

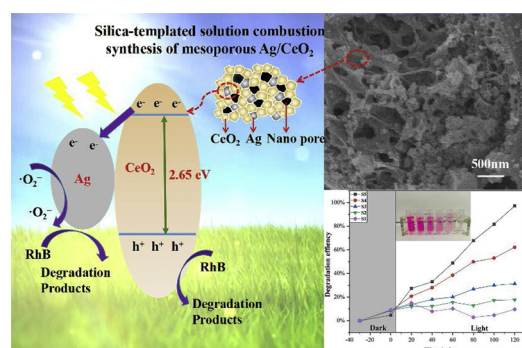
Ordered mesoporous Ag/CeO₂ nanocrystalline via silica-templated solution combustion for enhanced photocatalytic performance

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GRAPHICAL ABSTRACT



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ABSTRACT

The various ordered mesoporous Ag/CeO₂ catalysts were successfully prepared using a facile silica-templated solution combustion synthesis method (TSCS). Utilizing X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), Brunauer-Emmett-Teller (BET), photoluminescence (PL) and UV-vis diffuse reflectance spectrometry (DRS), etc., the morphological, structural, crystalline, surface and optical properties of Ag/CeO₂ were investigated. It was found that the removal of the template (SiO₂) resulted in the formation of ultrafine mesoporous Ag/CeO₂ composites, and the specific surface area increased to 98.6 m²/g. The 15 % Ag/CeO₂ composite showed the best photocatalytic performance (97 % at 120 min), which was approximately 10 times higher as compared to the conventional SCS (Solution Combustion Synthesized) CeO₂. In addition, a mechanism of the photocatalytic degradation of Rhodamine B (RhB) was proposed, where the reactive species ·O₂⁻ and h⁺ played important roles in the degradation of pollutants.

1. Introduction

With the rapid development of modern industry, the disposal of organic pollutants has become one of the most egregious environmental problems [1]. In recent years, various technologies have been applied to remove organic pollutants, including adsorption [2], biodegradation

[3], chemical oxidation [4], and electrochemical conversion/combustion [5], etc. Photocatalytic degradation of dyes using solar energy is an efficient and economical way among these methods [6,7]. Many existing oxide semiconductors, such as ZnO, TiO₂, and ZrO₂, etc., have been used to degrade organic dyes. Remarkably, cerium oxide (CeO₂) has attracted significant attention owing to its excellent oxygen

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storage/release capabilities [8], strong redox capacity, and non-toxicity. CeO₂ has been applied to environmental chemistry, pharmaceutical, and industrial applications [9–11], besides it has played a great effect in the field of photocatalysis [12].

Nevertheless, on account of its inherent wide band gap energy, Chen et al. [13] reported direct-band gap values ranging from 3.56 eV–3.71 eV for CeO₂ nanoparticles as prepared by a precipitation method [14]. The utilization efficiency of solar energy is relatively low, limiting the further application of CeO₂ in the treatment of environmental pollutants [15]. To improve the photocatalytic performance of CeO₂, some modification methods have been developed, such as loading ions, and/or noble metals [1,15–17]. As compared to noble metals including Au, Pd and Pt, etc. [18–25], silver (Ag) is more affordable and abundant. For example, Du et al. [26], utilized Ag to modify bismuth nitrate to increase the photocatalytic performance by 1.5 times; Grabchenko et al. [27] employed the interaction between Ag and CeO₂ to enhance its CO oxidation and soot combustion performance. Recently, several additional investigations of Ag/CeO₂ composites have been reported to focus on NO reduction, hydrocarbon oxidation and the antibacterial property [27,28]. However, Ag/CeO₂ composites applied as a photocatalyst for dye degradation are seldom investigated [29,30], especially for the degradation of Rhodamine B (RhB), which is toxic, carcinogenic to organisms and non-biodegradable [31,32].

Several methods are reported to prepare CeO₂ and Ag/CeO₂ composites in the literature, including hydrothermal, solvothermal, sol-gel, photodeposition. Saravanakumar et al. [31] synthesized Ag/CeO₂ using a facile hydrothermal method for the photocatalytic degradation of organic pollutants. Liu et al. [30] prepared Ag/CeO₂ via photodeposition method, and it exhibited good photocatalytic performance for methylene blue degrading. Compared to these techniques, solution combustion synthesis (SCS) [33] is an energy- and time-saving approach without the requirements of any surfactants or additional chemicals [25,34,35], and has been used to synthesize thousands of oxides [36–39]. Ravishankar synthesized CeO₂ using SCS to study its photocatalytic performance [40]; Negi et al. used SCS as a one-step approach to synthesize Ag/CeO₂ to investigate its antibacterial properties and photocatalytic performance [41]. However, the high combustion temperature of SCS typically leads to low surface area (20–50 m²/g) [40–43] and metal sintering over the prepared oxides, i.e., aggregating to a larger cluster. Both of the above issues are not beneficial to enhance their catalytic performance. Recently, template-assisted solution combustion synthesis (TSCS) has been proved effective for increasing the specific surface area of the prepared oxide [44–47]. Manukyan et al. [46] introduced mesoporous silica (SBA-15) into a reactive solution followed by removing the template via etching, the obtained α-Fe₂O₃ nanoparticles exhibited a high specific surface area at 132 m²/g. TSCS was also used to produce porous CeO₂ catalysts with high surface area (81.7 m²/g), in which colloidal SiO₂ nanoparticles were added as the template [47]. However, to the best of our knowledge, there is no report on using silica-templated solution combustion synthesis for preparing Ag/CeO₂ composites.

In the present work, CeO₂ and Ag/CeO₂ composites were synthesized via the TSCS approach using colloidal SiO₂ as the template. The photocatalytic property of the as-prepared samples was investigated in the Rhodamine B degradation experiment. The effects of the silica template and Ag amount on the morphology and catalytic performance were analyzed and discussed. It was found that Ag/CeO₂ composites exhibited higher photocatalytic activity than that of CeO₂ in the Rhodamine B degradation experiments. The objective of this work is to develop an effective photocatalyst for the treatment of waste organic pollutants.

