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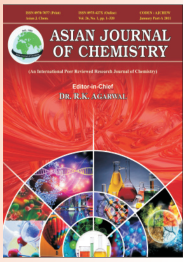

UV-Shielding and Photocatalytic Properties of $ZnO-CeO_2-TiO_2$ Composite

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The $ZnO-CeO_2-TiO_2$ composite oxide was rapidly synthesized by the combustion method using ascorbic acid as a new combustion agent. The composites were characterized by XRD, FT-IR, UV-visible and SEM. The experiments investigated the effect of molar ratio of burning agent, zinc, titanium and cerium ions on $ZnO-CeO_2-TiO_2$ (ZCT) composite. The $ZnO-CeO_2-TiO_2$ composite oxide with various morphologies, ultraviolet absorbing, photocatalytic and decolouring properties were obtained by changing molar ratio of burning agent, zinc, titanium and cerium ions. The composite oxide exhibited better properties of ultraviolet absorption, Light-stability of modified ZCT/paraffin wax and decolouration. Its ultraviolet properties are completely different from any monomer oxide. The composite oxide has better photocatalytic properties when molar ratio of burning agent, zinc, titanium and cerium ions is 8:4:0.25:1. Inorganic UV-shielding agent is firstly applied to improve light-stability of paraffin wax. The composite was modified in order to inorganic UV-shielding agent and paraffin wax can be mutually mixed.

Keywords: Composite oxide, Decolouration, UV absorbance, Photo-catalyst, light-stability, Paraffin wax.

INTRODUCTION

ZnO, TiO_2, CeO_2, Al_2O_3, SiO_2 and their composite oxides are better UV shielding agent, as inorganic UV shielding agent had good chemical stability, thermal stability, easy decomposition and non-toxicity. In addition, their shielding ultraviolet wavelength range was wide. So, more and more people were interested in them[1-4]. The chosen oxides TiO_2, ZnO and CeO_2 are broad band semiconductors with band gap (BG) widths of 3.2, 3.37 and 3.15 eV, respectively. These band gaps ensure effective absorption of UV light by these materials. Therefore, their composites can be used to protect polymers from UV degradation. The composites oxides not only retained properties of monomer oxides, but also is superior to monomer oxides. The use of different fillers was due to the fact that low cost zinc oxide, titanium oxide and ceria oxide are UV shielding agent, on exposure to UV light, they can shield UV light, whereas ceria is heat stabilize and has no photocatalytic activity[5-7], hence, cannot induce destruction of the polymer. The use of three zinc, titanium and ceria oxide nano-particles as UV absorbance agent may increase the wear resistance of the polymers.

Recently, much attention was paid to the combustion method due to its simple, high-yield, high-quality products. The composites prepared with combustion synthesis have been reported in many published papers[8-10]. In this study, the $ZnO-CeO_2-TiO_2$ (ZCT) composite was rapidly synthesized with ascorbic acid as a new burning agent through a novel combustion method. This method was simple and fast, which only needed 2 h from the solution to the product. The composite with high purity and high yield could be obtained without further washing and calcination. Moreover, it was found that the composite oxide exhibit the excellent ultraviolet absorbing properties, *e.g.*, this composite had stronger absorbance in UV region only (200-400 nm), better transmittance in the visible region (400-800 nm), high photocatalytic and decolouring ability. The aims were implemented by only changing molar ratio of metal ions. Three composite was different from two composite oxide of Zn, Ce and Ti[10-13], but superior to two composite.

EXPERIMENTAL

All chemical reagents are analytical grade purity without any further purification. The desired mole ratio of cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$, 99.9 %), zinc nitrate [$Zn(NO_3)_2{\cdot}6H_2O$, 99.9 %], titanium trichloride ($TiCl_3$, 40 %) and ascorbic acid ($C_6H_8O_6$), were mixed in the beaker. To obtain homogeneous solution, a minimum volume of deionized water around 10 milliliters were added to the mixed reactant. After that, the mixed solution was ultrasound for 10 min at 60 °C. The mixed solution was heated for 0.5 h by a 1000 W electric jacket. Through heating, the water was evaporated and a viscous colloid could be obtained. Continue heating, the colloid happened to

Self-igniting combustion for 0.5 h to produce milky ZnO-CeO_2-TiO_2 powder. According to this method, ZnO, CeO_2 and TiO_2 powder were prepared.

