Development of New Catalytic Pigments: Dual Functional $\text{SiO}_2/\text{TiO}_{2-x}$ Amorphous Photonic Crystals for Non-Iridescent Structural Color and Enhanced Photocatalytic Activity

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Abstract

Biomimetic synthesis of amorphous photonic crystals (APCs) is a significant approach to obtain non-iridescent structural colors. However, the structural colors of artificially prepared APCs are dim or even white due to the influence of incoherent scattering. In this paper, we present an innovative method was proposed to combine APCs with black TiO_{2-x} to construct non-iridescent structural color pigments with high visibility and photocatalytic activity. Due to absorption of incoherent scattered light by black TiO_{2-x} , the color saturation of structural colors has been significantly increased. In addition, the utilization rate of photogenic carriers was effectively enhanced by slow light effect generated from pseudo-band gap of SiO_2 APCs with TiO_{2-x} absorbed full spectrum. The tone and color saturation of catalytic pigments are controlled by the diameter of SiO_2 nanospheres and the ration of TiO_{2-x} nanoparticles, which provides a controllable application study in color related fields such as artwork, environmental coatings and textiles.

1 Introduction

Color is an important form of expression in inheriting social civilization by integrating art and reality and expressing complex emotions of human beings [1]. Human fascination and pursuit of color has never stopped. From Dunhuang murals [2] to modern and fashionable decorative pigments [3, 4], humans have continued to improve the color and visual effects of synthetic pigments. To find inspiration for synthetic pigments, they paid attention to the brightly colored morpho butterfly [5], peacock feathers [6], and chameleons [7] that can switch colors instantly. This also inspired scientists to study the physics of the appearance of colors. The sparkle of butterflies originates from the regular arrangement of scale cells. Bright color switching of chameleon is caused by a combination of transparent guanine nanocrystals and melanosomes in the inner layer of skin [7, 8]. Submicron-scale materials are regularly arranged in a specific structure in space by the diffraction, interference, and scattering of light at a specific wavelength, thus producing a structural color that never fades [9–11].

Structural color based on photonic crystals has bright color and iridescent effect [12, 13]. The independent structural color prepared by the doping of melanin with amorphous photonic crystals (APCs) has been widely studied by scientists owing to their soft colors and ability to satisfy the visual needs of human beings [14–17]. A short-disordered APCs structure produces incoherent scattering of light, making the color of the material white [18]. Current studies have introduced nanoscale carbon black material (carbon, nanotube, acetylene black, and graphene) into the APCs structure as the backside to absorb coherent scattered light, or heat treatment in the presence of carbon in a reducing atmosphere to obtain non-iridescent structural color when synthesizing photonic crystal structure units [19–22]. Pastel colors and timeless non-iridescent structural colors can replace traditional chemical colors in use, but in the application of home decoration coating, pigment, and other color decoration fields, it is still unable to reduce indoor environmental pollution [23–25].

Well-known environment-friendly material titanium dioxide (TiO_2) has excellent photocatalytic properties, but white TiO_2 can only be excited to provide redox ability under UV light accounting for 5% of the light

[26]. Therefore, preparation of black TiO_{2-x} capable of full-spectrum absorption has become a research focus [27]. Hydrogen heat treatment of TiO_2 , Al/Zn reduction of P25, hydrogen plasma reduction of TiO_2 nanotubes, and other preparation methods require high temperature and pressure and time-consuming, so the chemical reduction method is used to prepare TiO_{2-x} [28–31]. Black TiO_{2-x} particles effectively replace carbon black material and absorb coherent scattered light. Moreover, as a structural unit of APCs, SiO_2 can effectively increase the specific surface area of TiO_2 , and black TiO_{2-x} with enhanced light absorption efficiency and large specific surface area can effectively promote the separation of electrons and holes, and significantly enhance the photocatalytic effect on pollutants [32].