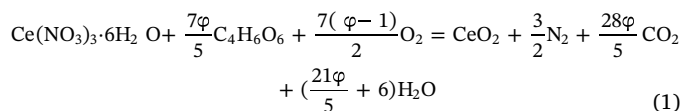
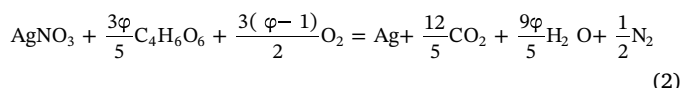
2. Experimental

2.1. Materials

All the following materials were purchased from Aladdin Chemical Reagent Co. Ltd, China, and used without any further purification: cerium nitrate hexahydrate ((Ce(NO₃)₃·6H₂O, AR 99.95 %), sodium hydroxide (NaOH, BP > 98 %) silver nitrate (AgNO₃, AR 99.8 %), tartaric acid (L-C₄H₆O₆, ACS 99.5 %), and Rhodamine B (RhB, AR 99.0 %).

2.2. Synthesis

The CeO₂ and Ag/CeO₂ powders were prepared via the silica-templated SCS. The metal nitrate–fuel (tartaric acid) molar ratio was selected according to the reaction stoichiometry for all experiments. The reaction between cerium nitrate hexahydrate and tartaric acid is written as Eq. (1); by the same token, the reaction between silver nitrate and tartaric acid is written as Eq. (2), in which φ is the ratio of fuel to oxidizer.



The case when φ = 1 means that the initial mixture does not require an additional atmospheric oxygen for the complete oxidation of the fuel, while φ > 1 (<1) indicates fuel-rich (-lean) condition [48]. In a typical synthetic process, 4.3412 g Ce(NO₃)₃·6H₂O and 1.6810 g C₄H₆O₆ in the stoichiometric ratio (φ = 0.8) were dissolved in 5 mL deionized water and mixed under vigorous magnetic stirring for 5 min at 353 K (Solution A). In a separate beaker, 0.0849 g of silver nitrate and 0.0360 g of tartaric acid were treated in the same way (Solution B). Both solutions were mixed and added 1 mL silica sol and stirred at 353 K until the solution became homogenous. Then the mixture was transferred into a muffle furnace followed by heating at 500 °C for 20 min. The entire collected powder was immersed in 4 M NaOH at 80 °C for 12 h. After rinsing and drying, the reaction of silica sol and sodium hydroxide can be written as Eq. (3).



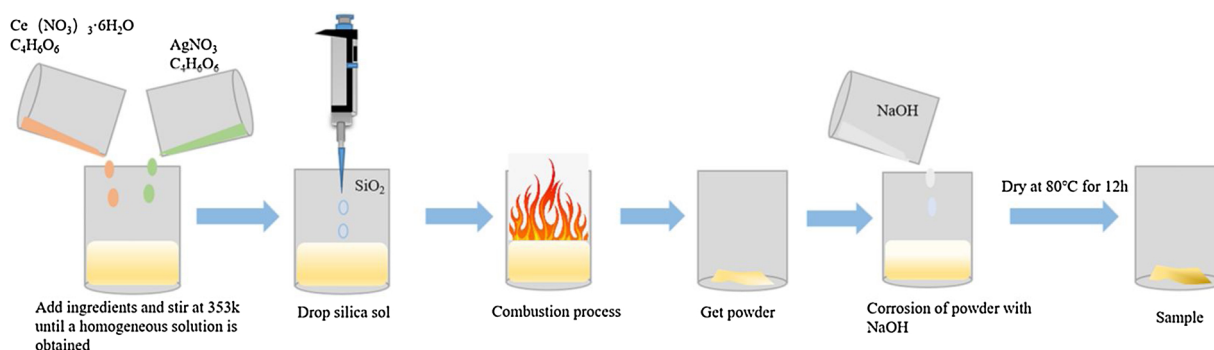
This sample is labeled as S3, where 5 % Ag means the molar ratio of Ag/Ce. Other samples denoted as CeO₂, 10 % Ag and 15 % Ag were synthesized using the same procedure by controlling the content of silver nitrate (see Table 1). The synthesis process is schematically illustrated in Fig. 1.

2.3. Characterization

The crystal phases and structures of the as-prepared samples were

Table 1
The amounts of reagents for each sample.

Samples	Solution A		Solution B		SiO ₂ (ml)
	Ce(NO ₃) ₃ ·6H ₂ O (g)	C ₄ H ₆ O ₆ (g)	AgNO ₃ (g)	C ₄ H ₆ O ₆ (g)	
S1	4.3412	1.8010	0	0	0
S2	4.3412	1.8010	0	0	1
S3 (5% Ag)	4.3412	1.8010	0.0849	0.0360	1
S4 (10 % Ag)	4.3412	1.8010	0.1699	0.0720	1
S5 (15 % Ag)	4.3412	1.8010	0.2548	0.1080	1

Fig. 1. Schematic illustration of Ag/CeO₂ synthesis.

characterized by powder X-ray diffraction (XRD, Bruker D8 advance, Germany) at 40 kV and 40 mA with Cu K α radiation. The reaction process was studied by thermogravimetry analyzer (TG, Netzsch STA409PC, Germany) and differential thermal analyzer (DSC, Netzsch 404F3, Germany) in air at a heating rate of 10 °C/min up to 500 °C. The microstructures were characterized by scanning electron microscopy (SEM, Quanta 250, USA). The morphologies and size of the resultant products were obtained by high-resolution transmission electron microscopy (HRTEM, TecnaiG2 F20, USA). The surface chemical composition was determined by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, USA) with Al K α radiation (20 eV pass energy, 900 μm spot size). The surface properties such as specific surface area, pore size and pore volume of the Ag/CeO₂ nanomaterials were determined using N₂ gas Brunauer-Emmett-Teller (BET, BELSORP-max, Japan). The optical properties were evaluated using an UV-vis spectrophotometer (Lambda 750 s, USA) at 554 nm, while the photoluminescence spectra were recorded using a fluorescence spectrophotometer (PL, Varian3000, UK) upon 325 nm excitation.

