Enhanced photocatalytic crystal-violet degradation performances of sonochemically-synthesized AC-CeO$_2$ nanocomposites

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ABSTRACT

Semiconductor-based photocatalysis is one of the favorable techniques for the wastewater treatment. Herein, we synthesized the activated carbon-decorated cerium dioxide (AC-CeO$_2$) nanocomposites via the facile ultrasonication method by using the biomass-derived AC nanoflakes and the sonochemically-synthesized CeO$_2$ nanoparticles. The AC-CeO$_2$ nanocomposites exhibited the aggregated morphology with the AC nanoflakes-anchored CeO$_2$ nanoparticles. Since the hybridization of conductive AC and semiconductive CeO$_2$ would lead to the increased photocarrier transport and the reduced photocarrier recombination, during the photocatalytic reaction, the AC-CeO$_2$ nanocomposites showed the enhanced crystal violet dye-degradation efficiency up to 97.9% within 135 min. The results suggest that the AC-CeO$_2$ nanocomposites hold promise as a prominent photocatalyst for future green environmental technology.

1. Introduction

Organic pollutants from various industries are one of the key culprits for water pollution [1–3]. Over the past decades, the oxide semiconductor (OS)-based photocatalysis has emerged as an effective way to resolve such a critical issue. For example, several kinds of hazardous pollutants such as organic/inorganic dyes, pharmaceuticals, heavy metals, herbicides, surfactants, microorganisms, and pesticides were amputated from industrial wastewater via the oxide semiconductor-based photocatalysis [4–9]. Among various OSs, cerium dioxide (CeO$_2$) has attracted significant attention as an efficient photocatalyst because of its high photo-stability, high oxygen storage capacity, non-toxicity, photocorrosion resistance behavior, low cost, high thermal stability, and strong light absorption in the ultra-violet (UV) wavelength region [10–12]. However, the large bandgap energy (3.2 eV) and the high photocarrier recombination rate of the CeO$_2$ nanostructures have somewhat degraded their photocatalytic activities [13,14]. To overcome such drawbacks, hybridization of CeO$_2$ with transition metal oxides [15–18], noble metals [19], and/or carbon nanostructures (e.g., reduced graphene oxide [20,21], carbon nanotubes [22], graphene [11,23], graphene oxide [24,25], and activated carbon (AC) [26,27]) has been conceived and demonstrated as an effective way for enhancing the photocatalytic performances of CeO$_2$. Among them, AC holds promise for materializing the high-performance photocatalytic AC-OS composites because of its extraordinary characteristics such as high absorption capacity, high chemical stability, large surface area, high porosity, high conductivity, and high microstructural tunability [26–28]. Thus, the anchorization of OS with AC (i.e., formation of AC-OS nanocomposites) could be advantageous for improving the specific surface area and the conductivity, both of which are vital for the effective photocatalytic actions. Furthermore, AC could not only improve the charge transfer characteristics of the AC-hybridized OS composites but also reduce the photocarrier recombination at the AC-OS interface [29–31]. This could eventually lead to the enhanced photocatalytic performances of the AC-OS nanocomposites [32,33]. Recently, it is reported that high-performance AC could be derived from various biomass resources such as bamboo leaf [34], food waste [35], nartangai leave [36], palm tree [37], rice husk [38,39], coconut shells [40], green tea waste [41], apple tree branches [42], and neem leaves [43,44]. Because of its environmental friendliness, cost-effectiveness, massive availability, and...
morphological tunability [45,46], biomass-derived AC has been widely used as an effective additive for various catalytic, electrocatalytic, and photocatalytic applications. Owing to numerous benefits of both CeO₂ and AC, many researchers have investigated the synthesis and the characterization of the AC-CeO₂ nanocomposites for the energy conversion [26,27] and energy storage applications [47–49]. However, the AC-CeO₂ nanocomposites have rarely been utilized for the degradation of environmental hazardous pollutants [26]. To our best knowledge, particularly, no previous studies have reported on the photocatalytic crystal-violet (CV) degradation performances of the AC-CeO₂ nanocomposites even though the dye degradation of extremely harmful CV is of great importance in future environmental technology as well as modern chemical industry [50–53].

All the above backgrounds prompt us to investigate the synthesis of the high-quality AC-CeO₂ nanocomposites for demonstrating the highly efficient photocatalytic CV degradation performance. In this study, we therefore fabricated the AC-CeO₂ nanocomposites through the facile sonochemical process that can offer many advantages over other techniques, for example, a cost-effectiveness, an easiness, a facileness, a low thermal budget, an ambient pressure, and a short reaction time. The sonochemically-synthesized AC-CeO₂ nanocomposites showed an excellent photocatalytic CV degradation activity with a high efficiency of 97.9 % under visible light irradiation because of the effective charge separation of photoexcited electrons and holes in the present composite system. Herein, the material synthesis, material characterization, photocatalytic performance test, and photocatalytic reaction mechanisms of the AC-CeO₂ nanocomposites are systematically examined and discussed in detail.