Herein, black TiO_{2-x} with excellent photocatalytic performance was prepared by thermally reducing P25 with NaBH_4 for a certain period of time, and it was used as a black additive to reduce the incoherent scattering in APCs. A certain amount of TiO_{2-x} was added to the substrate by blending. In ethanol-activated SiO_2 nanospheres, TiO_{2-x} particles were distributed on the surface of SiO_2 nanospheres after stirring for a certain period of time at room temperature. After drying in a constant-temperature drying oven at 50 °C, $\text{SiO}_2/\text{TiO}_{2-x}$ APCs with photocatalytic properties and noniridescent structural color were obtained. Different colors can be adjusted by controlling the diameter of SiO_2 nanospheres, and the color saturation can be controlled by varying the amount of TiO_{2-x} . The concentration of TiO_{2-x} is related to the photocatalytic performance. Therefore, introduction of black TiO_{2-x} not only provides a direction for the functionalization of structural colors, but also improves the photocatalytic activity.

2 Experimental Section

2.1 Materials

Tetraethoxysilane (TEOS, 98%), ethanol (99%), and ammonium hydroxide (28–30%) were purchased from Sinopharm Chemical Reagent, China. P25 (98%) and sodium metaborate (NaBH_4 , 97%) were purchased from Tianjin Kermel Chemical Reagents. Deionized water (18.2 MΩ cm resistivity) was used in the experiments. All the other chemical reagents were of analytical grade and used as received without further purification.

2.2 Preparation of monodispersed SiO_2 nanospheres

Monodispersed SiO_2 nanospheres were synthesized using a modified Stöber method [33]. Appropriate amounts of ethanol (0–10 mL) and TEOS (3 mL) were poured into a mixture of ethanol (40–50 mL) and ammonia (4 mL), and the solution was magnetically stirred at 40 °C and mixed well. A homogeneous solution of ethanol and TEOS was added dropwise to the mixture of ethanol and ammonia, and the dropping rate was controlled at 0.2 mL/s. After the addition was completed, the system was continuously stirred at 40 °C and 500 rpm for 4 h. Finally, the uniform solution obtained was centrifuged, washed, dispersed in ethanol, and dried in an oven at 50 °C to obtain white SiO_2 nanospheres.

2.3 Synthesis of black TiO_{2-x} nanoparticles

Chemical reduction method was used to prepare black TiO_{2-x} P25 (4 g) and NaBH_4 were mixed at room temperature for 30 min. The mixture was added into a combustion boat; the reduction reaction was carried out in a vacuum tube furnace, and the temperature was increased to 380 °C at a rate of 7 °C/min for 2 h. A series of samples was obtained by controlling different molar ratios of P25 and NaBH_4 (4:0, 4:0.5, 4:0.75). The samples were washed with water to neutrality to remove unreacted NaBH_4 and then dried in an oven at 45 °C, producing powdered black TiO_{2-x} .

2.4 Fabrication of colorful $\text{SiO}_2/\text{TiO}_{2-x}$ APCs

Certain amounts of black TiO_{2-x} nanoparticles were added to the SiO_2 ethanol dispersion solution. Then, 50 mL of the dispersion solution was dispersed by ultrasonication for 4 h and stirred at room temperature for 7 h. The reaction process is shown schematically in Scheme 1. Anhydrous ethanol and deionized water were centrifuged, washed, and dried in an oven at 50 °C to obtain a $\text{SiO}_2/\text{TiO}_{2-x}$ APCs with excellent photocatalytic activity and non-iridescent structural color.

2.5 Characterization and property measurement

The surface morphology of $\text{SiO}_2/\text{TiO}_{2-x}$ APCs was observed using a field-emission scanning electron microscopy (FESEM, Hitachi FE-S4800). The reflection and absorption spectra of $\text{SiO}_2/\text{TiO}_{2-x}$ APC pigments were measured using a Cary 5000 UV-Vis-NIR spectrometer (Agilent), covering a wavelength range from 250 nm to 800 nm. The interplanar crystal spacing and crystalline structure of TiO_{2-x} nanoparticles were determined by transmission electron microscopy (TEM, FEI Tecnai G2F20S-TWIN) and X-ray diffraction (XRD; D/max-2200PC) analyses. The Raman scattering spectra of TiO_{2-x} was acquired using a Renishaw-in Via instrument equipped with a 532 nm red laser and CCD detector. The optical photographs of synthesis samples were recorded using an optical microscope (Leica DM2500 M) connected with a CCD camera.

