Interface Template Synthesis of Zein-Based Amorphous TiO_2 Composite Microcapsules with Enhanced Photocatalysis

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Abstract

In order to further enhance the application field of zein-based microcapsule. Zein-based amorphous TiO_2 composite microcapsules (ZTCMs) were innovatively prepared from zein, tetra butyl ortho titanate (TBOT) and $\text{PEO}_{106}\text{PPO}_{70}\text{PEO}_{106}$ (F127) via interface template synthesis. The Effects of TBOT amount on ZTCMs structures and photo-catalytic performances were mainly investigated. Chemical structure and microstructure of the obtained composite microcapsules were characterized mainly by fourier-transform infrared spectroscopy (FTIR), transmission electron microscope (TEM), scanning electron microscope (SEM) and energy disperse spectroscopy (EDS). The results show ZTCMs exhibited evident hollow structure with titanium dioxide (TiO_2) wrapped in the outer layer. The average size of ZTCMs₃₀₀ was approximately 4 μm , which increased as the increase of TBOT dosage. Significantly, ZTCMs showed excellent photo-catalytic ability on dyes, red wine and coffee alike. The degradation rate of Rhodamine B (RB) was more than 80% after irradiation for 5 h under sunlight. This study provides a facile method to fabricate natural-based photo-catalytic material, which will be a good candidate in many fields such as medicine, food packaging, leather and textile.

1 Introduction

In the past few decades, massive use of fossil resources has led to the rapid consumption of global oil reserves and soaring oil prices. Therefore, it's meaningful to research and develop renewable resources. As a kind of plant protein, zein is derived from corn yellow powders [1–3]. There are a large number of hydrophobic amino acids and non-polar amino acid residues in zein, meanwhile zein is lacking of charged acidic, alkaline and polar amino acids [4–6]. Zein owns excellent performances including degradability, self-assembly ability and special solubility [7–9]. Hence, zein has significant potential to replace part of mineral resources which can be applied in medical, packaging, leather, textile fields, etc [10–13].

With the increasing of environmental awareness, consumers' active lifestyles and green consumption concepts have brought new challenges to daily necessities. For example, clothing is always stained by oils, juices or coffee, which can provide an easeful environment for microbial growth but a bad influence on people's daily lives and works. Owing to the advantages of high chemical stability and photo-catalytic activity, titanium dioxide (TiO_2) has been widely developed to degrade organic contaminants [14–16]. According to researches, TiO_2 own four kinds of natural polymorphs (TiO_2 (B), brookite, anatase and rutile) and at least five polymorphs that are produced synthetically [17]. Although the crystalline TiO_2 has a well defined structure, a large fraction of the atoms located on the surface show structural disorder, leading to them having unique properties different to their bulk crystalline counterparts [18]. This explains why the amorphous TiO_2 , with their disordered structure can have different properties, for advanced applications, relative to the crystal structures that have well-defined properties [19, 20]. Meanwhile, amorphous TiO_2 has also captured a great deal of attention due to the characteristic of the processability at room temperature and the high specific surface area [21, 22]. So, there is a growing interest in studying

the performances of amorphous TiO_2 which can possess a strong surface activity compared to crystalline TiO_2 of the same size [23, 24].

Up to now, the synthesis of functional materials based on TiO_2 and zein by combining the photo-catalytic performance of TiO_2 and the film-forming property of zein has been reported. Li et al. demonstrated a novel method to prepare composite films by using zein, poly propylene carbonate and anatase TiO_2 , which indicated TiO_2 can endow composite films with photo-catalytic activity [25]. Qu and co-workers reported an effective method to improve the photo-catalytic performance of composite films by adding highly dispersible TiO_2 nanoparticles [26]. Sajed et al. created a new nanofibers based on zein and sodium alginate incorporated with TiO_2 nanoparticles and betanin by using the electrospinning technique, and the nanofibers were beneficial to improve the shelf life and quality of food as the food packaging [27]. However, there is few reports on the combination of zein and amorphous TiO_2 , not to mention the design and research of the microstructures of composite materials containing zein and amorphous TiO_2 .

