  and unmodified  $\text{CeO}_2@\text{SiO}_2$  nanoparticles.

### 3.3 Preparation of PF/ $\text{M-CeO}_2@\text{SiO}_2$ latex coatings

The above-synthesized nanoparticles were applied to the acrylate emulsion system *via* a mini-emulsion polymerization process to improve the performance of polyacrylate resin.

The morphology of the latex particles was observed using TEM to investigate the formation mechanism of the composite films. Hybrid latex containing 1.0 wt%  $\text{M-CeO}_2@\text{SiO}_2$  nanoparticles was dropped onto a copper grid. As can be observed from Fig. 4a, the hybrid particles show a raspberry-like structure with several polymeric particles grafted onto the surface of the nanoparticles. The amount of PF/ $\text{M-CeO}_2@\text{SiO}_2$  particles is small because of the low content of the  $\text{M-CeO}_2@\text{SiO}_2$  nanoparticles. This structure is formed because of the good compatibility between nanoparticles and organic monomers.

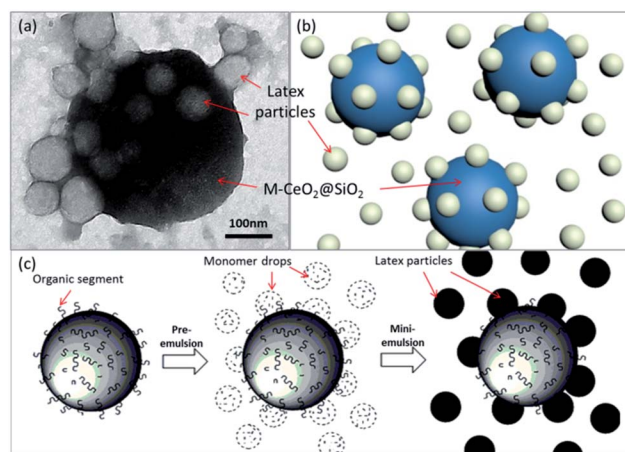


Fig. 4 (a) A TEM image of PF/ $\text{M-CeO}_2@\text{SiO}_2$  particles; schematic representations of (b) PF/ $\text{M-CeO}_2@\text{SiO}_2$  particles and (c) the growth of PFA latex particles.



Fig. 4c illustrates the preparation of the PF/M-CeO<sub>2</sub>@SiO<sub>2</sub> latex using a mini-emulsion polymerization process. In the pre-emulsification process, the organic segments on the surface of the nanoparticles attract the surrounding acrylic monomers. After that, these monomers polymerize directly to form raspberry-like structures during the mini-emulsion. The uneven distribution of polymeric particles on the M-CeO<sub>2</sub>@SiO<sub>2</sub> surface is probably due to steric hindrance among polymeric particles. The raspberry-like structures would benefit the even dispersion of M-CeO<sub>2</sub>@SiO<sub>2</sub> particles in the latex system and subsequent coatings (as shown in Fig. S2†).

The chemical composition of the PF/M-CeO<sub>2</sub>@SiO<sub>2</sub> film was characterized by FT-IR as shown in Fig. 5. The absorption peaks at 2956 cm<sup>-1</sup> and 2874 cm<sup>-1</sup> are the stretching vibrations peaks of C-H, while the peak at 1723 cm<sup>-1</sup> is assigned to the stretching vibration peak of C=O. Absorption at 3345 cm<sup>-1</sup> belongs to -OH. Furthermore, the characteristic peaks at 1236 cm<sup>-1</sup> and 1143 cm<sup>-1</sup> are the stretching vibration peaks of C-F. Compared with PFA0, few changes can be observed after the incorporation of M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles due to the small amount of nanoparticles in the hybrid latex. Only a weak peak at 800 cm<sup>-1</sup>, which corresponds to Si-O, indicates the existence of M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles within fluorinated polyacrylate.