Photocatalytic activity and photoelectrochemical properties were determined to illustrate the ability of catalyst to degrade pollutants. During the measurement of photocatalytic activity, 0.05 g $\text{SiO}_2/\text{TiO}_{2-x}$ APC catalytic pigments were added to a 50 mL RhB solution (5×10^{-6} M) each time, which was evaluated by visible-light irradiation from a BL-GHX-V photocatalytic reactor connected with a 500 W xenon lamp. To verify the adsorption and degradation balance, the solution was stirred magnetically under dark conditions for 60 minutes. After a period of illumination, 5 mL suspension was taken out every 30 minutes and the photocatalyst was removed by centrifugal separation. The degradation product was detected by UV-Vis spectrophotometer. Photoelectrochemical measurement was performed on electrochemical workstation (CHI760E) using a normative three-electrode, equipped with the Ag/AgCl electrode and platinum plate as the reference electrode and counter electrode, and the prepared photocatalysts as the working electrode. 2 mg photocatalysts was added to the mixture of 0.5 mL dimethylformamide and 1 mL ethanol to acquire the emulsion, which was coated in 1.0 cm³ FTO glass as the working electrode. Electrolyte is 0.5 M NaSO_4 aqueous solution. The photocurrent curve was

remarked by amperage under intermittent irradiation. Electrochemical impedance spectroscopy (EIS) was obtained in the frequency range of 0.01–100,000 Hz.

3 Results And Discussion

3.1 Morphology and structure of SiO₂ nanospheres

According to the Bragg diffraction law, the particle size of SiO₂ is related to the photonic bandgap of photonic crystals; photonic bandgaps produced iridescent structural colors [10, 34]. To obtain vivid color from colloid assembly, it is important to control the size of colloidal particles. Firstly, SiO₂ nanospheres with different particle sizes were prepared using the improved Stöber method. The reaction mainly includes hydrolysis and polycondensation. The amount of TEOS (3 mL) and ammonia (4 mL) is fixed. By controlling the concentration of ammonia and rate of TEOS hydrolysis, SiO₂ nanospheres with uniform size and different particle sizes were obtained. The specific reagents used in the reaction are shown in Table 1.

Table 1 Diameters of SiO₂ nanospheres

Samples	NH ₃ ·H ₂ O	CH ₃ OH	TEOS	CH ₃ OH	Particles size
1	4 mL	49 mL	3 mL	1 mL	221 nm
2	4 mL	45 mL	3 mL	5 mL	245 nm
3	4 mL	41 mL	3 mL	9 mL	287 nm

The SEM images of SiO₂ nanospheres with different particle sizes are shown in Fig. 1. The particle sizes of obtained SiO₂ nanospheres are 221 nm, 245 nm, and 287 nm. SiO₂ distribution is uniform, and the particle surface is smooth and flat. The structural unit of APCs was prepared. When the amount of TEOS and ammonia is unchanged, the particle size of SiO₂ depends on the ratio of ethanol. As the ratio of ethanol increases, the degree of alcoholysis of SiO₂ in ethanol increases, and SiO₂ crystal nuclei continue to grow, resulting in SiO₂ nanospheres with increased particle size.