In our previous researches, the method of interface template synthesis has been used to craft chitosan-coated silica nanocapsules with a double-shelled structure, which was proved as an effectively method for preparing organic-inorganic double-shell materials [28]. Herein, in this study, amorphous TiO_2 -coated zein microcapsules (ZTCMs) were also prepared by interface template synthesis to improve the utilization of zein and the specific surface area of amorphous TiO_2 , and the possible synthesis strategy of ZTCMs was proposed as exhibited in Scheme 1. Firstly, the mixture was obtained after the blending, containing F127, TBOT, THF, was dropwise added into zein ethanol solution. And then, the microcapsules based on zein and F127 gradually formed with the volatilization of ethanol and THF. Meanwhile, the TBOT coated in the micelles was also gradually hydrolyzed. Finally, ZTCMs were obtained after spray drying the microcapsules emulsion.

2 Materials And Methods

2.1 Materials

Zein was obtained from Gaoyou Rixing Medical Supplementary Materials Co., Ltd. (Jiangsu, China). Ethyl alcohol was supplied by Tianjin Tianli Chemical Engineering Co., Ltd. (Tianjin, China).

PEO₁₀₆PPO₇₀PEO₁₀₆ (F127) was procured from Sigma-Aldrich. (Shanghai, China). Tetrahydrofuran (THF) and tetra butyl ortho titanate (TBOT, 99%) were purchased from Tianjin Kemiou Co., Ltd. (Tianjin, China). Rhodamine B (RB) was procured from Aladdin Reagents (Shanghai, China) Co., Ltd. All above chemicals were analytical grade and used without further treatment. Waterborne polyurethane was bought from Yantai Daocheng Chemical Co., Ltd. (Yantai, China). Red wine and coffee were bought from a supermarket in Xi'an, China.

2.2 Preparation of ZTCMs

Briefly, 5.0 g of zein was added into 500.0 mL of 85% (v/v) aqueous ethanol solution with magnetic stirring at 1000 rpm for 4 h at 40°C by heating in water bath. Meanwhile, a series of TBOT blends were prepared by dissolving 0.750 g of F127 in 9.0 mL of THF and adding different volumes of TBOT, before magnetic stirring solutions at 1000 rpm for 4.0 h at ambient temperature. Afterwards, 9.1 mL of different kinds of TBOT blends were added dropwise into 100.0 mL of zein stock solution with continuous stirring at 1200 rpm for 24 h at 40°C also by heating in water bath. Finally, all compound emulsions were stored at 4°C and powder samples were spray-dried by using a laboratory-scale spray-dryer (Spray Dryer, SD-Basic, Jia sheng technology co. LTD, Hong Kong, China) with air-inlet and air-outlet temperatures were 120°C and 80°C, separately. In this work, zein-based amorphous TiO₂ composite microcapsules (ZTCMs) with different TBOT volumes (300.0, 400.0, 500.0, 600.0 and 700.0 µL) were termed respectively as ZTCMs₃₀₀, ZTCMs₄₀₀, ZTCMs₅₀₀, ZTCMs₆₀₀ and ZTCMs₇₀₀. At the same time, microcapsules without TBOT (ZMs) were used as the blank control. What's more, ZMs film and ZTCMs film were obtained by mixing 0.1 g of ZMs and ZTCMs₆₀₀ with 50.0 g of aqueous waterborne polyurethane solution respectively (Support information 1, S1).

2.3 Characterization of ZTCMs

2.3.1 Particle size measurement

The particle size distribution (PSD) of ZMs and ZTCMs were measured by a dynamic light scattering instrument (DLS, Master Sizer 2000; Malvern instruments Ltd.). Samples were diluted by 50 times with deionized water prior measurement to avoid multiple scattering effects. Each test was repeated in triplicate at 25 ± 0.2°C.

2.3.2 Fourier transform infrared spectroscopy

The infrared spectra of spray-dried samples including ZMs and ZTCMs were measured by using a fourier transform infrared spectroscopy (FTIR, Bruker, Germany) described by zhu in the wavenumber range of 500–4000 cm⁻¹ by using the KBr pellet method.¹²

2.3.3 X-ray diffraction

An X-ray diffractometer (XRD, Bruker D8 Advance, Germany) was used to confirm the crystalline behavior of obtained ZMs and ZTCMs, with Cu K α radiation at a scanning rate of 8°/min. The diffraction angle 2 θ was set from 5° to 40°.