### 3.4 Performance of PF/M-CeO<sub>2</sub>@SiO<sub>2</sub> latex coatings

Due to the excellent UV absorption capacity of ceria, the hybrid films containing M-CeO<sub>2</sub>@SiO<sub>2</sub> also show the ability of UV absorption. The UV-vis absorption capacity of hybrid latex films with different M-CeO<sub>2</sub>@SiO<sub>2</sub> content was measured, and the results are shown in Fig. 6. Obviously, hybrid latex films containing M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles show considerably stronger absorption of light below 600 nm than the pristine film, especially in the wavelength range of 250–400 nm. Furthermore, the UV-vis absorption capacity of the films increases gradually with the amount of nanoparticles present in the final film.

Surface hydrophobicity is an important property of fluoropolymers. Thus, water contact angle measurements were taken to evaluate the wettability properties of PF/M-CeO<sub>2</sub>@SiO<sub>2</sub>

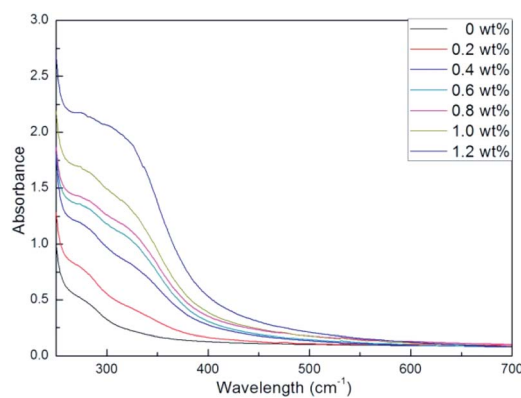


Fig. 6 UV-vis spectra of PF/M-CeO<sub>2</sub>@SiO<sub>2</sub> coatings.

films, and the results are displayed in Fig. 7. It can be seen that the surface hydrophobicity of the hybrid films significantly improved with a small amount of M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles added. As shown in Fig. 7, the bare PFA0 film exhibits an average WCA of 84.2°. When 0.2 wt% M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles were added, however, the WCA dramatically increased to 90.5°. When the content of M-CeO<sub>2</sub>@SiO<sub>2</sub> was increased further, the hydrophobicity of the hybrid films gradually increased initially, and then decreased. The PFA10 film, which contains about 1.0 wt% M-CeO<sub>2</sub>@SiO<sub>2</sub>, shows the highest water contact angle of 98.2°. All the hybrid films containing M-CeO<sub>2</sub>@SiO<sub>2</sub> show a higher level of surface hydrophobicity than that of PFA0. As is well known, solid surface hydrophobicity is determined by the surface microstructure and chemical composition. The altered WCA data indicate that some changes have taken place on the surface after the addition of M-CeO<sub>2</sub>@SiO<sub>2</sub>. To investigate the changes, AFM and EDS tests were performed to study the film surface properties.

Fig. 8 shows the AFM height and R<sub>q</sub> (root mean square roughness) of the hybrid films. It can be seen that the hybrid films containing M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles displayed rougher surfaces than that of PFA0. As shown in Fig. 8a, bare PFA0 shows a rather smooth surface, with R<sub>q</sub> = 0.268, and revealed good compatibility of the fluorinated segment with the polyacrylate system. After the addition of M-CeO<sub>2</sub>@SiO<sub>2</sub>, the

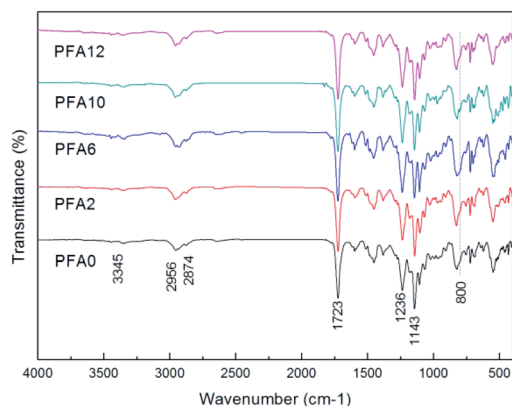


Fig. 5 FT-IR spectra of PF/M-CeO<sub>2</sub>@SiO<sub>2</sub> coatings.