Sample characterization: The phase purity and crystallinity of the as-prepared composite were characterized by the X-ray diffraction (XRD, Model D8 advance, Bruker, X-ray apparatus) at a scanning rate of 5 min^{-1} in the 2θ range from 10° to 80°, with CuK_α radiation (λ = 1.5406 Å) at 40 kV and 40 mA. The morphologies of the as-prepared samples are observed by field emission scanning electron microscope (SEM; JSM-4800, JEOL, Japan). UV-visible spectrophotometer (Model UV1100 Meike Intrument, Shanghai, China) and FI-IR spectrophotometer (WQF-520 Ruili Intrument, Beijing, China) were used to check their absorbance properties.

Modification of ZCT: The ZCT was modified as follows: at first, 4 shares sodium stearate and 96 shares ethylalcohol were dropped into the desired amount of ZCT powder and water in the beaker. The beaker was immersed in a constant temperature bath. The mixed powder was magnetically stirred under 55-65 °C and was kept 60 min. Then the powder was dried at 110 °C overnight and obtained modified ZnO-CeO_2-TiO_2 composite (MZCT).

Application of modified ZCT: The desired amount of MZCT and paraffin wax were thoroughly mixed by an ultrasonic mixer for 0.5 h in organic glass containers. Different proportions MZCT in paraffin wax were used, yielding mixtures bearing 0, 0.08, 0.1, 0.2 and 0.3 wt. % MZCT. The mixture of MZCT and paraffin were radiated under UV light. The light-stability of MZCT/paraffin wax was measured by Saybolt Chromometer (US66M/K13009, China) at set intervals.

RESULTS AND DISCUSSION

Conditions of composite oxides prepared: Figs. 1-3 shows the XRD patterns of ZCT composite prepared for different molar ratio of burning agent and metal ions. The peaks of ZCT phase was increased in Fig. 1 when the dose of burning agent increased. With molar ratio of cerium increased, the peak intensity of composites increased and the number of peak decreased as shown in Fig. 2. While molar ratio of titanium and cerium was fixed to be 0.25:1, the molar ratio of zinc was changed in Fig. 3. It is shown that with molar ratio of zinc increased, the peak intensity of composites increased while the number of peak decreased. In case of the molar ratio of zinc is equal to 4, it is found that many peaks of ZnO appeared in XRD patterns. Hence, when increased zinc and cerium and decreased titanium, the peak intensity of composites increased and the crystallinity of composite tend to be better. When the molar ratio of Zn, Ti, Ce and burning agent is equal to 1:0.25:1:8, the crystallinity of composite oxide was best and the number of peak was less. According to the intensity of diffraction peak, it can be learned the ceria is the main phase. The same result is showed in literature[14].