2.3.4 Transmission electron microscopy

The morphology and structure of ZMs and ZTCMs were investigated by a FEI transmission electron microscope (TEM, FEI Tecnai G2-F20, America) operated with an acceleration voltage of 200 kV. The freshly prepared dispersions were diluted using water, and one drop of the diluted dispersion was placed on a 200-mesh carbon-coated copper grid.

2.3.5 Scanning electron microscopy

The morphology of ZMs and ZTCMs were also studied by a scanning electron microscope (SEM, TESCAN-Vega 3 SBH, Czech) operated with an acceleration voltage of 10 kV. To study the morphology of microcapsules which were obtained after spray-drying, each sample was covered with a layer of gold and the sample imaging was performed in different magnifications. The surface elemental composition of ZMs and ZTCMs were also observed by this instrument equipped with an energy-dispersive spectroscopy (EDS).

2.3.6 Super depth-of-field microscopy (SDOFM)

The appearance and structure of ZMs and ZTCMs were observed by a super depth of field microscope (SDOFM, HIROX Corporation KH-8700, Japan). The AAE@Z-SMs were added dropwise on a silicon wafer before detection.

2.3.7 Photo-catalytic degradation of dye in the solution

As a water soluble xanthene organic dye, Rhodamine B (RB) is widely used as colourant in many industry processes [29–31], so it's meaningful to choose RB as the model dye. Photo-catalytic degradation experiments were performed in Xi'an, China (34°32'N, 108°55'E) in August 2019, and the sun exposure time was from 10.00 to 15.00 and the UV-light power of input solution was kept constant (10 W). The absorbance changes occurred in RB was evaluated by UV spectrophotometer (TU-1900, Beijing Purkinje General Instrument Co., Ltd). All the samples mentioned above were analyzed in a quartz cuvette with 1 cm path length over the wavelength range from 350 to 700 nm. The absorbance values of RB were recorded at the wavelength of 554 nm, meanwhile the absorbance values were converted to the corresponding concentration values on the basis of Lambert-Beer's law.

Precisely, 50.0 mL RB solution (10.0 mg/L) were poured into different glass reaction bottles which containing 25.0 mg ZMs, ZTCMs₃₀₀, ZTCMs₄₀₀, ZTCMs₅₀₀, ZTCMs₆₀₀ and ZTCMs₇₀₀, separately. At the same time, in order to verify the effects of the presence or absence of light on RB degradation, some samples were placed under light directly, while others were placed under light after wrapped in tin foil, the former was labeled (light) or (L) and the latter was labeled (dark) or (D). All experiments were tested three times, and the absorption rates and degradation rates were calculated using Eq. (1, 2).

$$\text{Absorption rate (\%)} = \frac{RB_{ai} - RB_{af}}{RB_{ai}} \times 100\% \quad (1)$$

$$\text{Degradation rate (\%)} = \frac{RB_{di} - RB_{df}}{RB_{di}} \times 100\% \quad (2)$$

Where RB_{ai} and RB_{af} represent the initial and final RB concentration of adsorption-dissociation equilibrium, RB_{di} and RB_{df} are the initial and final RB concentration of photo-catalysis degradation reaction, respectively.

In order to further examine the photo-catalytic performances of ZTCMs, three reaction cycles were carried out. Briefly, the spent ZTCMs samples were recovered via centrifugation and poured into distilled water under stirring on a magnetic stirrer. After the mixtures were filtered, the filter cakes were washed by distilled water and then were dried in a vacuum oven at 60°C. The dried again ZTCMs can be applied for the next photo-catalytic reaction. All the cycles were carried out maintaining a constant ZTCMs concentration (50% m/v). The degradation rate in each sample was obtained after irradiation for 20 h under a constant UV-light power of 10 W.

2.3.8 Photo-catalytic decomposition of stains on the film

Besides, to deeper investigate the photo-catalytic activity of the prepared capsules, a similar test was also conducted by dropping 50.0 μL of red wine or coffee solution onto ZMs or ZTCMs films, and the dimension of the two kinds of rectangular films were 2 cm $\times$ 2 cm. These films were exposed to UV-light (DOHO D60 10W, China) for certain time intervals to observe the photo-catalytic behaviors. Subjective stains degradation performances were evaluated by obtaining color photographs of the films.