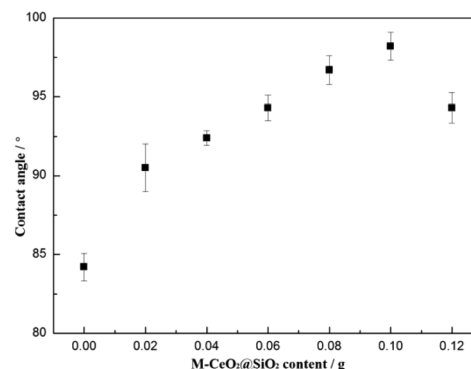


Fig. 7 The water contact angles of PF/M-CeO<sub>2</sub>@SiO<sub>2</sub> coatings with various amounts of M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles.



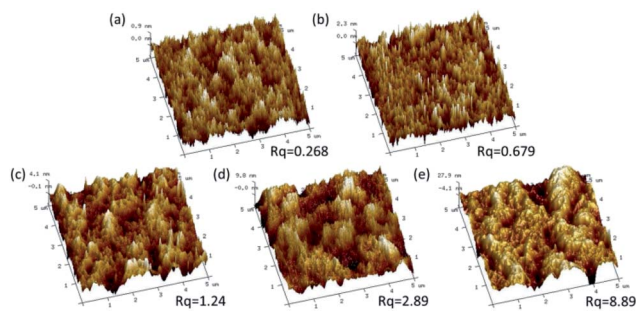


Fig. 8 AFM images of PF/M-CeO<sub>2</sub>@SiO<sub>2</sub> coatings: (a) PFA0, Rq = 0.268; (b) PFA2, Rq = 0.679; (c) PFA6, Rq = 1.24; (d) PFA10, Rq = 2.89; and (e) PFA12, Rq = 8.89.

film surface roughness increased. As the M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticle content increased from 0 wt% to 1 wt%, Rq increased slowly from 0.268 to 2.89. However, as the nanoparticle content continued to increase to 1.2 wt%, there was a dramatic change in the surface roughness, with Rq increasing to 8.89. This sharp increase is likely ascribed to the partial agglomeration of nanoparticles, according to our group's previous work.<sup>35</sup> Although the M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles exhibit relatively good compatibility with the polymeric system, when too many nanoparticles are added during the polymerization process, partial agglomeration might happen, resulting in the sharp increase in surface roughness. The Wenzel and Cassie–Baxter models are two well-known classic wetting models that are commonly used to explain the relationship between wettability and surface roughness. According to those theories, the WCA of a hydrophobic surface can be improved by a rough surface, which is consistent with our experimental results.

Table 2 presents the chemical composition at the air–film interface of the PF/M-CeO<sub>2</sub>@SiO<sub>2</sub> hybrid films. With the addition of M-CeO<sub>2</sub>@SiO<sub>2</sub> into PFA copolymers, a remarkable increase of fluorine content on the film surface can be observed. It can be seen from Table 2 that only 6.80 wt% fluorine content can be detected from the latex film containing no M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles. As the M-CeO<sub>2</sub>@SiO<sub>2</sub> content increases from 0 wt% to 1.2 wt%, the fluorine content on the film surface increases significantly from 6.80 wt% to 9.45 wt% at first, and then decreases slightly to 8.54 wt%. This result indicates that the addition of M-CeO<sub>2</sub>@SiO<sub>2</sub> helps the enrichment of fluorine on the surface because of the unique structure of the hybrid particles. By constructing a raspberry-like structure, parts of the latex particles grow directly on the M-CeO<sub>2</sub>@SiO<sub>2</sub> surface. During the film formation process, those latex particles concentrate on the surface along with the M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles.<sup>33</sup> Furthermore, the fluorine-containing groups

always migrate to the surface during the film formation process due to their relatively low surface energy. By the addition of the nanoparticles, the surface roughness and the specific surface area of the film layer increase, which helps to increase the content of the F element per unit area. A slight decrease of fluorine content when more nanoparticles were added resulted from the partial agglomeration of nanoparticles, as mentioned before.