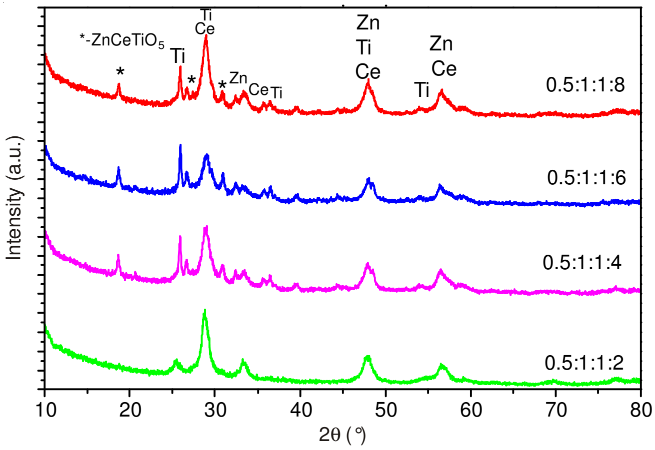

Fig. 1. Effect of burning agent on the composite

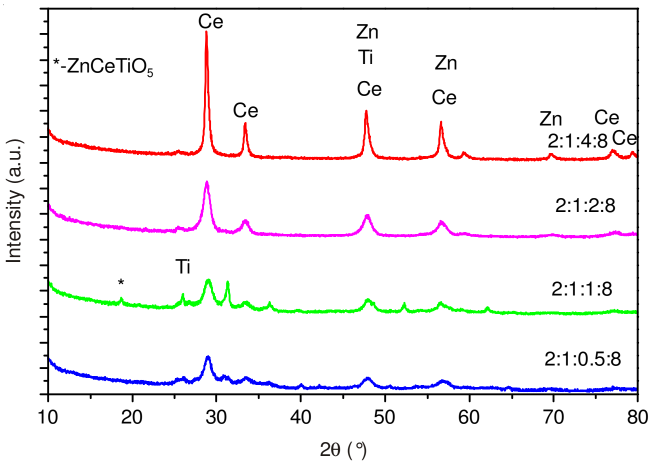

Fig. 2. Effect of molar ratio of cerium on composite

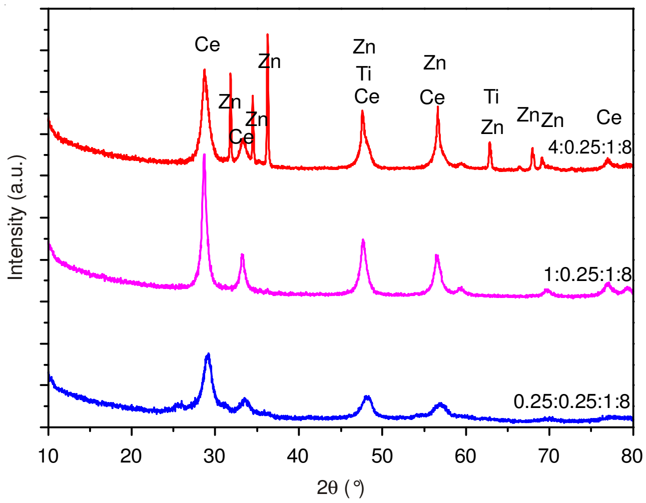

Fig. 3. Effect of molar ratio of Zinc on composite

Microstructural analysis of ZCT composite: Scanning electron micrographs of ZnO-CeO_2-TiO_2 composite are shown in Fig. 4. There are three XRD pattern graphs in Figs. 1-3. When molar ratio of Zn, Ti and Ce is equal to 1:1:1, the composite is compound of powder, particles and rods in Fig. 4(a). ZnO is short rod in Fig. 4(d), CeO_2 is powder in Fig. 4(e) and TiO_2 is particles in Fig. 4(f). The ZnO, CeO_2 and TiO_2 were prepared in accordance with the preparing methods of ZnO-CeO_2-TiO_2 composite. The hexagonal sheet structure of layers and powder are observed when molar ratio of Zn, Ti and Ce is equal to 4:0.25:1, which can be ascribed to two phases mixed in Fig. 4(c). When the molar ratio of Zn, Ti and Ce is equal to 1:0.25:1, the composite oxide was hexagonal columnar in Fig. 4(b).