3 Result And Discussion

3.1 Characterization of ZTCMs

3.1.1 Particle size of ZTCMs

Controlling microcapsule size plays an important role in governing the stability of dispersion and DLS was conducted to show the particle size distribution of ZMs and ZTCMs. As shown in Fig. 1, the mean diameter of ZMs at neutral condition was about 550 nm and previous study also reported similar results [32, 33]. From ZTCMs₃₀₀ to ZTCMs₆₀₀, the particle size sharply increased from 0.9 μm to 5.2 μm . With the continuous feeding of TiO_2 , the transparency of the dispersions were continuously reduced and the turbidity of that were gradually increased (inset in Fig. 1). One suggestive reason is that, during the process, zein self-assembly formed a spherical morphology and TiO_2 adsorbed on the hydrophilic groups around zein. However, the PSD of ZTCMs₇₀₀ overlapped most that of ZTCMs₆₀₀ but the PSD of ZTCMs₇₀₀ was not uniform. ZTCMs₇₀₀ possessed a wider PSD than that of ZTCMs₆₀₀, but the former average particle size was just slightly larger than that of the later. It's maybe that, with the increasing of TiO_2 dosage, the hydrophilic group vacancies on zein surface were reduced and a cross-linking was formed when reached adsorption saturation [18].

3.1.2 Structure characterization of ZTCMs

It's evident from Fig. 2(A) to find ZMs and ZTCMs have similar spectra. The primary characteristic peaks of zein were 1671 cm^{-1} (amide I, C = O stretching and C - N stretching), 1538 cm^{-1} (amide II, N-H bending) and 1240 cm^{-1} (amide III, secondary structures) [34]. In addition, some other featured peaks of

zein appeared at $3100 - 2800\text{ cm}^{-1}$ (a set of C - H vibrations of CH_3 and CH_2 groups), 1448 cm^{-1} (benzene ring respiratory vibrations) and 1166 cm^{-1} (secondary alcohols stretch and vibrations) [9]. Meanwhile, the characteristic absorption peaks in ZMs were partially different from those appeared in ZTCMs. As provided in Fig. 2(B), the stretching vibration absorption peak and bending vibration absorption peak of O-Ti-O bond appeared at 953 cm^{-1} and 842 cm^{-1} proved the existence of TiO_2 in the microcapsules [35]. By comparing the spectra of ZMs and ZTCMs, the characteristic peaks of hydroxyl group were respectively shifted from 3307 cm^{-1} and 3420 cm^{-1} to 2876 cm^{-1} and 3303 cm^{-1} , implying the formation of hydrogen bonds between zein and TiO_2 .

The crystalline behaviors of as-prepared ZMs and ZTCMs were carried out by XRD as provided in Fig. 3. Obviously, not other peaks could be observed in ZMs except two broad diffraction peaks at 8° and 20° , confirming zein is an amorphous structure [36, 37]. Simultaneously, two sharp diffraction peaks at 19° and 23° appeared in all diffraction lines of ZTCMs, this phenomenon can be illustrated by the formation of PEO crystals of F127, the similar results were also reported by other researches [38, 39]. At the same, the absence of the amorphous TiO_2 related peaks may arise from their amorphous structure with low crystallinity and the overlapping of the diffraction peaks of Zein or F127, which was in good agreement with the results of Kong et al [40]. So, the ZTCMs own an amorphous structure and the micromorphology of ZTCMs have been further researched by TEM, SEM and EDS.

3.1.3 Micromorphology characterization of ZTCMs

To investigate the effects of TiO_2 on the morphology and size of microcapsules, the microstructural features of ZMs and ZTCMs_{300} were determined by TEM. Figure 4 shows the morphology of both ZMs and ZTCMs_{300} were spherical, and these phenomena were due to the self-assembly of zein when the polarity changes in the microenvironment [28]. ZMs showed smaller diameters ranging from approximately $0.5\text{ }\mu\text{m}$ to $3.0\text{ }\mu\text{m}$ than that of ZTCMs_{300} , verifying the presence of TiO_2 shell can increase the diameter of ZMs. Under different contrasts, a well delimited wall demonstrated the hollow spherical structure of ZMs, while ZTCMs revealed a dense, solid and dark morphology with a microcapsule shape. The strong contrast between the dark edges and bright centers under different contrasts confirmed that zein was evenly coated by TiO_2 , and the result was also verified by other reports [28, 41].