2. Experimental section

2.1. Synthesis of CeO₂ nanoparticles

Fig. 1 schematically illustrates the experimental steps for the fabrication of the AC-CeO₂ nanocomposites via the simple sonochemical technique. Initially, the CeO₂ nanoparticles were synthesized by using bulk CeO₂ (Sigma-Aldrich, St. Louis, MO, USA). Bulk CeO₂ (1 g) was blended in deionized (DI) water (100 ml) and stirred for 10 min. After that, the prepared mixture solution was transferred into the glass vessel and sonicated at the ultrasonic power of 240 W under 35 kHz for 1 h. During the sonication process, the high intensity of the ultrasound provides a sufficient energy to break the larger aggregates into the smaller species [54–56], and it could eventually lead to the high dispersity of the nanostructures. After completing the sonication process, the CeO₂ nanoparticles could be obtained through following sequential processes of ‘collecting, washing, filtrating, and drying’ at 120 °C for 10 h in an electric oven.

**Fig. 1.** Schematic representation of the experimental procedures for the sonochemical synthesis of the CeO₂ nanoparticles and the AC-CeO₂ nanocomposites.

2.2. Synthesis of activated carbon nanoflakes

Neem leaves (Azadirachta indica, NLs), which had been harvested from Tamil Nadu, India, were used as a biomass carbon resource. Initially, the raw NLs were detached, rinsed, and dried at 20 h in sunlight. Next, the dried NLs were carbonized in a muffle furnace to collect their ashes. Namely, to burn the dried NLs, carbonization was performed at 500 °C for 1 h in air. After carbonization, the NL ashes (3 g) were mixed with KOH (12 g) by using a mortar and annealed at 600 °C for 2 h. After the KOH activation, the KOH-NL ash products were filtrated five-times by using DI water (100 ml) for 8 h to remove the unwanted potassium complexes. Finally, the AC nanoflakes in the form of colloidal powders were collected, filtered, washed, and dried at 120 °C for 8 h.

2.3. Synthesis of AC-CeO₂ nanocomposites

The AC-CeO₂ nanocomposites were synthesized via an ultrasound process by using the prepared AC nanoflakes and CeO₂ nanoparticles. Here, we note that the AC : CeO₂ ratio was fixed to 0.3 : 1 because previous studies [20,25–27,57] reported that, when using the AC-CeO₂ composites as a catalyst, the optimal ratio of AC : OSs was 0.3 : 1 for demonstrating better catalytic performances. Initially, 1 g of CeO₂ nanoparticles were dispersed in DI water (100 ml) and stirred for 10 min. Next, 0.3 g of AC nanoflakes were mixed with the above CeO₂-blended solution by continuous stirring for 20 min. After that, the AC-CeO₂ blended solution was sonicated for 1 h at the ultrasonic power of 240 W under 35 kHz. Finally, the sonicated colloidal suspension was strained, washed, and dried at 150 °C for 10 h to achieve the nanopowder form of the AC-CeO₂ nanocomposites.

2.4. Measurements of material characteristics

The surface morphology and the elemental composition of the prepared materials were examined through field-emission scanning electron microscopy (FE-SEM, Inspect-F50, FEI, Mahwah, NJ, USA) and in-situ energy-dispersive X-ray (EDX) spectroscopy, respectively. Additionally, the topographical insights of the prepared materials were further inspected by transmission electron microscopy (TEM, JEM 2100F, JEOL, Tokyo, Japan). The structural properties were investigated by X-ray diffractometry (XRD, D8-Advence, and Bruker, USA). The chemical vibration properties of the samples were evaluated through Raman scattering spectroscopy (LabRAM HR-800, Jobin Yvon, and Longjumeau, France), and the optical absorption properties were studied by UV–visible (UV–vis) spectrophotometry (T90 + UV spectrometer, PG Instruments Ltd., Wibtoft, England). The bandgap energies of the samples were also evaluated by ultraviolet photoelectron spectroscopy (UPS) (VersaProbe II, ULVAC-PHI, and Kanagawa, Japan). The electrochemical impedance spectroscopy (EIS) analysis was performed by using a VersaSTAT3 system (Ametek Scientific Instruments, USA) at a frequency range of 1 Hz – 10 kHz.
2.5. Measurements of photocatalytic performances