2.4. Photocatalytic performance test

The photocatalytic performance was evaluated by degrading 20 mg/L Rhodamine B in an aqueous solution under UV and visible light, as RhB is a stable dye. The photocatalytic degradation experiments were carried out in a 50 mL beaker, which was placed on a magnetic stirrer with horizontally fitted 500 W Xe lamp as an irradiation source above it. In each set of experiments, 50 mg catalyst sample was added into 50 mL Rhodamine B (RhB) solution (20 mg/L), and was magnetically stirred in the dark for 30 min to reach an adsorption/desorption equilibrium [49]. An aliquot of 5 mL of this solution was taken out after 20-min intervals and centrifuged at 10,000 rpm for 5 min to remove photocatalyst solid. The concentration of residual RhB was then measured by UV-vis spectroscopic analysis at 554 nm. The catalytic efficiency is calculated as Eq. 4:

$$\text{Catalytic efficiency \%} = \left(\frac{C_0 - C_i}{C_0} \right) \times 100\% \quad (4)$$

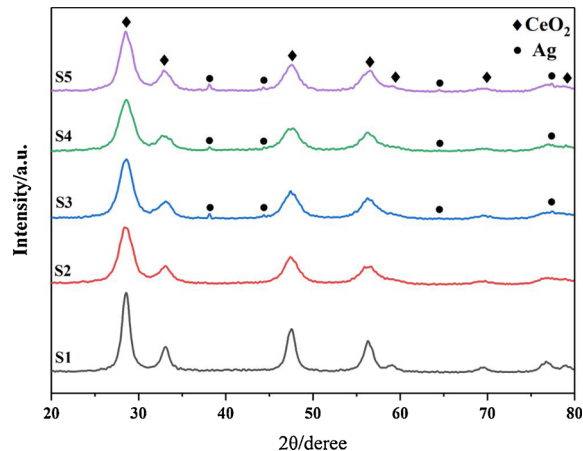
where C_i is the Rhodamine B concentration after degradation and photocatalysis, while C_0 is the initial concentration.

To further investigate the photocatalytic mechanism isopropyl alcohol (IPA, 1 mg/mL), 1 mL 1,4-benzoquinone (BQ, 1 mg/mL) and 1 mL ammonium oxalate (AO, 1 mg/mL) were added into RhB solution as the reactive species scavengers to clear $\cdot\text{OH}$, $\cdot\text{O}_2^-$ and h^+ , respectively. Then the above photocatalytic performance tests were repeated to confirm the influence of the reactive species.

3. Results and discussion

3.1. Phase composition and microstructure analysis

Fig. 2 shows the XRD patterns of the as-prepared CeO₂ and Ag/CeO₂

Fig. 2. XRD patterns of CeO₂ and Ag/CeO₂ composites.

composites. For samples S1 and S2, cubic fluorite structure of CeO₂ (JCPDS 34-0394) is the only phase of products, where the major peaks at $2\theta = 28.55^\circ, 33.08^\circ, 47.48^\circ, 56.33^\circ, 59.09^\circ, 69.40^\circ, 76.70^\circ$ and 79.07° correspond to diffraction peaks of the (111), (200), (220), (311), (222), (400), (331) and (420) planes, respectively. No diffraction peaks of silica can be detected in the products of silica-templated SCS. And the diffraction peak of sample S2 was broadened significantly, indicating that the grain size was refined (the particle sizes of samples S1 and S2 were 7.5 nm and 5.6 nm, respectively). It also implies that SiO₂ can absorb the heat of reaction as a diluent [50,51], representing a different role in addition to a templating agent. Thus, SiO₂ helps reduce the combustion heat and make the reaction more gentle to achieve the effect of grain refinement. The diffraction peaks of Ag/CeO₂ samples are also significantly broadened, further confirming the role of SiO₂ as a diluent. According to the Scherrer formula combined with XRD diffraction peak width, the crystalline grain size of S3, S4 and S5 were calculated as 5.0 nm, 4.8 nm and 5.1 nm, respectively. In addition to diffraction peaks of CeO₂, several new peaks appear at $2\theta = 38.12^\circ, 44.28^\circ, 64.43^\circ$ and 77.42° when AgNO₃ was added, which are related to cubic Ag planes of (111), (200), (220) and (311). This indicates the presence of metallic Ag in samples S3, S4 and S5. The XRD results imply that highly crystalline CeO₂ and Ag/CeO₂ composites are successfully prepared via the silica-templated SCS method.

Fig. 3 demonstrates the SEM images with different magnifications of the as-synthesized catalyst samples. As shown in Fig. 3 (a), SCS CeO₂ solids are composed of non-continuous thin flakes with irregular shapes. And from the high-magnification image (Fig. 2 (d)), these flakes are composed of many fine particles that with highly ordered crystalline. As for the silica-templated SCS CeO₂ (Fig. 3 (b) and (e)), there are many macro- and mesopores in the sample. These holes may be caused by the silica-template introduced in SCS. The melting point of SiO₂ is about 1600–1700 °C [46,47], generally higher than the reaction