3.2 Structure and properties of TiO_{2-x} nanoparticles

3.2.1 Crystal structure and morphology of TiO_{2-x} nanoparticles

Short-range disordered SiO₂ APCs have a white appearance and require black additives to absorb incoherent scattered light to eliminate the iridescent effect and achieve a single color that can be used in pigments and inks. As a new black additive, TiO_{2-x} is produced by the vacuum heat treatment of P25 (white TiO₂) and NaBH₄ in a tube furnace to hypoxia. The morphology and structure of TiO_{2-x} was

characterized by SEM, TEM, XRD analysis, and Raman spectroscopy. The SEM and TEM of TiO_{2-x} obtained with different contents of reducing agent are shown in Fig. 2. The particle size of TiO_{2-x} without reducing agent is about 30 nm, and the dispersibility is better (Fig. 2a-c). When 0.5 g of NaBH_4 was added for reduction, a part of the particles agglomerated, and the particle size increased. Some particles bonded together to form larger agglomerates. Fig. 3A-C illustrates that before P25 is reduced, the TiO_2 nanocrystals exhibit a high degree of crystallinity and good lattice characteristics. Fig. 3-5B testifies that the sample had a P25/ NaBH_4 mass ratio of 4:0.5 and reacted at 380 °C for 3 h. Samples showed a clear core-shell structure after NaBH_4 reduction. A highly crystalline inner core with an amorphous outer shell was observed. Fig. 3-6C shows that when the mass ratio was increased to 4:0.75, the proportion of amorphous shell in the sample in the entire crystal grain increased, and the thickness of shell also increased. As the degree of reduction increased, the inside of TiO_{2-x} lattice fringes became curved. With the thickening of amorphous shell on TiO_2 surface, the ordered lattice structure is almost invisible in the TEM image, and the lattice almost disappears.

XRD and Raman spectra of crystal structure are shown in Fig. 3. The XRD spectrum of TiO_{2-x} sintered at 380 °C for different ratios of P25 and NaBH_4 is illustrated in Fig. 3a. the diffraction peaks of two samples with a ratio of 4:0 and 4:0.5 appear at $2\theta = 25.4^\circ, 37.8^\circ, 47.5^\circ, 53.9^\circ, 54.9^\circ$, and 62.4° , corresponding to anatase (101), (004), (200), (105), (211), and (204) crystal faces of mineral TiO_2 (JCPDS 21-1272), respectively. When the ratio of P25 to NaBH_4 is 4:0.75, the diffraction peak of brookite phase appeared, indicating that excess reducing agent, TiO_2 was completely reduced to form Ti_2O_3 with a lower valence state.

Raman scattering spectrum further illustrates the crystal structure of TiO_{2-x} series samples, as testified in Fig. 3b. Four peaks appeared in the Raman diffraction pattern of TiO_{2-x} , 146, 394, 515, and 645 cm^{-1} , indicating that TiO_{2-x} and P25 have typical anatase phases. With the decrease in the molar ratio of P25 and NaBH_4 , the degree of reduction of TiO_{2-x} increased. Concentration of oxygen vacancies gradually increased, and the thickness of amorphous shell increased. This is consistent with the phenomenon observed by TEM, indicating that with the increase in the degree of reaction, the concentration of oxygen vacancies and the thickness of amorphous shell both increased. The peak corresponding to E_g shifted to the right, and the phase changed. This also shows that when the molar mass ratio of TiO_2 to NaBH_4 is 4:0.5, the anatase phase and other phase samples exist.

In a word, as the mass ratio decreases, the degree of TiO_2 reduction increases and order of crystal lattice decreases, and the crystallinity decreases. Meanwhile, the thickness of amorphous shell increases and color of TiO_2 deepens with the progress in reaction. Black TiO_{2-x} is more conducive to absorbing UV-Vis light and acts as a black additive to absorb incoherent scattered light in APCs.

3.2.2 Photocatalytic activity and enhanced mechanism of TiO_{2-x} nanoparticles

To rapidly and accurately analyze the light absorption mechanism of TiO_{2-x} , UV-Vis diffuse reflectance analysis was performed for TiO_{2-x} samples prepared under different ratios. The results are demonstrated in Fig. 4a. Untreated P25 showed strong absorption of UV light, but weak absorption in the visible-light range. TiO_{2-x} sample prepared by chemical reduction reaction showed not only strong absorption of UV light, but also significantly increased the absorption of visible light, consistent with the results of other studies where it was found that an amorphous shell and Ti^{3+} enhance the absorbance through a synergistic effect. After improving the experimental method, the absorbance of TiO_{2-x} significantly changed. With the increase in NaBH_4 , the appearance of TiO_{2-x} gradually darkened (yellow-black blue-black), and the performance shows that TiO_{2-x} powder not only gradually increased the absorption of visible light, but also gradually increased the absorption of light in the NIR region. Especially, When the ratio of TiO_{2-x} and NaBH_4 is 4:0.5, the light absorption performance of TiO_{2-x} becomes significantly stronger in the full spectrum and shows the same absorption intensity for UV light, indicating that the reduction of TiO_2 significantly improves the absorption for different bands of light.