The photocatalytic degradation performances of the bare CeO$_2$ nanoparticles and the AC-CeO$_2$ nanocomposites were assessed by using the CV dye under visible light irradiation (halogen lamp, $\lambda_{\text{lamp}}$ = 350 – 3500 nm, $I_{\text{opt}}$ = 72 W). Initially, CeO$_2$ (20 mg) and AC-CeO$_2$ (20 mg) were separately dispersed in each quartz beaker (100 mL), in which 60 mL of CV (20 ppm) was contained. To confirm the equilibrium adsorption-desorption characteristics, before light illumination, the UV-vis measurement was performed for 30 min in a dark space. Next, the light source was turned on to start the photocatalytic dye degradation. During the degradation process, at certain time intervals (every 15 min duration), 3 mL of aliquots were extracted, and then the aliquots were subsequently centrifuged to separate the nanosize photocatalyst. Next, the residual CV concentration was determined by assessing the UV-vis absorbance at the maximum absorption wavelength of 590 nm. Here, the CV degradation efficiency ($\eta_{\text{deg}}$) was determined by using the following equation:

$$\eta_{\text{deg}} (%) = \left(1 - \frac{C_t}{C_0}\right) \times 100$$  \hspace{1cm} (1)

where $C_0$ is the initial concentration of the CV dye and $C_t$ is the CV dye concentration at a certain time $t$.

3. Results and discussion

The morphological properties of the bare CeO$_2$ nanoparticles and the AC-CeO$_2$ nanocomposites were monitored by the FE-SEM measurements. Fig. 2(a) and (b) display the FE-SEM images of bare CeO$_2$. The sample exhibits an aggregated morphology with the irregular-shaped CeO$_2$ nanoparticles-aggregated morphology. In the case of AC-CeO$_2$ nanocomposites, we confirm the mixture phases with polycrystalline CeO$_2$ and amorphous AC (Fig. 3(h)). To help understand the chemical mechanisms during the ultrasonication process. For the ultrasonication process in aqueous solution, the water (H$_2$O) provides the two significant radicals; i.e., one is hydroxyl (OH*) and the other is hydrogen (H*). Those radicals act as the reactants during sonication of bulk materials [58–62]; therefore, bulk CeO$_2$ (nCeO$_2$) could be reduced into small CeO$_2$ nanoparticles (CeO$_2$(m)) under the high ultrasonic power in H$_2$O. Such a sonochemical reduction can be expressed as below:

$$\text{H}_2\text{O} \rightarrow \text{OH}^* + \text{H}^*$$  \hspace{1cm} (2)

$$n\text{CeO}_2 + \text{OH}^* + \text{H}^* \rightarrow \text{CeO}_2(n)$$  \hspace{1cm} (3)

$$n\text{CeO}_2 + \text{AC} + \text{OH}^* + \text{H}^* \rightarrow \text{CeO}_2(n) - \text{AC} - \text{CeO}_2(n)$$  \hspace{1cm} (4)
Fig. 4 (a) shows the XRD patterns of the bare CeO\(_2\) nanoparticles and the AC-CeO\(_2\) nanocomposites. Both CeO\(_2\) and AC-CeO\(_2\) samples exhibit the diffraction peaks at 28.59, 33.08, 47.42, 56.33, 58.97, 69.36, 76.65, 78.97, and 88.36°, which are attributable to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (4 2 0), and (4 2 2) planes of cubic CeO\(_2\) (JCPDS card no: 34–0394), respectively \([63,64]\). Here, we note that no carbon-related peaks were observed in AC-CeO\(_2\) because of low volumetric distribution of AC in the entire composite system \([63]\). In addition, no other impurities and secondary phases were detected in both samples, and it signifies that the present samples hold a high crystal quality. To further elucidate the structural vibration mode of CeO\(_2\) and AC-CeO\(_2\), Raman scattering spectroscopy measurements were conducted. As shown in Fig. 4(b), both CeO\(_2\) and AC-CeO\(_2\) exhibit a strong Raman band at 465 cm\(^{-1}\), arising from the symmetric stretching vibration of Ce-O\(_8\) (i.e., F\(_{2g}\) mode) in CeO\(_2\) \([20,65]\). In addition to F\(_{2g}\), the AC-CeO\(_2\) nanocomposites display two additional Raman bands at 1345 and 1599 cm\(^{-1}\), which are denoted by D and G bands, respectively. The G band originates the E\(_{2g}\) vibration mode of the sp\(^2\)-hybridized carbon, and the D band sprouts from the defective and disordered features of graphite structures \([66–70]\). Such a simultaneous observation of F\(_{2g}\) and D/G depicts an effective hybridization of CeO\(_2\) and AC in a nanocomposite system.