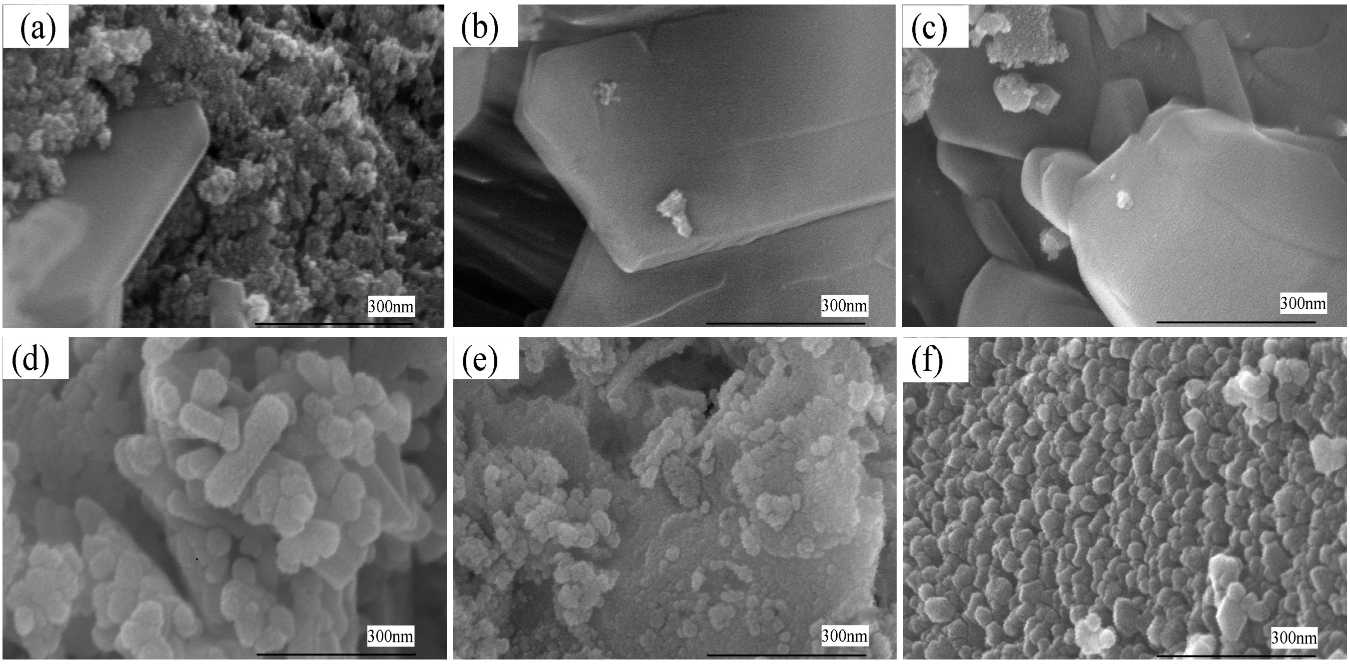

Fig. 4. SEM images of ZnO-CeO$_2$-TiO$_2$ Composite, (a) Zn:Ti:Ce = 1:1:1 (b) Zn:Ti:Ce = 4:0.25:1 (c) Zn:Ti:Ce = 1:0.25:1 (d) ZnO (e) CeO$_2$ (f) TiO$_2$

UV-visible spectra of ZCT composite: Fig. 5 shows UV-visible spectra of nano-ZnO-CeO$_2$-TiO$_2$ composite. The composite has only strong absorbance in 200-240 nm when the molar ratio of Zn, Ti and Ce is equal to 1:1:1. The composite with Zn, Ti and Ce mole ratio of 1:0.25:1, 2:1:4 and 4:0.25:1 all have stronger absorbance in UVC (200-280 nm), UVB (280-320 nm) and UVA (320-410 nm). Modi-fied-ZCT still retain stronger ultraviolet absorbent properties. The composite has the strongest and the widest range absor-bance in the UV region and especially the composite still retains strong absorbance peak of ZnO when molar ratio of Zn, Ti and Ce is equal to 4:0.25:1. Moreover, this composite oxide remains better transmission properties in the visible region. Therefore, the experimental results demonstrate that the composite is a perfect ultraviolet absorbing and visible light transmittance material.