Calculation and analysis of band gap showed that the reducing agent increased the reduction reaction of TiO_{2-x} , gradually darkening the appearance of catalyst. Meanwhile, the bandgap of catalysts decreased from 3.13 eV to 0.61 eV. The change in band gap shown in Fig. 4b indicates that the material has a corresponding response to the light of different bands. As the band gap becomes smaller, the response of TiO_{2-x} to light gradually becomes stronger. It is very important to acquire vividly visible structural colors.

In this experiment, by sequentially adjusting the ratio of P25 and NaBH_4 to 4:0, 4:0.5, and 4:0.75 and reducing in a vacuum tube furnace at 380 °C for 3 h, the colors of prepared TiO_{2-x} changed from white to black. With the increase in the amount of NaBH_4 , the concentration of reducing hydrogen increases by the thermal decomposition of NaBH_4 , thereby increasing the concentration of intermediate (reducing hydrogen) required for the reduction reaction. When the concentration of intermediates increases, the reduction of iron dioxide intensifies at the same time, and the reaction degree increases. Thus, increasing the oxygen vacancy of TiO_{2-x} , the oxygen vacancy of TiO_{2-x} increases. Which manifested in continuous color deepening (yellow-black-blue-black) on the macro level (inset of Fig. 4a), and the amorphous shell structure becomes thicker in turn. However, an appropriate oxygen vacancy can promote the separation of electrons and holes, reduce the combination rate of electrons and holes, and improve the utilization rate of light [35], The photocatalytic data are shown in Fig. 4c. TiO_{2-x} shows a relatively strong degradation efficiency of RhB, it is indicated that the appropriate oxygen vacancy concentration can effectively promote photocatalytic reaction in this experiment.

3.3 Morphology and structure of $\text{SiO}_2/\text{TiO}_{2-x}$ APCs

$\text{SiO}_2/\text{TiO}_{2-x}$ APCs with photocatalytic activity and non-iridescent structural colors were prepared from a mixture of TiO_{2-x} with excellent photocatalytic activity and activated 245 nm SiO_2 nanospheres. Their microscopic morphology was characterized by SEM, TEM, and EDS analyses, as shown in Fig. 5. Since

the activated SiO_2 provides a site for TiO_{2-x} to support and avoid agglomeration, it can be clearly seen that Ti, Si and O elements are evenly distributed in the microstructures.