The morphology of ZMs and ZTCMs were also assessed by SEM. Figure 5(A) depicts that, although a few particles appeared to be collapsed, mostly-spherical particles were observed, and this result was similar to that of Fig. 4(A). Differences in PSD of ZMs could be explained that high hydrophobicity can promote the formation of smaller protein microcapsules [42]. From Fig. 5(B-F), rough surfaces of ZTCMs were observed with less-uniform diameters from approximately $2.5\text{ }\mu\text{m}$ to $7.0\text{ }\mu\text{m}$. It could be observed that diameters of ZTCMs became larger with increasing TBOT usage, and this phenomenon further confirmed the results of DLS. It could be clearly seen from Fig. 5(F) that the diameter of ZTCMs_{700} was equal to that of ZTCMs_{600} , moreover, the agglomerated morphology can be observed but the boundary

between zein and TiO_2 seemed not clear. It maybe that, when more and more hydrophilic TiO_2 adsorbed onto the zein microcapsules, TiO_2 will combine with each other thus to form cross-linking structure [18].

EDS was used to investigate the elements distribution based on ZTCMs₅₀₀ surface displayed in Fig. 5(G-I). The elliptical auxiliary line showed where ZTCMs₅₀₀ exist. As is shown in Fig. 5(G), elements distribution on the surface of ZTCMs₅₀₀ was homogeneous indicating an uniform structure. It can be seen from Fig. 5(H) that nitrogen was mainly concentrated in circles, confirming the existence and the morphology of zein. What's more, Fig. 5(I) presents titanium exactly has same even distribution as nitrogen, which proved TiO_2 was uniformly distributed on the surface of microcapsules. Through the results we can assume zein and TiO_2 have a stable combination, meanwhile ZTCMs₅₀₀ possessed the best uniform and stable structure.

Meanwhile, the morphology of ZMs and ZTCMs were also observed by SDOFM. As shown in Fig. 6(A), the morphology of ZMs is relatively flat and the overall picture is blue-green. The particle size of ZMs is relatively small, with an average particle size of 1.4 μm . As shown in Fig. 6(B), in yellow-green and red states, ZTCMs have a relatively large particle size, with an average particle size of about 1.7 μm . At the same time, by comparing the 2D pictures, it was noted that the outline of ZMs is smooth, while that of ZTCMs is rough. The results show the size of the microcapsules increased with the addition of TiO_2 , which is consistent with the characterization results of SEM and TEM.

3.2 Photo-catalytic performance of ZTCMs

3.2.1 Photo-catalytic degradation of RB

RB has a good linear relationship between absorbance and mass concentration in the concentration range of 1–10 mg/L (Figure S1). In order to avoid the interference of dye adsorption on RB photo-degradation, a type of adsorption-dissociation equilibriums between the dye molecules and ZMs or ZTCMs were obtained (S2). The results of adsorption-dissociation equilibrium experiments were given in Fig. 7, which noted the RB absorption rates of ZTCMs increased as the increasing of TiO_2 dose. This phenomenon can be attributed to the augment of available active sites on ZTCMs surface [43].

To verify the photo-catalytic ability of ZTCMs, the effects of UV-light irradiation time on the photo-degradation rate of RB was studied. As reported in Fig. 8(A) and 8(B), with the increasing of irradiation time of ZTCMs₃₀₀, the absorbance value reduced from 0.60 at the 1st h to 0.43 at the 20th h and the concentration decreased from 8.16 to 7.38 mg/L. Meanwhile, the concentration curves of other types of ZTCMs had the similar trends. In fact, it can be illustrated that, as time prolong, the dye molecules have enough chances to adsorb on the surface of ZTCMs thus to be degraded under UV-light irradiation [43]. What's more, ZTCMs₃₀₀ almost have no ability to degrade RB in the absence of UV-light, and this result revealed ZTCMs have photo-catalytic ability only under irradiation. Figure 8(C) shows that, under UV-light, pure RB had scarcely degradation in the absence of ZTCMs. The obviously increase in degradation rates of RB is likely to arises from the increasing of TiO_2 content in ZTCMs. The color changes of RB in the