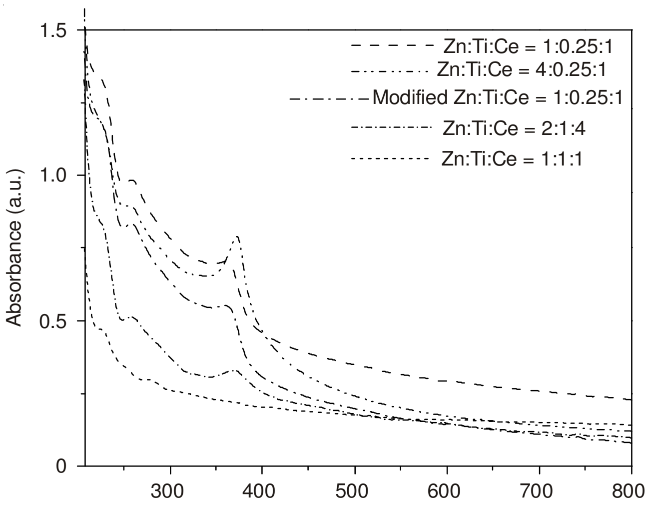

Fig. 5. UV spectra of ZnO-CeO$_2$-TiO$_2$

IR spectra of ZCT composite: Fig. 6 shows the FT-IR spectra for the ZnO-CeO$_2$-TiO$_2$ composite with molar ratio of Zn, Ce and Ti in the 1:0.25:1 and 4:0.25:1 and modified composite. It is observed that the composite exhibits one absorption peak from 600-485 cm^{-1} region. The absorption peak is attributed to the characteristic stretching vibration of ZnO, CeO$_2$ and TiO$_2$ bond. The peak of the composite with Zn, Ti and Ce is equal to 4:0.25:1 was stronger and wider than the composite with Zn, Ti and Ce molar ratio is equal to 1:0.25:1. The reasons can be attributed to high mole ratio of Zn in the composite with Zn, Ti and Ce molar ratio is equal to 4:0.25:1.The organic matters have been completely decomposed and a kind of metal oxide formed in the product. The peaks of 3400-1630 cm^{-1} are H$_2$O and OH$^-$ which are attributed to peak of composite oxide surface adsorbed water. The purity of ZCT composite is high because no impure peak is observed. The characteristic peak of MZCT happened red-shift and the presence of modifier resulted in more and stronger infrared absorption peaks.

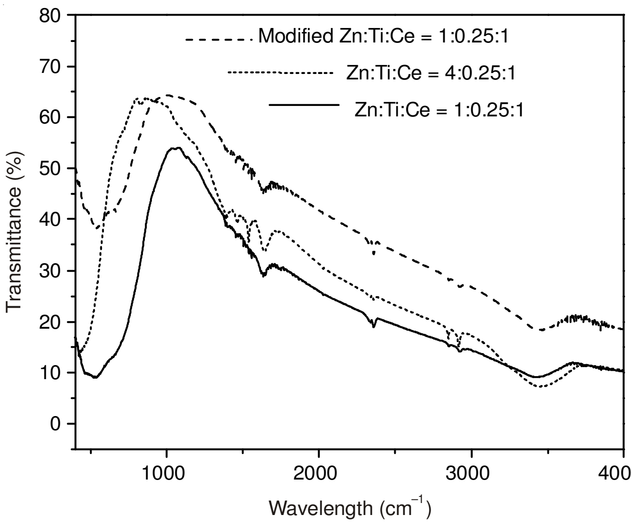

Fig. 6. IR spectra of ZnO-CeO$_2$-TiO$_2$ composite

Photocatalytic and decolouring properties of ZCT composite: Fig. 7 presents the results for decolouring experiments of the composite with molar ratio of Zn, Ti and Ce was 1:0.25:1.2 mL aqueous solution, containing 60 mg composite decolourized 100 mL methylene blue in 25 °C water bath. The decolouration of methylene blue was completed in approximately 150 min. However, the composite with molar ratio of Zn, Ti and Ce was 4:0.25:1, the 2 mL H_2O_2 and 60 mg composite photocatalyzed methylene blue in 25 °C water bath, the decolouration of methylene blue completed in approximately 1 h as shown in Fig. 8. Bearing in mind these facts, we might conclude that when the molar ratio of Zn:Ti:Ce was 4:0.25:1, the composite prepared by combustion method possess better photocatalytic activity and they were suitable photocatalysis in ultraviolet absorbing range of the spectrum. The reason for that might be attributed to the composite showed a number of peaks of ZnO (Fig. 3) as better photocatalyst, the changes in the band gap and increasing the number of surface defects as a result of combustion synthesis. When molar ratio of Zn, Ti and Ce was 1:0.25:1, the composite prepared by combustion method possess better decolouring activity. The reason for that might the composite has the same XRD pattern as CeO$_2$ (Fig. 2), but possess better crystallinity, so exhibit higher decolouring activity.