Fig. 5(a) displays the UV–vis absorption spectra of CeO\(_2\) and AC-CeO\(_2\). Both samples exhibit the strong absorption peak at around 250 nm. According to literature \([71,72]\), the observed optical absorption band is attributed to the charge carrier transition from the O\(^{2–}\) (2p) state to the Ce\(^{4+}\) (4f) state in CeO\(_2\). By using Tauc’s plot \([73]\), the optical bandgap energy of CeO\(_2\) and AC-CeO\(_2\) were determined to be 2.8 and 2.1 eV, respectively (Fig. 5(b)), and these values are in good agreement with those obtained from the UPS data (Fig. S1). The smaller bandgap energy of AC-CeO\(_2\) than CeO\(_2\) can be ascribed to the formation of the localized band at the CeO\(_2\)-CeO\(_2\) interface, which might be created by anchoring of CeO\(_2\)-CeO\(_2\) surfaces by AC. Namely, AC provides the charge carriers at the CeO\(_2\) surface, and the charges accumulated at the CeO\(_2\)-CeO\(_2\) interface could lead to band bending \([73–75]\) along the aggregated CeO\(_2\)-CeO\(_2\) nanoparticles (Fig. 5(c)). This would eventually create the localized band at the CeO\(_2\)-CeO\(_2\) interface, and then the effective optical bandgap energy would be decreased in comparison with that of bare CeO\(_2\).

After characterizing the material properties of the fabricated products, we further investigate the electronic and optical properties of the fabricated materials. The results are shown in Fig. 6, where we can see that the fabricated materials exhibit high optical transparency and strong light absorption in the visible range. The bandgap energy measured from the UPS data is in good agreement with the optical absorption results. These findings suggest that the fabricated materials have potential applications in various fields such as photovoltaics and optoelectronics.
catalysts, we assessed their photocatalytic CV degradation performances. Fig. 6 (a) and (b) display the UV–vis absorption spectra of the CeO\textsubscript{2}– and AC-CeO\textsubscript{2}-added CV solutions under visible light irradiation (halogen lamp, $\lambda_{\text{lamp}} = 350–3500$ nm, $P_{\text{opt}} = 72$ W), respectively. Prior to CV degradation, the controlled adsorption test was performed in a dark space to confirm the adsorption/desorption stability (Fig. S3). Initially, the CV dye shows the maximum intensity of its intrinsic absorption peak at $\sim 580$ nm. After adding the prepared catalysts and performing the photocatalytic degradation processes, the absorption peak intensity at 580 nm starts to decrease in both CeO\textsubscript{2} and AC-CeO\textsubscript{2} cases. In addition, the CV-related absorption peak drastically decreases with increasing light irradiation time. Particularly, in the case of AC-CeO\textsubscript{2}, the CV-related absorption peak completely disappeared after 135 min (Fig. 6(a)). In the case of bare CeO\textsubscript{2}, however, the CV feature still remains even after 195 min (Fig. 6(b)). Furthermore, bare AC exhibited a poor CV degradation activity with $\eta_{\text{deg}} \approx 66.1\%$ after 165 min (Fig. S4). Namely, the AC-CeO\textsubscript{2} nanocomposites exhibit a faster and higher CV degradation activity ($\eta_{\text{deg}} \approx 97.9\%$ after 135 min) than that of bare CeO\textsubscript{2} ($\eta_{\text{deg}} \approx 78.8\%$ after 195 min) and bare AC ($\eta_{\text{deg}} \approx 66.1\%$ after 165 min) (Fig. 6(c), 6(d), and Fig. S4).