3.4 Non-iridescent structural color analysis of $\text{SiO}_2/\text{TiO}_{2-x}$ APCs

Owing to the presence of incoherent scattering in APCs, the saturation of structural color is low to white. In this study, 10% TiO_{2-x} nanoparticles were added to SiO_2 colloidal particles of different diameters and mixed with 10 mL ethanol to form a mixture, which was uniformly dispersed by ultrasonication and dried at 45 °C. Blue, green, and purple structural color materials were obtained, as shown in Fig. 6A-C. The particle diameters of SiO_2 colloidal nanospheres are 221 nm, 245 nm, and 287 nm. The colors of $\text{SiO}_2/\text{TiO}_{2-x}$ pigments prepared under different particle diameters of SiO_2 nanospheres are quite different, indicating that SiO_2 APCs have different colors. This is because the microstructure of APCs is long-range disordered and short-range ordered. Nanospheres act as a structural unit, and the particle size affects the wavelength position of reflection peak, conforming to the Bragg-Snell law: . In addition, when the size of SiO_2 nanospheres gradually increases, the color of prepared structural color pigment starts to shift in the direction of long-wavelength light. Fig. 6d shows that with the continuous increase in particle size, the position of reflection peak of powder moves to the long wavelength direction, and its reflection spectrum shows obvious characteristic peaks at 439 nm, 512 nm, and 635 nm. The total amount of reflection on both sides is low, consistent with the color observed with the naked eye. If the amount of TiO_{2-x} added is too low, the color of powder will be uneven and white. Therefore, the effect of 10%, 30%, and 50% TiO_{2-x} addition on the color was evaluated. With the increase in the amount of addition, the color gradually changed to dark green. By observing the morphology with SEM, it was found that with the increase in the amount of TiO_{2-x} , particle aggregation occurred at 50%. However, as shown in Fig. 6e, after SiO_2 with a particle size of 245 nm was introduced with different amounts of TiO_2 , the position of reflection peak did not move. Therefore, the introduction of TiO_{2-x} has slight effect on the tonal change of structural color, but absorbs the incoherent scattering in APCs. Thus, the structural color has no angle dependence, and the saturation of color is improved.

3.5 Photocatalytic activity and enhanced mechanism of $\text{SiO}_2/\text{TiO}_{2-x}$ APCs

The active sites of photocatalysis are important for the production of redox reaction. A large specific surface area increases the number of active sites. Fig. 7a shows the N_2 adsorption-desorption isotherms of prepared TiO_{2-x} and $\text{SiO}_2/\text{TiO}_{2-x}$. According to the IUPAC classification, all the samples have similar type IV isotherms, and the relative pressure range is 0.7-0.95, producing a H3 hysteresis loop, a characteristic of mesoscopic materials [26]. In the range of (10, 30, and 50 wt%) TiO_{2-x} , the specific surface area increases with the increase in loading, significantly higher than TiO_{2-x} . Therefore, SiO_2 provides dispersion sites for TiO_{2-x} , which can effectively increase the specific surface area of photocatalyst, increase the active sites, and promote the transport of photogenerated carriers. The charge separation and transfer behavior of photocatalyst after light excitation can be analyzed by transient photocurrent and impedance measurements. Fig. 7b shows the transient photocurrent response of

SiO₂/TiO_{2-x} sample. After 30 s of visible-light excitation, all the samples produced a constant current. The current of SiO₂/50 wt% TiO_{2-x} is 3.1 $\mu\text{A}/\text{cm}^2$, indicating that it has good charge separation efficiency and migration rate, which can be further explored. The semicircle in high-frequency EIS diagram is a characteristic of charge transfer process, and the radius of EIS semicircle is equal to the semiconductor charge transfer resistance. Fig. 7c shows that the surface charge of TiO_{2-x} after chemical reduction is less, almost 5 times smaller than that of P25. Meanwhile, with the increase in TiO_{2-x} content in SiO₂, the transfer resistance of SiO₂/TiO_{2-x} gradually decreased, indicating that SiO₂/TiO_{2-x} APCs can be used as photocatalysts. In summary, structural color and photocatalysis were achieved by integrating the functions of catalyst.

UV-Vis-NIR absorption spectrum is generally used to measure the light utilization rate of a substance. When the response of a substance to light is high, the utilization efficiency of substance to light increases in the photocatalytic reaction. SiO₂ has almost no absorption of light, while after adding TiO_{2-x}, SiO₂/TiO_{2-x} has strong absorption characteristics in both UV and visible light (Fig. 8a). With the increase of TiO_{2-x} addition, the absorption rate of SiO₂/TiO_{2-x} gradually increased. Because a pseudo-band gap exists in the amorphous photonic crystal, its structural color is purple-red relative to 287 nm SiO₂/TiO_{2-x}, and double reflection peaks appear in the reflection spectrum. The corresponding reflection wavelengths are 406 nm and 635 nm. The absorption intensity decreased at 406 nm and 635 nm, but peaks appeared at 375 nm and 561 nm due to the edge effect of photonic band gap. Therefore, the introduction of TiO_{2-x} can enhance the light absorption, while the existence of pseudo-band gap of APCs produces a local optical effect and slow photon effect and synergistic enhancement of photon utilization ratio.