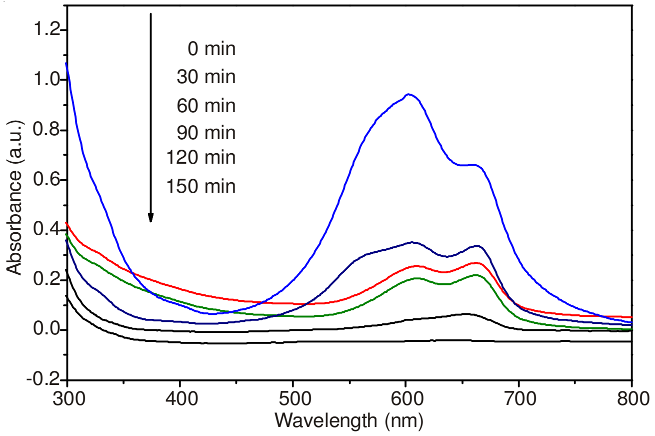

Fig. 7. ZCT composite decoloured methylene blue

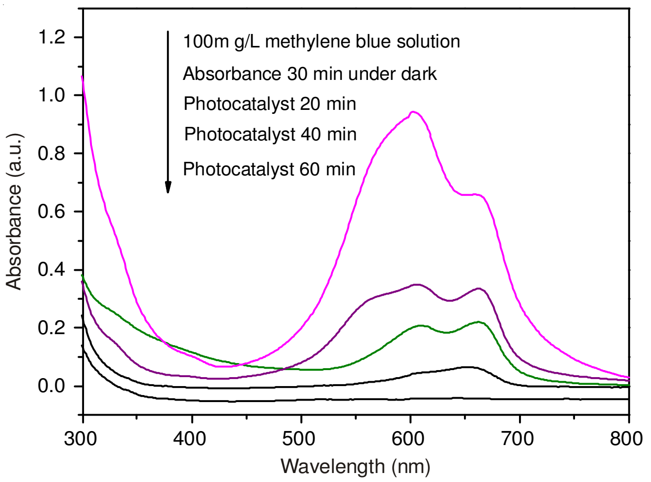

Fig. 8. ZCT composite photo-catalyzed methylene blue

Effect of surface modification: Lipophilic degree is as evaluation standard of modified effects. The dispersion degree of powder in organic medium is better, lipophilicity is higher. methanol was added drop-wised into mix solution of 0.5 g modified nano-powder and 40 mL distilled water. When the floating powder on the surface of water was completely wet, recorded added methanol quantity (mL) was "a", usable the following formula to calculate the lipophilic degree. Fig. 9 shows the lipophilicity of ZCT and MZCT in methanol. The fact shows that the compatibility between MZCT and methanol is better than that between ZCT and methanol. Because of the larger surface area of ZCT, it is easy for ZCT to absorb water molecules, which tend to polarize and produce polar hydroxyl groups on the surface of ZCT. The polar hydroxyl makes it difficult for ZCT to disperse in organic media. The modifier includes hydrophilic and oleophilic groups. The polar hydroxyl groups on the surface of ZCT arrest the former and the latter groups are exposure in media to improve the compatibility between MZCO and organic media.

$$\text{lipophilic degree} = \left(\frac{a}{40} + a\right) \times 100\,\% \qquad (1)$$