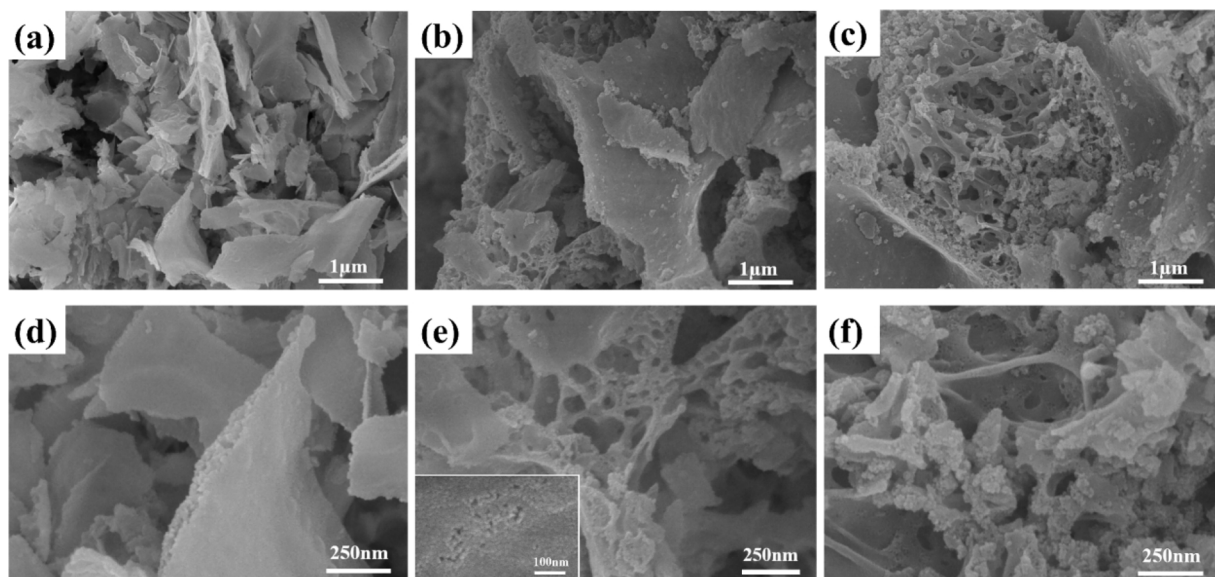


Fig. 3. SEM images of (a,d) SCS CeO₂, (b,e) TSCS CeO₂ and (c,f) TSCS 15 % Ag/CeO₂.

temperature of SCS. Therefore, SiO₂ will remain in the combustion products, and lead to pores after being etched by NaOH. In addition to the macropores, mesopores (diameter 7–10 nm), which nested in the micropores, also appear in the CeO₂ grains (see inset image of Fig. 3 (d)). This porous structure is beneficial for enhancing the specific surface area of the catalyst. And in accordance with the XRD results, the grain size of CeO₂ is 7–10 nm. As shown in Fig. 3 (c) and (f), 15 % Ag/CeO₂ were successfully achieved via the silica sol templated solution combustion synthesis (TSCS) exhibits similar morphology with the TSCS CeO₂.

The detailed structure and morphology of the as-prepared Ag/CeO₂ composites nanostructured materials were investigated by TEM and HRTEM (Fig. 4). From Fig. 4(a), it can be seen that many spherical nano-particles (diameter ranging from 1.4 nm to 4.3 nm) were distributed on these flakes. In HRTEM images (Fig. 4 (b) and (c)), the appearance of clear and ordered lattice fringes indicates that the composite are highly crystalline. The lattice fringes of spherical particles with the measured lattice spacing of 0.23 nm match well with the crystallographic planes (111) of face centered cubic Ag phase, while the lattice spacing (0.31 nm) of the flakes match well with crystal face (111) of cubic fluorite CeO₂. The TEM observations fit well with the XRD results, further demonstrating that the Ag-decorated CeO₂ composite has been successfully synthesized in the present study.

More detailed information regarding the chemical state and bonding environment of the Ag/CeO₂ composites (S5) were ascertained using X-ray photoelectron spectroscopy (XPS) (see Fig. 5). The binding energy positions of all the peaks were calibrated using C 1s' standard binding energy of 284.5 eV as a reference. Fig. 5(a) shows the XPS survey spectra of the S5 sample, in which the characteristic peaks of Ce, O, Ag

and C elements are detected. As can be seen from Fig. 5(b), in the high-resolution XPS spectrum of Ce 3d, the spectra were analyzed to four pairs of spin-orbit-split doublets. The peaks located at binding energies of 917.4 eV, 907.5 eV and 901.7 eV can be assigned to the Ce 3d_{3/2} level of Ce⁴⁺ [52]. Moreover, the peaks 899.1 eV, 889.9 eV and 882.8 eV were respectively to the Ce 3d_{5/2} level of Ce⁴⁺ [53]. While the other peaks were assigned to Ce³⁺ [54,55]. The O 1s core-level spectrum in Fig. 5(c) could be fitted with two peaks, which were related to O₂[−] (529.6 eV) confined by Ce⁴⁺ ions and O₂[−] (531.8 eV) ions to Ce³⁺ ions, respectively [56]. According to the XRD results, CeO₂ is the only oxide in S5 sample, and no diffraction peaks of Ce₂O₃ have been detected, which means that Ce³⁺ ions exit in the crystal lattice of CeO₂. It is known that the existence of Ce³⁺ ions on the surface of CeO₂ nano-crystals can induce their average lattice distortion of surface atoms and the production of more oxygen vacancies [57]. The oxygen vacancies could capture light-generated electrons and transfer the captured electrons to the adsorbed species of the catalyst, thus effectively preventing the charge carriers' recombination, which is beneficial to the enhancement of the photocatalytic activity [58]. Therefore, solo CeO₂ also has certain photocatalytic performance. However, the concentration of Ce³⁺ and the corresponding surface oxygen vacancies in cerium oxide will decrease with the incorporation of Ag due to the interaction between the Ag metal and CeO₂ (Ag⁺ + Ce³⁺ → Ag⁰ + Ce⁴⁺). And the interaction will become stronger with the increase of Ag content, which ultimately makes Ag play a leading role in the process of improving photocatalytic performance [59]. As for Fig. 5(d), the binding energies at around 368.5 eV and 374.6 eV are in agreement with Ag 3d_{5/2} and Ag 3d_{3/2}, respectively. These binding energies of Ag 3d are attributed to Ag⁺ ions and Ag⁰ [60], which further proves that Ag ions have been

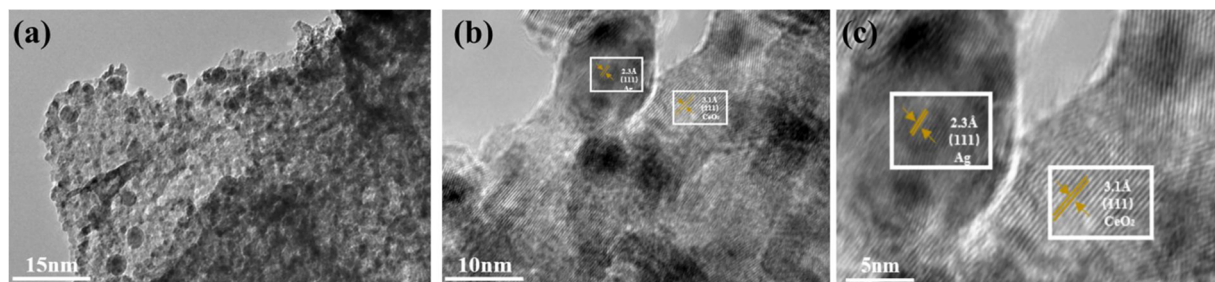


Fig. 4. The TEM (a) and HRTEM (b and c) images of the 15 % Ag composite.