In the recycling test (Fig. 7(a)), both CeO\textsubscript{2} and AC-CeO\textsubscript{2} showed a reasonable recyclic performance with a small change in their CV degradation efficiencies (i.e., $\Delta \eta_{\text{deg}} = (\eta_{\text{deg(1st)}} - \eta_{\text{deg(5th)}})/\eta_{\text{deg(1st)}} \approx 12\%$ loss after 5 cycles). Although there is a small decrease in $\eta_{\text{deg}}$ after multiple use of the catalysts, AC-CeO\textsubscript{2} still holds a better CV degradation performance than that of CeO\textsubscript{2}. To help understanding the enhanced photocatalytic CV degradation activities of AC-CeO\textsubscript{2}, we here explain the possible reaction mechanism. Fig. 7(b) schematically illustrates the photocatalytic reaction process when using AC-CeO\textsubscript{2} as a photocatalyst for CV degradation. When irradiating the light onto the AC-CeO\textsubscript{2} photocatalyst-added CV mixture, the electrons ($e^-$) are excited from the valence band ($E_V$) to the conduction band ($E_C$) in CeO\textsubscript{2}. Correspondingly, the holes ($h^+$) are generated in $E_V$ of CeO\textsubscript{2}. Due to the band bending effect from AC-CeO\textsubscript{2} hybridization, a great number of $e^-$ and $h^+$ are provided from AC.
are confined inside the CeO₂ particles. At this point, one needs to remind that, in the AC-CeO₂ nanocomposites, the CeO₂ particles are anchored with the AC nanoflakes. In this circumstance, the AC nanoflakes would play a key role as the charge-carrier sink paths because of their high electrical conductivity. This could lead to the swift charge separation of photogenerated e⁻ and h⁺, and it would eventually reduce the e⁻•h⁺ recombination [76,77]. In other words, due to the existence of highly conductive AC, the photogenerated e⁻ and h⁺ could rapidly transfer to the pollutant through the AC nanoflakes (i.e., charge-carrier sink paths). For example, in EIS measurements (Fig. S2), the AC-CeO₂ nanocomposites exhibited a lower solution resistance (−2.93 Ω) than that of the bare CeO₂ nanoparticles (−6.14 Ω). Owing to the enhanced charge separation, photocarriers would strongly contribute to the dye-degradation reaction while the e⁻•h⁺ recombination would be considerably reduced. Namely, the photogenerated e⁻ would easily react with O₂ (dissociated from H₂O) to form the superoxide radical anions (O₂⁻), and the photogenerated h⁺ would freely react with the OH⁻ so that the hydroxyl radicals (•OH) could be effectively created. These highly reactive radicals (i.e., •OH and O₂⁻) would vigorously react with the pollutants via following chemical reactions. Then, such a vigorous reaction would eventually result in a higher photocatalytic dye-degradation efficiency.

\[
\text{AC} - \text{CeO}_2 + h\nu \rightarrow \text{CeO}_2(e_{\text{CB}}^+) + \text{AC}(h^+) \quad (5)
\]
\[
\text{CeO}_2(e_{\text{CB}}^+) + \text{O}_2 \rightarrow \text{O}_2^- \quad (6)
\]
\[
2e_{\text{CB}}^- + 2\text{H}^+ + \text{O}_2^- \rightarrow \text{OH}^- + \text{OH}^- \quad (7)
\]
\[
\text{AC}(h_{\text{CB}}^+) + 2\text{H}^+ + \text{H}_2\text{O} (\text{OH}^-) \rightarrow \text{H}^+ + \cdot\text{OH} \quad (8)
\]
\[
\text{CV} + \cdot\text{OH} \text{(or } \cdot\text{O}_2^-) \rightarrow \text{Intermediates} \rightarrow \text{Degraded Pollutants (CO}_2 + \text{H}_2\text{O)} \quad (9)
\]

4. Summary and conclusions

The AC-CeO₂ nanocomposites were successfully synthesized through the facile sonication method and showed the enhanced CV dye degradation performances. The nanocomposites showed the aggregated morphology with the AC nanoflakes-anchored CeO₂ nanoparticles. When using AC-CeO₂ as a photocatalyst, a high CV degradation efficiency was attained up to 97.9 % under visible light irradiation within 135 min. The superb photocatalytic CV degradation activity of AC-CeO₂ can be imputable to the hybridization of semiconductive CeO₂ with highly conductive AC. Namely, AC could decrease the effective optical bandgap energy of CeO₂ and increase the photocarrier transport in the composite system. The former would lead to the increased photocarrier generation because of the increased light absorption at the wider visible wavelength region. Then, the latter could enhance the photocatalytic reaction in the pollutant medium because the effective photocarrier transport would hinder the photocarrier recombination in semiconductive CeO₂. Based upon all the experimental results, the AC-CeO₂ nanocomposites can be suggested as an excellent candidate of the highly efficient photocatalyst, particularly, for the industrial wastewater treatment via photocatalytic dye degradation.

CRediT authorship contribution statement

Sankar Sekar: Investigation, Methodology, Formal analysis, Writing – original draft. Chinna Bathula: Methodology, Formal analysis. Iqra Rabani: Methodology, Formal analysis. Jin Woo Lee: Methodology, Formal analysis. So Hyun Lee: Methodology, Formal analysis. Young-Soo Seo: Data curation, Validation. Sejoon Lee: Conceptualization, Supervision, Funding acquisition, Writing - review & editing.

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.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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