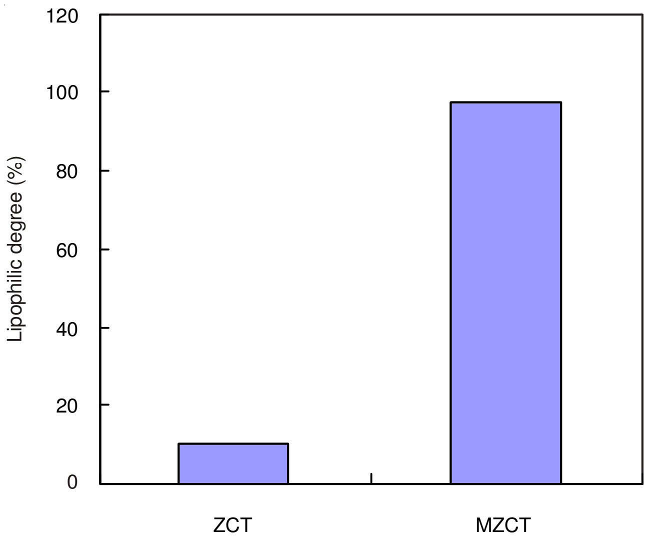

Fig. 9. Lipophilic degree of ZCT and MZCT

Light-stability of MZCT/paraffin wax: The light-stability of paraffin wax decreases because paraffin wax absorbs UV-light result in degradation and increasing chromaticity of paraffin wax. Table-2. shows different dose of MZCT effected on light-stability of paraffin wax. The paraffin wax with MZCT possess more excellent light-stability than the blank paraffin wax. That means MZCT can improve the light-stability of paraffin wax. The composite with molar ratio of Zn, Ti and Ce is 1:0.25:1, 0.2 %, light-stability of paraffin wax is optimum because the chromaticity of paraffin wax only change from 1 to 2 by UV light irradiating of 90 days in Table-1. The reason may be the composite possess better crystal and ultraviolet absorbing property, when molar ratio of Zn, Ti and Ce was 1:0.25:1. The composite absorbed ultraviolet light prevented paraffin wax from degradation and oxidation. The chromaticity of blank paraffin wax change from 5 to 10 by irradiating of UV-light after 90 days and the light-stability of paraffin wax obviously decreases. Table-1 shows other UV shielding agents protect paraffin wax to UV degradation in 14 days. Table-2

TABLE-1
EFFECT OF DIFFERENT MODIFIED COMPOSITE ON LIGHT-STABILITY OF PARAFFIN WAX

Irradiating time	Paraffin wax	Zn:Ce:Ti =1:1:1	Zn:Ce:Ti 4:0.25:1	Zn:Ce:Ti 1:0.25:1	TiO_2 0.2 %	ZnO 0.2 %	CeO_2 0.2 %
0	5	4	2	1	2	1	4
7 d	6	4	2	1	2	1	4
14 d	7	4	2	1	2	1	4
30 d	9	5	2	1	3	2	5
60 d	11	7	3	2	4	2	6
90 d	13	9	4	2	5	3	7

TABLE-2
EFFECT OF COMPOSITE DOSE ON LIGHT-STABILITY OF PARAFFIN WAX

Radiation time	Paraffin wax	Zn-Ce-Ti 0.08 %	Zn-Ce-Ti 0.1 %	Zn-Ce-Ti 0.2 %	Zn-Ce-Ti 0.3 %
0	5	4	3	1	2
7 d	6	4	3	1	2
14 d	7	4	3	1	2
30 d	9	5	4	1	2
60 d	11	6	4	2	3
90 d	13	7	5	3	3

shows dose of MZCT is more, light-stability of paraffin wax is better. But dose of MZCT in paraffin wax is 3 %, light-stability of paraffin wax change worse. So, the composite which molar ratio of Zn, Ti and Ce is 1:0.25:1, 0.2 %, light-stability of paraffin wax is optimum. The reason can be attributed to the composite with molar ratio of Zn, Ti and Ce is 1:0.25:1 exhibited stronger UV absorbance. The composite exhibits completely different UV absorbance properties from ZnO[16], TiO_2[17], CeO_2[8,12], TiO_2-CeO_2[11], ZnO-CeO_2[13]. The composite has stronger absorbance in total ultraviolet region, moreover exhibit three very strong absorbance peaks such as UVC (200-280 nm), UVB (280-320 nm) and UVA (320-410 nm). So, the composite can well protect paraffin wax from degradation by absorbing all ultraviolet.

Conclusions

- The high purity ZnO-CeO_2-TiO_2 composite was rapidly synthesized by combustion method using ascorbic acid as new combustion agent. The composite was prepared within 2 h from solution to product. Meanwhile, this synthetic route is simple and easy to implement.
- The composite oxide not only had a strong absorption in the UV region, retained the strong absorption peak of ZnO and better transmittance in the visible region, but also possess better photocatalytic and decolouring properties.
- The light-stability of paraffin wax are improved by the composite with strong UV-shielding ability could be attributed to the composite retains UV-shielding properties of CeO_2, ZnO and TiO_2 and super to any monomer[15]. Inorganic UV-shielding agent and paraffin wax can be mutually mixed by modification of the composite. This is first that inorganic UV-shielding agent is applied to improve light-stability of paraffin wax.

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