inset in Fig. 8(C) also show ZTCMs had abilities of adsorption and photo-catalytic (S3). There is a good probability that increasing the dosage of TiO_2 can improve the active site and active oxygen radical concentration [44]. However, RB degradation rate of both ZTCMs₆₀₀ and ZTCMs₇₀₀ were kept at about 50% at the 20th h. Two factors can account for this observation (Scheme S1). One is the saturation of active sites by dye molecules after a specific time [43]. Another is the contact area where ZTCMs combine with RB molecules decreased due to the accumulation of excess TiO_2 , and this reason can also be demonstrated by Figs. 5 and 6.

In order to simulate natural environment, the photo-catalytic activity of ZTCMs was further studied under sunlight. As displayed in Figure S2(A), RB's maximum absorption peaks shifted from 554 nm to 545 nm, which can be attributed to the formation of a series of N-deethylated intermediates of RB [45]. It could be seen clearly from Figure S2(B) that the concentration changes of RB degraded by ZTCMs under sunlight were similar to that under UV-light, but pure RB was still degraded about 7% even the absence of ZTCMs and the RB didn't degraded by ZTCMs₃₀₀ in the dark. We can know more details from Figure S2(C) that ZTCMs owned larger degradation rates under sun light than that under UV-light. In the meantime, RB showed more pronounced color changes under sunlight according to the inset in Figure S2(C). There are two reasons to explain this phenomenon. One is sun can provide a wider wavelength range including UV-light and a large amount of near infrared ray, so the RB molecules may be destroyed by sunlight. Another is the generation of photo-generated electrons and photo-generated holes could be promoted, thus benefiting the photo-catalytic efficiency of ZTCMs [46].

ZTCMs were recycled three times to investigate the changes of their photo-catalytic by degrading fresh RB. As represented in Fig. 9, ZTCMs₃₀₀ held dye adsorption ability in the absence of irradiation. During the first cycle, RB degradation in ZTCMs₃₀₀ (light) was 26.5%. However, with the increasing of TiO_2 content, catalytic behaviors of ZTCMs were enhanced, RB degradation rates of both ZTCMs₆₀₀ (light) and ZTCMs₇₀₀ (light) could reached about 40%. Then, in the second and third cycles, RB degradation rates of ZTCMs₃₀₀ (light) were respectively reduced to 20.4% and 19.5%, and other ZTCMs also showed relatively downward trends. The decrease in photo-catalytic efficiency can be explained by that, during recycling, ZTCMs formed hydrolysate on the surface when in contact with RB, which affected the effective contact between RB and photo-electron, photo-hole of ZTCMs [47–49]. The results are similar to those of Sharma et al [50], indicating the as-obtained ZTCMs, especially ZTCMs₆₀₀, still owned a reasonable photo-degradation efficiency after three cycles.

3.2.2 Photo-catalytic decomposition of red wine and coffee stains

In our daily life, dirt and greasiness can easily attack daily necessities' surfaces, which may cause inconvenience and troubles. Therefore, in this research, self-cleaning behaviors of ZTCMs composite films by using red wine and coffee as stains were conducted. Pictures of red wine and coffee on composite films before and after irradiation were listed in Table 1. It is clear to see that with the prolongation of photo-catalysis time, only slight changes in shapes and colors of droplets occurred on

ZMs films, indicating the weak photo-catalytic activity of ZMs films. For ZTCMs films, red wine and coffee stains gradually decomposed as the irradiation time increased from 1 h to 24 h. It was obvious that colors faded away and the outline became a bit fuzzy, suggesting a relatively higher decomposition, which was in complete agreement with the previous study [51]. The results pointed ZTCMs composite films own expected photo-catalytic activity.

Table 1
Discoloration of red wine and coffee stains on ZMs films and ZTCMs films under UV-light.