Fig. 8b shows the photocatalytic degradation curves of SiO₂/TiO_{2-x} prepared with 10%, 30%, and 50% introduction of RhB. The introduction of black TiO_{2-x} into SiO₂ provided photocatalytic performance. SiO₂/TiO_{2-x} shows amorphous photonic crystals structure color. As the percentage of TiO_{2-x} increased, the rate of photodegradation of pollutants under simulated sunlight gradually increased. The photocatalytic degradation rate constant of SiO₂/50 wt% TiO_{2-x} is 0.01363 min⁻¹, which can be attributed to photocatalysis (Fig. 8c). Excellent performance requires sufficient photocatalyst support. Moreover, compared with pure TiO_{2-x}, its photocatalytic degradation rate constant is 0.00775 min⁻¹, smaller than SiO₂/50 wt% TiO_{2-x}. Therefore, in this experiment, the prepared SiO₂/TiO_{2-x} APCs has a synergistic effect due to the optical localization effect and blue-edge slow photon effect produced by the pseudo-band gap and TiO_{2-x} with a large surface area, thus effectively enhancing the photocatalytic performance by improving the photon absorption.

Conclusion

In summary, we developed a novel catalytic structural color pigment that not only provides vivid physical structural colors, but also eliminates indoor pollutants. Black TiO_{2-x} with full-spectrum absorption prepared by reducing white TiO₂ with NaBH₄ was used as an additive to prepare noniridescent structural

colors, achieving one-step synthesis of dual functional $\text{SiO}_2/\text{TiO}_{2-x}$ APCs. Compared with pure TiO_{2-x} , colored $\text{SiO}_2/\text{TiO}_{2-x}$ APCs exhibited excellent photocatalytic activity. SEM and TEM characterization showed that SiO_2 nanospheres promoted the dispersion of TiO_{2-x} nanoparticles and provided active sites for catalytic reactions. DRS spectroscopy showed that the slow-light effect produced by the pseudo-band gap of APCs promotes the photon utilization of catalytic colorant, thereby improving the photoelectrochemical reaction and photocatalytic activity. The hue and color saturation of catalytic color can be controlled by controlling the diameter of SiO_2 nanospheres and the ratio of TiO_{2-x} . This provides a basis for the application of catalytic colorants in artworks, home decoration, and wall printing to decorate public places. Compared with traditional chemical colorants, these catalytic structural colors with decorative and photocatalytic functions can effectively satisfy the needs of mental and physical health.

Declarations

Conflicts of 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

SEM images of SiO₂ nanospheres with different particle sizes.

Figure 2

SEM (a-c) and TEM (A-C) images of TiO_{2-x} nanoparticles obtained with different content reductants (A: 4:0, B: 4:0. 5, C: 4:0. 75).

Figure 3

XRD patterns of TiO_{2-x} nanoparticles with different content of reductants (a). Raman diffraction spectrum of TiO_{2-x} (b).

Figure 4

TiO_{2-x} samples and absorption spectra of reductants with different contents (a); Curve of

Figure 5

SEM of SiO₂ and SiO₂/TiO₂-x (a-b). TEM of SiO₂/TiO₂-x (c). EDS element analysis (d).

Figure 6

Photos of SiO₂/TiO₂-x structural color with different particle sizes of SiO₂ (A-C). SEM of SiO₂/TiO₂-x (10%; b: 30%; c: 50%), the experimental sample is shown in the illustration (a-b). Reflection spectra of SiO₂/TiO₂-x APCs (d-e).

Figure 7

Nitrogen adsorption-desorption isotherm (a). Transient photocurrent responses (b). Nyquist plots of the $\text{SiO}_2/\text{TiO}_{2-x}$ sample (c)

Figure 8

UV-Vis absorption spectra (a). Photodegradation of $\text{SiO}_2/\text{TiO}_{2-x}$ APCs (b-c).

Supplementary Files

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- [Scheme1.png](#)