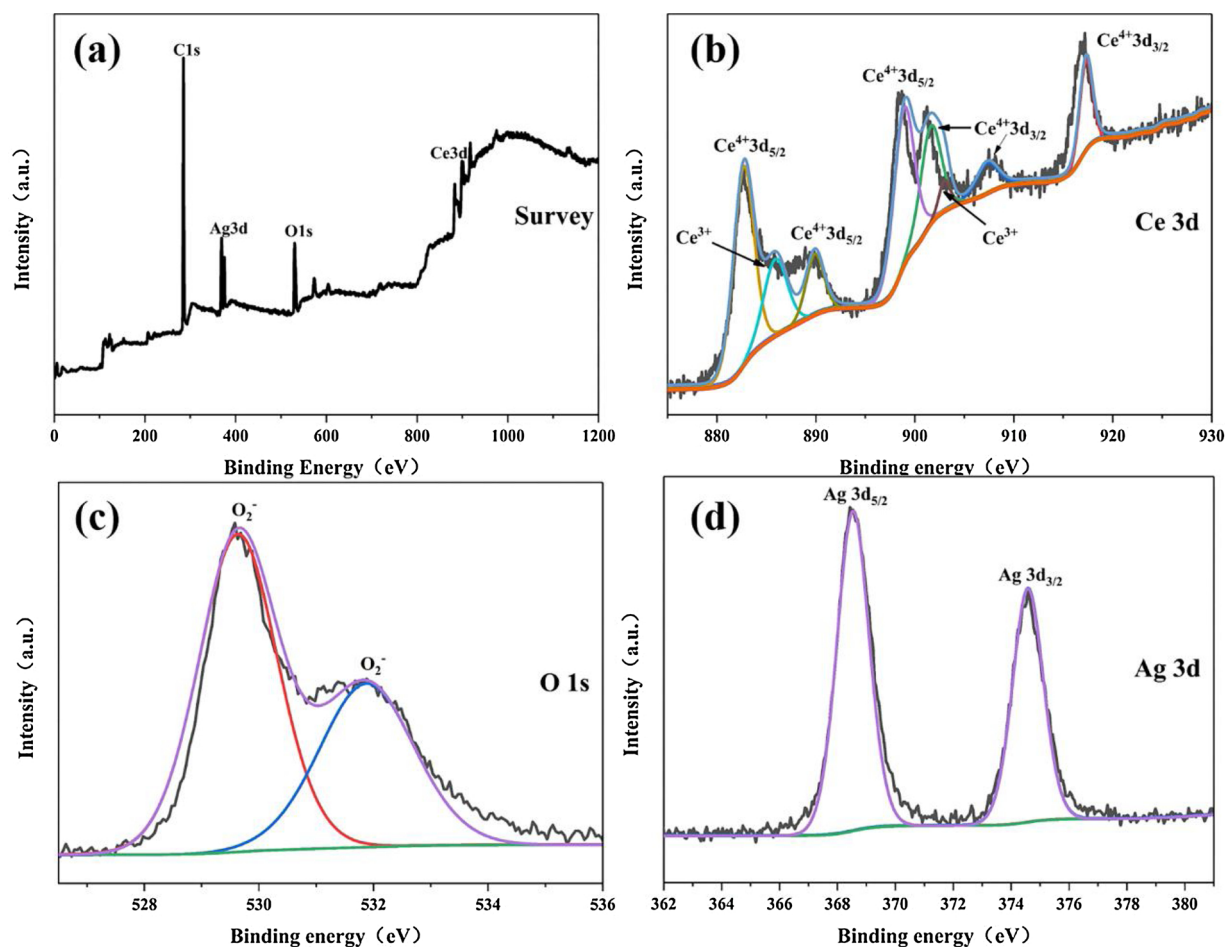


Fig. 5. XPS spectrum of S5 (a), High-resolution XPS spectra of Ce 3d(b), Ag 3d (c) and O 1s (d).

successfully loaded on the CeO₂ matrix.

The porosity of the as-synthesized material was confirmed from N₂ gas BET adsorption-desorption and Barret-Joyner-Halenda (BJH) pore size distribution analysis (see Fig. 6 and Table 2). It can be seen that the isotherm profiles of all samples displays type-IV [61] with a hysteresis loop, suggesting the mesoporous nature of the as-prepared samples composite. For SCS ceria (S1), the specific surface area and the volume is 43.466 m²/g and 9.9864 cm³/g, respectively, similar to the reported surface area of CeO₂ as prepared via solution combustion synthesis [61,62]. When the silica sol template was added, the specific surface area of as-prepared CeO₂ increases 127 % to 98.622 m²/g (Fig. 6 (b)), while the pore volume has also been improved to 22.659 cm³/g. The silica sol can help increase the surface area and the pore volume due to the following reasons: 1) the SiO₂ template could act as diluent in SCS

Table 2

The main textural characteristics (surface area, pore volumes, particle sizes) of representative as synthesized material.