## 4. Conclusions

Ceria was uniformly incorporated into polymeric matrices and maintained high stability when a three-layer nanoparticle structure was constructed. The synthesized nanoparticles are about 360 nm in diameter. Monodispersed silica spheres with controlled sizes ensure the even distribution of ceria. An MPS/SiO<sub>2</sub> layer protects the catalytic activity of ceria and improves the compatibility between the nanoparticles and the organic matrix. The synthesized M-CeO<sub>2</sub>@SiO<sub>2</sub> nanoparticles were incorporated into fluorinated polyacrylate resin *via* a mini-emulsion method. After the addition of M-CeO<sub>2</sub>@SiO<sub>2</sub>, the hydrophobicity of the hybrid coatings improved significantly from 84.2° to a maximum of 98.2°, due to the enrichment of fluorine and an increase in the surface roughness. Furthermore, the UV absorption capacity of the hybrid coating was improved, as expected, with the use of M-CeO<sub>2</sub>@SiO<sub>2</sub>. The hybrid coating is a promising candidate material for outdoor coatings.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors are very grateful for support from the National Natural Science Foundation of China (Grant No. U1637204).

## References

- 1 L. Feng, S. H. Li, Y. S. Li, H. J. Li, L. J. Zhang, J. Zhai, Y. L. Song, B. Q. Liu, L. Jiang and D. B. Zhu, *Adv. Mater.*, 2002, **14**, 1857–1860.
- 2 J. W. Ha, I. J. Park, S. B. Lee and D. K. Kim, *Macromolecules*, 2002, **35**, 6811–6818.
- 3 J. Wu, R. Zhang, P. Li, G. Ma, C. Hou and H. Zhang, *J. Coat. Technol. Res.*, 2019, **16**, 681–688.
- 4 K. Li, X. Zeng, H. Li and X. Lai, *Appl. Surf. Sci.*, 2014, **298**, 214–220.
- 5 V. Sabatini, E. Pargoletti, V. Comite, M. A. Ortenzi, P. Fermo, D. Gulotta and G. Cappelletti, *Polymers*, 2019, **11**, 1190.
- 6 S. D. Vacche, S. Forzano, A. Vitale, M. Corrado and R. Bongiovanni, *Int. J. Adhes. Adhes.*, 2019, **92**, 16–22.
- 7 J. Tsibouklis, P. Graham, P. J. Eaton, J. R. Smith, T. G. Nevell, J. D. Smart and R. J. Ewen, *Macromolecules*, 2000, **33**, 8460–8465.
- 8 A. Asakawa, M. Unoki, T. Hirono and T. Takayanagi, *J. Fluorine Chem.*, 2000, **104**, 47–51.

Table 2 Elemental content of the hybrid film surfaces *via* EDS (wt%)

| Sample | PFA0  | PFA2  | PFA6  | PFA10 | PFA12 |
|--------|-------|-------|-------|-------|-------|
| C      | 63.76 | 62.57 | 62.19 | 63.17 | 60.58 |
| O      | 29.28 | 29.11 | 27.89 | 27.89 | 30.90 |
| F      | 6.80  | 7.76  | 9.45  | 8.91  | 8.54  |