Films		Irradiation time					
		0 h	1 h	3 h	5 h	8 h	24 h
Red wine	ZMs film
	ZTCMs film
Coffee	ZMs film
	ZTCMs film

To give a guidance, a feasible mechanism was used to illustrate the photo-catalytic activity of ZTCMs. Surface atoms and internal atoms have so large differences in electronic states and bond states, which makes ZTCMs possess more active sites and enables TiO₂ a higher catalytic activity [52]. When the photon energy radiated by light source was greater than or equal to the band gap energy, TiO₂ outer shell can be excited to produce photo-generated electrons (e⁻) and photo-generated holes (h⁺) [53]. As shown in scheme 2, e⁻ and h⁺ can undergo four reactions: (a) both of them recombine in TiO₂; (b) both of them recombine on TiO₂ surface; (c) e⁻ migrates to the surface of TiO₂ and reduces electron acceptors and (d) h⁺ also migrates to the surface of TiO₂ and oxidizes electron donors. More importantly, only reactions (c) and (d) can participate in photo-catalysis reaction. Therefore, in this case, RB, red wine and coffee all could be degraded into H₂O, CO₂ and other degradation products by ZTCMs under reaction (c) and (d) (S Eqs. (1–4)).

Conclusions

ZTCMs with double-shelled structure were successfully prepared via interface template synthesis. The as-obtained microcapsules possessed an inner shell of zein and an outer shell of amorphous TiO₂. This

double-shell structure endowed ZTCMs with high photo-catalytic performance, and it still owned reasonable photo-degradation efficiency after three cycles of use. Most interesting, the composite films has good self-cleaning performance and can be used to degrade red wine and coffee under UV-light. What's more, double-shelled structure of ZTCMs may also be available for imparting kinds of functions, such as keeping stable and controlling delivery of nutrients, medical drugs, flavor fillers and so on.

Declarations

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CRediT authorship contribution statement

Prof. Xu, Mr. Bai and Mr. Wu carried out experimental research and collected data. Prof. Xu, Mr. Bai and Miss. Huang prepared the article. Mr. Qiu offered help in the materials preparation and instrumental analysis. Prof. Xu and Prof. Ma conducted the data interpretation, refined manuscript and choose the submission of article for publication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

Figure 1

Size distribution of ZMs and ZTCMs dispersions. Inset in it: dispersions appearances of (a) ZMs, (b) ZTCMs₃₀₀, (c) ZTCMs₄₀₀, (d) ZTCMs₅₀₀, (e) ZTCMs₆₀₀ and (f) ZTCMs₇₀₀.

Figure 2

FTIR spectra of ZMs and ZTCMs with (A) full spectra and (B) expanded spectra at 1700-700 cm^{-1} .

Figure 3

XRD pattern of ZMs and ZTCMs.

Figure 4

TEM images of ZMs (A) and ZTCMs300 (B).

Figure 5

SEM images of spray-dried microcapsules: (A) ZMs, (B) ZTCMs300, (C) ZTCMs400, (D) ZTCMs500, (E) ZTCMs600 and (F) ZTCMs700. EDX spectra of ZTCMs500: the distribution of (G) all elements, (H) nitrogen, (I) titanium, and the corresponding SEM image was inset in (D).

Figure 6

SDOFM (3D) images of (A) ZMs and (B) ZTCMs, and the corresponding 2D pictures of (A') ZMs and (B') ZTCMs.

Figure 7

RB adsorption rates of ZMs and different kinds of ZTCMs.

Figure 8

(A) Effects of UV-light catalytic time of ZTCMs₃₀₀ on absorbance of RB; (B) Effects of ZTCMs kinds on concentration of RB under UV-light; (C) Effects of ZTCMs kinds on degradation rates of RB and inset in (C): the visual inspection of the degradation of RB by different ZTCMs under UV-light for 20 h, including (a) pure RB (light), (b) ZTCMs₃₀₀+RB (dark), (c) ZTCMs₃₀₀+RB (light), (d) ZTCMs₄₀₀+RB (light), (e) ZTCMs₅₀₀+RB (light), (f) ZTCMs₆₀₀+RB (light), (g) ZTCMs₇₀₀+RB (light) and (h) pure water.

Figure 9

Photo-catalytic measurement of ZTCMs under UV-light for 3 cycles.

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