Samples	V _m [cm ³ (STP) g ⁻¹]	S _{BET} (m ² g ⁻¹)	Mean pore diameter(nm)
S1	9.9864	43.466	10.479
S2	22.659	98.622	9.388
S5 (15 % Ag)	19.319	84.086	9.663

procedure, making the reaction more gentle to achieve smaller grains, as shown in the XRD results; 2) nano silica particles remain in the combustion products, and lead to nano pores after being etched by NaOH. As for the S5 sample (15 % Ag composite), the specific surface

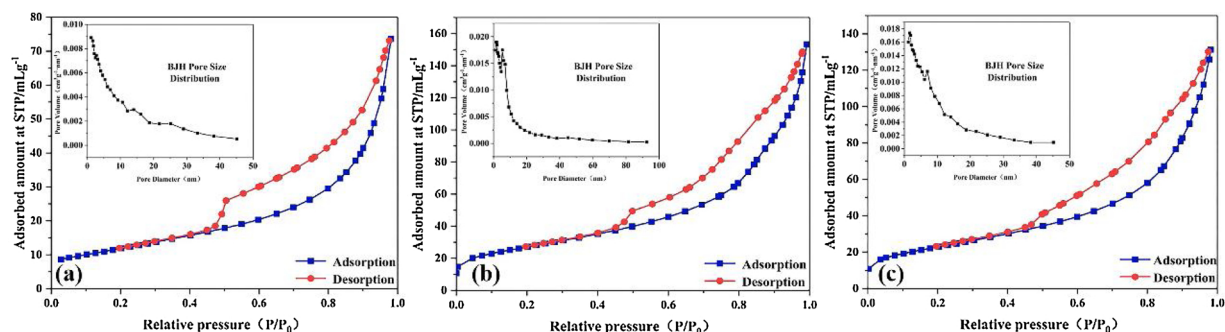


Fig. 6. Nitrogen adsorption-desorption isotherms of the SCS CeO₂ (a); TSCS CeO₂ (b) and 15 % Ag (c) composite. (inset shows pore size distribution of the corresponding components).

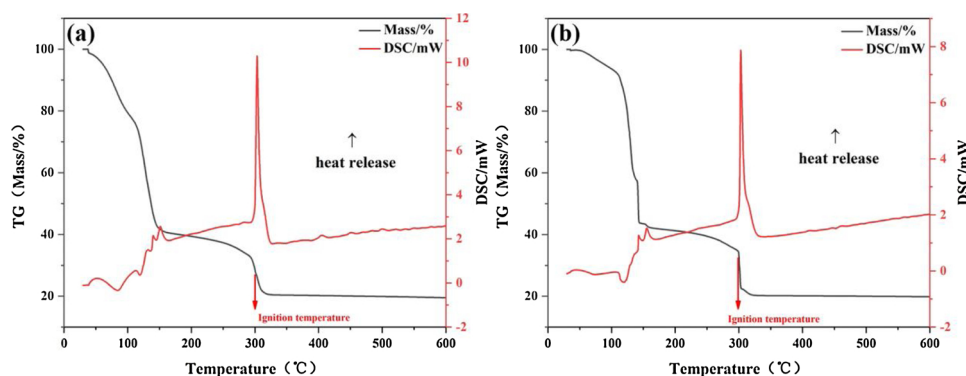


Fig. 7. DSC and TG curves of (a) SCS precursor of CeO_2 and (b) TSCS precursor of CeO_2 .

area is $84.086 \text{ m}^2/\text{g}$, which is slightly lower than that of sample S2 (TSCS CeO_2). However, the pore volume $19.319 \text{ cm}^3/\text{g}$, was found to decrease only slightly in comparison to S2. This trend is consistent with previous reports [41].

Fig. 7 shows DSC-TG linkage analysis of the combustion precursor in air. For precursor solution of sample S1 (Fig. 7 (a)), the DSC curve shows several minor endothermic peaks before 400°C , as similar to that of cerium nitrate (see S1 in S.I.). When the temperature reaches 301°C (ignition temperature), a great exothermic peak appears on the DSC curve, along with a rapid weight loss on the TG curve, indicating that a strongly exothermic reaction proceeds. This phenomenon differs with the thermal deposition of cerium nitrate and tartaric acid, in which the entire process remains endothermic. These results confirm the solution combustion reaction in the precursor, and the small endothermic peaks appearing in the early stage are due to the evaporation of the solvent, dehydration of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and early decomposition of cerium nitrate [63,64].

The TG and DSC curves of sample S2 (Fig. 7 (b)) are similar to that of sample S1, in which the combustion reaction starts at 304°C , only 3°C higher, indicating that the addition of SiO_2 does not affect the reaction mechanism of the cerium nitrate-tartaric acid system. For both samples, the TG curves become stable after combustion, and the stabilization of the mass proves that no organic residue remains in the product after combustion. Therefore, the heating temperature of 500°C in the present experiments is suitable for ensuring the complete combustion of organics and obtaining pure CeO_2 .

3.2. Photocatalytic characterization

The energy band feature of a semiconductor photocatalyst is one of the most important factors determining its photocatalytic performance. UV-vis absorption spectra of the as-synthesized CeO_2 and Ag/CeO_2 composites (S1-S5) are shown in Fig. 8 (a). Unlike SCS CeO_2 , TSCS CeO_2

and TSCS Ag/CeO_2 samples reveal a more intense continuous absorption in the visible light region of $400-800 \text{ nm}$. The absorption peak of TSCS CeO_2 is higher than that of SCS CeO_2 . The large specific surface area of TSCS CeO_2 contributes to this phenomenon. And the absorption edges of TSCS Ag/CeO_2 exhibit a red shift with the increase of Ag content, which can be ascribed to the increasing plasmon absorption of Ag particles at $\sim 510 \text{ nm}$ [65]. The band gap energy (E_g) of a semiconductor can be estimated according to Eq. (5):

$$E_g(\text{eV}) = 1240/\lambda_g(\text{nm}) \quad (5)$$

In this equation, E_g and λ_g represent band gap energy and wavelength, respectively [66]. The band gap energies of the SCS CeO_2 , TSCS CeO_2 , TSCS 5 % Ag, 10 % Ag and 15 % Ag composites are estimated to be 2.65 eV, 2.56 eV, 2.39 eV, 2.25 eV and 1.70 eV, respectively. These results indicate that all these TSCS Ag/CeO_2 samples have suitable band gap for photodegradation of RhB under UV and visible light irradiation, and higher Ag loading will obviously reduce the band gap of the catalyst.