- 9 M. Aguirre, M. Goikoetxea, L. A. Otero, M. Paulis and J. R. Leiza, *Surf. Coat. Technol.*, 2017, **321**, 484–490.
- 10 H. Xiu, X. Qi, H. Bai, Q. Zhang and Q. Fu, *Polym. Degrad. Stab.*, 2017, **143**, 136–144.
- 11 A. Ehsani, F. Babaei and M. Nasrollahzadeh, *Appl. Surf. Sci.*, 2013, **283**, 1060–1064.
- 12 G. Ren, Y. Song, X. Li, B. Wang, Y. Zhou, Y. Wang, B. Ge and X. Zhu, *J. Colloid Interface Sci.*, 2018, **522**, 57–62.
- 13 M. Aguirre, M. Barrado, M. Iturrondobeitia, A. Okariz, T. Guraya, M. Paulis and J. Ramon Leiza, *Chem. Eng. J.*, 2015, **270**, 300–308.
- 14 M. Aklalouch, A. Calleja, X. Granados, S. Ricart, V. Boffa, F. Ricci, T. Puig and X. Obradors, *Sol. Energy Mater. Sol. Cells*, 2014, **120**, 175–182.
- 15 C. Sun, H. Li and L. Chen, *Energy Environ. Sci.*, 2012, **5**, 8475–8505.
- 16 T. Masui, M. Yamamoto, T. Sakata, H. Mori and G. Adachi, *J. Mater. Chem.*, 2000, **10**, 353–357.
- 17 S. Xie, Z. Wang, F. Cheng, P. Zhang, W. Mai and Y. Tong, *Nano Energy*, 2017, **34**, 313–337.
- 18 S. Parwaiz, M. M. Khan and D. Pradhan, *Mater. Express*, 2019, **9**, 185–202.
- 19 M. Aguirre, E. J. Salazar-Sandoval, M. Johansson, A. Ahniyaz, M. Paulis and J. Ramon Leiza, *J. Mater. Chem. A*, 2014, **2**, 20280–20287.
- 20 H. Ye, L. Zhu, W. Li, G. Jiang, H. Liu and H. Chen, *Chem. Eng. J.*, 2017, **321**, 268–276.
- 21 M. Aguirre, M. Paulis, J. Ramon Leiza, T. Guraya, M. Iturrondobeitia, A. Okariz and J. Ibarretxe, *Macromol. Chem. Phys.*, 2013, **214**, 2157–2164.
- 22 R. Francis, N. Joy, E. P. Aparna and R. Vijayan, *Polym. Rev.*, 2014, **54**, 268–347.
- 23 L. Qi, A. Sehgal, J. C. Castaing, J. Fresnais, J. F. Berret and J. P. Chapel, *Redispersible Hybrid Nanopowders: Cerium Oxide Nanoparticle Complexes with Phosphonated-PEG Oligomers*, 2008.
- 24 O. Parlak and M. M. Demir, *ACS Appl. Mater. Interfaces*, 2011, **3**, 4306–4314.
- 25 B. Chanteau, J. Fresnais and J. F. Berret, *Langmuir*, 2009, **25**, 9064–9070.
- 26 I. A. Siddiquey, T. Furusawa, Y.-i. Hoshi, E. Ukaji, F. Kurayama, M. Sato and N. Suzuki, *Appl. Surf. Sci.*, 2008, **255**, 2419–2424.
- 27 S. C. Zhang and X. G. Li, *Powder Technol.*, 2004, **141**, 75–79.
- 28 A. Guerrero-Martinez, J. Perez-Juste and L. M. Liz-Marzan, *Adv. Mater.*, 2010, **22**, 1182–1195.
- 29 F. Dang, N. Enomoto, J. Hojo and K. Enpuku, *Ultrason. Sonochem.*, 2010, **17**, 193–199.
- 30 G. Marcelo, E. Perez, T. Corrales and C. Peinado, *J. Phys. Chem. C*, 2011, **115**, 25247–25256.
- 31 J. Wang, Z. H. Shah, S. Zhang and R. Lu, *Nanoscale*, 2014, **6**, 4418–4437.
- 32 L. Tian, W. Li, H. Ye, L. Zhu, H. Chen and H. Liu, *Surf. Coat. Technol.*, 2019, **377**, 892–899.
- 33 W. Yang, L. Zhu and Y. Chen, *RSC Adv.*, 2015, **5**, 58973–58979.
- 34 W. Stober, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62–69.
- 35 W. Yang, L. Zhu, Y. Chen, H. Ye and Z. Ye, *Colloids Surf., A*, 2015, **484**, 62–69.