Fig. 8 (b) shows the PL spectra of as-prepared samples. It can be seen that all samples exhibit four emission peaks at the wavelengths of 468, 486, 508 and 531 nm respectively. As compared to CeO_2 , Ag/CeO_2 samples exhibit a significant decrease in the PL intensity. The PL spectrum associated with the transport behavior of photo-electrons and holes can reflect the separation efficiency of photo-generated carriers [67]. Therefore, it is generally believed that lower PL intensity showing the decreased recombination of photogenerated charges will provide the potential for photoinduced charge carriers to participate in the photocatalytic reactions taking place on the semiconductor surface [68]. It implies that 15 % Ag composites (sample S5) shows the lowest recombination rates of electrons and holes, which is beneficial for the enhancement of the photocatalytic properties.

The photocatalytic activities of the as-synthesized samples are shown in Fig. 9 (a). For SCS CeO_2 , the photocatalytic efficiency is 9.6 %

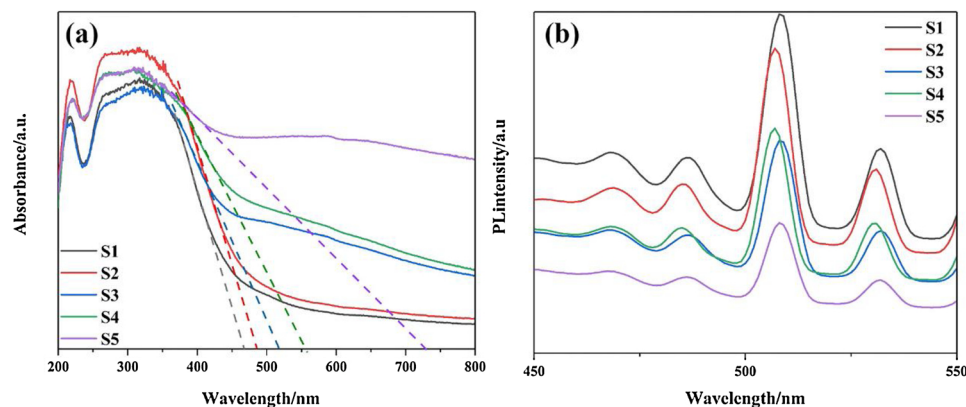


Fig. 8. (a) UV-vis diffuse reflectance spectra (DRS) of all CeO_2 and Ag/CeO_2 composites. (b) PL spectra of all CeO_2 and Ag/CeO_2 composites.

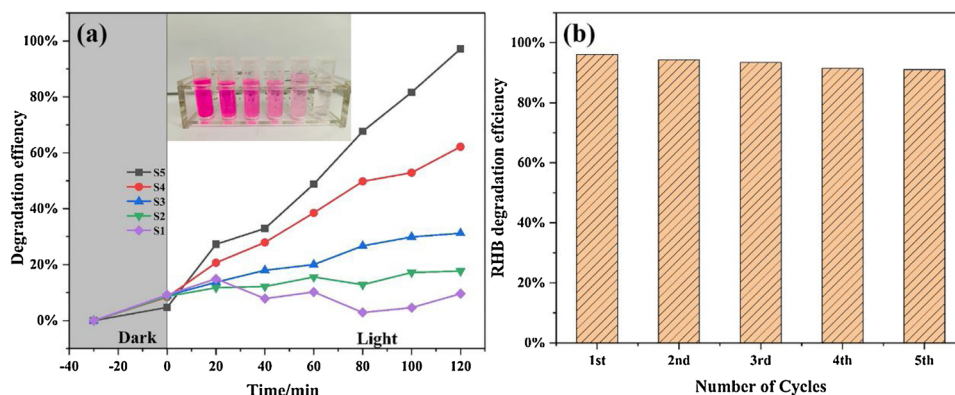


Fig. 9. (a) Time profiles of photocatalytic degradation of RhB over the as-prepared samples and inset shows the color change of RhB for the Ag-15 % composite as a photocatalyst; (b) cycle test of Ag-15 % composite.

within 120 min, while the degradation efficiency of the TSCS CeO₂ (17.7 %) is almost doubled, which is in accordance with the change of the specific surface area. These results indicate that the specific surface area has a significant influence on the catalytic activities of the CeO₂ catalysts. In general, a larger specific surface area means the matrix is more accessible to promote the photocatalytic reaction. When TSCS Ag/CeO₂ was employed, the improvement of photocatalytic performance can be clearly observed. The photocatalytic efficiency increases with the increase of the Ag amount, and 15 mol% Ag/CeO₂ shows the best photocatalytic performance (97.2 % in 120 min), which is approximately 10 times that of SCS CeO₂. This phenomenon can be attributed to the fact that the addition of Ag leads to a lower electron load rate and makes the band gap narrower. Moreover, according to the Mars van Krevelen mechanism [69], the oxygen availability and oxygen regeneration capacity are the most important factors in the catalytic performance, and the reverse spillover effect of Ag can powerfully promote the utilization of oxygen. The above results indicated that Ag modification significantly improves the photocatalytic performance of CeO₂.

As shown in Fig. 9 (b), the stability of the 15 % Ag composite photocatalyst was evaluated through recycling experiments. It shows remarkable photostability, where the photocatalytic efficiency of the sample decreased slightly, but still maintained at a high degradation rate of 91.1 % after five cycles of experiments.

By employing isopropyl alcohol (IPA) [70], 1,4-benzoquinone (BQ) and ammonium oxalate (AO) [71], trapping experiments of hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\cdot\text{O}_2^-$) and electron holes (h^+) were

performed over the 15 % Ag/CeO₂ composite in order to further investigate the photocatalytic mechanism. Fig. 10 (a) shows that the addition of the scavengers leads to the decrease of RhB degradation efficiency, which is especially true for BQ and AO. The RhB degradation efficiency sharply reduces to only 8.8 % and 18.4 % when BQ and AO were used as the scavenger, respectively. The presence of IPA has a limited effect on the RhB degradation (87.5 %). These results indicate that reactive $\cdot\text{O}_2^-$ and h^+ species play an important role in the photocatalytic degradation of RhB.

As shown in Fig. 10 (b), combined with the experimental results, a postulated mechanism for the enhanced photocatalysis of Ag/CeO₂ composites was proposed, including the optical absorption, the generation of photo induced electrons and holes, the transfer of the photogenerated charges and the surface reactions of photogenerated electrons and holes. The photocatalytic processes of the CeO₂ can be described as follows: upon light excitation with an energy higher than the band gap, the transition of electrons from the valence band to the conduction band of CeO₂ forms photogenerated electron-hole pairs. Photogenerated electrons and holes will transfer to the surface of CeO₂ and partially recombine by emitting photons in this process. The holes can degrade organic compounds directly when they are captured by the organic compound on the CeO₂ surface. The combination of electrons and dissolved O₂ in solution produces superoxide radicals $\cdot\text{O}_2^-$ which are also active in organics' degradation [72].

The modification with Ag nanoparticles plays an important role due to the following aspects: upon light excitation, photo-generated electrons and holes are generated on CeO₂. The silver-modified CeO₂

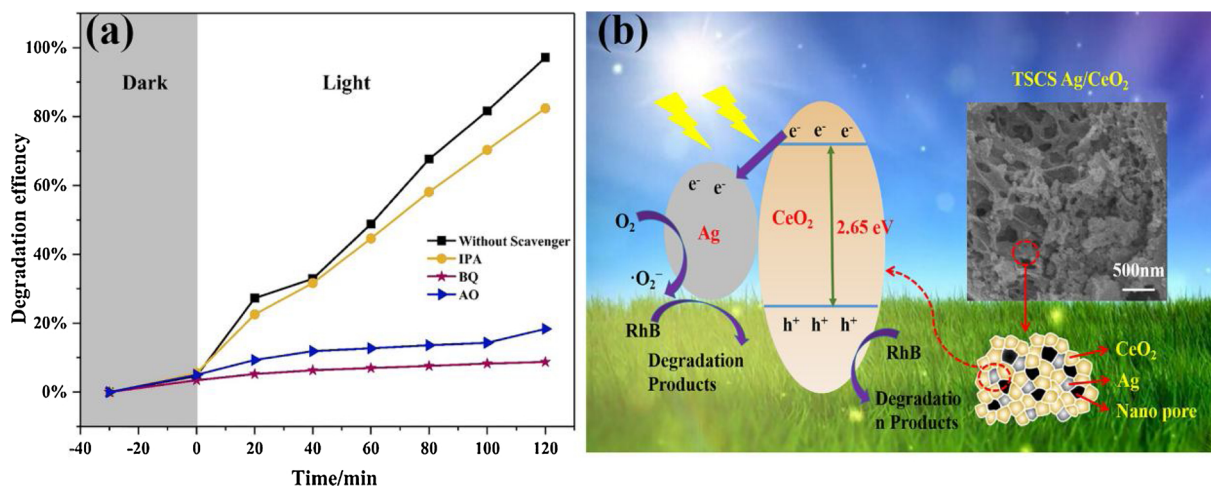


Fig. 10. (a) Effect of scavengers on the photocatalytic degradation of RhB by the 15 % Ag composite; (b) Photocatalytic mechanism of RhB degradation over Ag/CeO₂ composites.

accepts photo-generated electrons and prolongs the lifetime of charge carriers by the surface plasmon resonance (SPR) effect [73], resulting in a decrease in the recombination rate of electrons and holes and an improvement in photocatalytic efficiency, as confirmed by the photoluminescence (PL) spectra already. According to the Mars van Krevelen mechanism, the oxygen availability and oxygen regeneration capacity are the most important factors in the catalytic activity [69]. The oxygen availability is deeply associated with the content of oxygen vacancies in bulk ceria and can be promoted powerfully by Ag attribute to the reverse spillover effect [74,75]. And photogenerated electrons on the Ag surface can also react with O_2 to generate $\cdot O_2^-$ species. Finally, the reactive oxygen radicals ($\cdot O_2^-$) can react with RhB to form CO_2 and H_2O in photocatalytic reaction. In a nutshell, the Ag nanoparticle modification on CeO_2 nanosheets enhances the photocatalytic performances under both UV and visible light irradiation.

4. Conclusion

In summary, ordered mesoporous Ag/ CeO_2 catalysts were successfully achieved via the silica sol templated solution combustion synthesis (TSCS) method, which is cost-effective and suitable for large-scale production of metal oxide nanostructures with high porosity and surface area. The introduction of silica template into SCS is helpful to produce nanoporous (7–10 nm) structures with ultrafine grains (7–10 nm), making the specific surface area of CeO_2 increase to $98.6\text{ m}^2/\text{g}$. In particular, the addition of Ag effectively narrows the band gaps of Ag/ CeO_2 composites, reducing the recombination rate of photo-generated electron-hole pairs. The 15 % Ag/ CeO_2 shows the highest degradation efficiency of RhB dye (97.2 % in 120 min) under UV and visible light irradiation, which is approximately 10 times than that of SCS CeO_2 . The trapping experiments of radicals show superoxide radicals ($\cdot O_2^-$) and photogenerated holes (h^+) are the primary active species. A photocatalytic mechanism is proposed based on active species trapping experiments, the holes can degrade organic compounds directly when they are captured by the organic compound on the CeO_2 surface. It is concluded that the combination of electrons and dissolved O_2 in solution produces superoxide radicals $\cdot O_2^-$ which are also active in organics' degradation. This work provides an effective method to prepare ordered mesoporous Ag/ CeO_2 nanocrystalline with enhanced photocatalytic performance, which also shows a potential for synthesizing other kinds of mesoporous oxides.

CRediT authorship contribution statement

Zhichao Shang: Formal analysis, Data curation, Writing - original draft. **Zhongxiang Yang:** Investigation, Data curation. **Yang Xiao:** Conceptualization, Writing - original draft, Writing - review & editing, Funding acquisition. **Xiaohong Wang:** Investigation, Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Funding acquisition.

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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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.colsurfa.2020.125301>.

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