Photocatalysis of bifunctional Cr- and Fe-doped CeO$_2$ nanoparticles toward selective oxidation of 5-hydroxymethylfurfural and decomposition of high-density polyethylene

Jeong-Woo Nam  
Yeungnam University

Vy Ngoc Pham  
Sookmyung Women's University

Jeong Min Ha  
Yeungnam University

Minjeong Shin  
Sungshin Women's University

Hangil Lee  
Sookmyung Women's University

Young-Sang Youn (✉️ ysyoun@yu.ac.kr)  
Yeungnam University

Article

Keywords: Transition metal-doped CeO2 nanoparticles, Oxygen vacancy, Photocatalytic property, 5-Hydroxymethylfurfural, High-density polyethylene

Posted Date: November 29th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-2299917/v1

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Abstract

Oxygen vacancies ($V_o$) present in CeO$_2$ nanoparticles (NPs) can effectively boost their photocatalytic activity under ultraviolet (UV) light. To improve photocatalytic performance, Cr- and Fe-doped CeO$_2$ NPs with increased $V_o$ were prepared using a simple method of doping Cr and Fe ions into CeO$_2$ NPs, which was confirmed by an in-depth analysis of the structural and electronic changes. Through photocatalytic degradation (PCD) experiments with 5-hydroxymethylfurfural (HMF), we found that the PCD rates of the two doped CeO$_2$ NPs were approximately 1.6 times faster than that of the CeO$_2$ NPs. In addition, the conversion of HMF to 2,5-furandicarboxylic acid (FDCA) using the doped CeO$_2$ NPs occurred only through the mechanism of the selective oxidation to 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), with a conversion efficiency of 40%, exhibiting approximately 3.7 times better efficiency than using CeO$_2$ NPs. Furthermore, we confirmed that the photocatalytic reaction with the two doped CeO$_2$ NPs leads to the degradation of high-density polyethylene (HDPE) through C-H bond breakage in the polymer backbone of HDPE, resulting in the doped CeO$_2$ NPs enhancing the decomposition rate of HDPE microplastics by more than 1.7 times compared to CeO$_2$ NPs.

1. Introduction

Over the last few decades, metal oxides, such as CeO$_2$, ZnO, and TiO$_2$, have been studied for applications in various commercial fields.$^{1-3}$ Among metal oxides, CeO$_2$ is considerably attractive because it has the unique characteristics of a reversible valence change between Ce$^{4+}$ and Ce$^{3+}$ and oxygen vacancies ($V_o$),$^4$ leading to the engineering of $V_o$ to improve its photocatalytic performance.$^5-7$ With the tunable photocatalytic properties of CeO$_2$, photocatalysis by its action has been highlighted as a promising method for solving energy and environmental issues with plentiful sunlight.$^8,9$

Among various energy and environmental problems, the depletion of petroleum-based fuels and increasing environmental pollution are primary tasks to be solved because they directly affect the welfare of humanity. In this regard, cheap and abundant biomass is being considered as a potential alternative to petroleum-based fuels. The effective utilization of biomass can play a crucial role in solving the current energy crisis.$^{10,11}$ To this end, a facile strategy involves the oxidation of biomass and its derivatives using CeO$_2$ nanoparticles (NPs) as photocatalysts, and numerous efforts have been made to understand the mechanism of such reactions for various practical applications.$^{12-14}$ One of the most widely explored molecules as a biomass platform compound is 5-hydroxymethylfurfural (HMF), which is capable of being selectively oxidized through its two different functional groups: an aldehyde and alcohol.$^{15,16}$ To be precise, HMF can be converted to 2,5-furandicarboxylic acid (FDCA) through two distinct pathways; one is through 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) by the preferential oxidation of the aldehyde group of HMF and the other is via 2,5-diformylfuran (DFF) by that of its alcohol group (Scheme 1).$^{12,17,18}$ HMFCA and FDCA produced by HMF are considered suitable replacements of furanic polyester and phthalic acid obtained from fossil resources, respectively.$^{19-21}$ In particular, FDCA is recognized by
the U.S. Department of Energy as one of the top 12 bio-based chemicals.\textsuperscript{22,23} Therefore, the selective production of HMFCA and FDCA from HMF and the increase in conversion efficiency using CeO$_2$ NPs as photocatalysts have become a research hotspot.\textsuperscript{24}

Meanwhile, demand for the development of technology to solve environmental problems has increased dramatically. Among various environmental concerns, pollution caused by the excessive use of plastic is of utmost importance. Various types of microplastics, such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polyester, can flow along rivers and groundwater to the sea, and they can be absorbed by the human body through convection processes.\textsuperscript{25–27} Therefore, to minimize the potential influence of microplastics, it is necessary to develop a technology that can easily decompose microplastics. Research efforts, such as biodegradation using organisms and thermal/mechanical decomposition, have been implemented to break down the chemical structure of microplastics.\textsuperscript{28–35} However, these methods are time consuming, expensive, and often produce toxic byproducts. While many studies have reported the use of photocatalytic methods to decompose organic compounds in wastewater, research efforts on decomposing microplastics using photocatalysts have been limited to date.\textsuperscript{36–38} Recently, CeO$_2$ NPs have received attention as candidates for eco-friendly photocatalysts that can be adjusted to achieve high decomposition efficiency.\textsuperscript{39}

In pursuit of highly selective and efficient production of HMFCA/FDCA and the effective decomposition of microplastics under abundant solar energy, we introduced simple transition metal (TM)-ion doping into CeO$_2$ NPs. It is known that the amount of $V_0$ in CeO$_2$ NPs, which is directly related to the photocatalytic efficiency, increases with the modification of the CeO$_2$ surface from Cr- and Fe-ion doping.\textsuperscript{9,40} Therefore, we explored the photocatalytic activity of three distinct CeO$_2$, Cr-doped CeO$_2$ (Cr@CeO$_2$), and Fe-doped CeO$_2$ (Fe@CeO$_2$) NPs through photocatalytic experiments with HMF and high-density polyethylene (HDPE). In addition, the structural and electronic changes between CeO$_2$ and the doped CeO$_2$ NPs were thoroughly analyzed using a combination of high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDS), X-ray diffraction (XRD), Raman spectroscopy, and X-ray absorption spectroscopy (XAS).

We found that FDCA was produced through the pathway of the selective oxidation of HMFCA from HMF in all three NPs, and the conversion yield of HMF to FDCA in the presence of TM@CeO$_2$ NPs was approximately 40\%, as determined by high-performance liquid chromatography-mass spectrometry (HPLC-MS). Furthermore, the decomposition efficiency of HDPE was estimated by the change in average particle size calculated using scanning electron microscopy (SEM) images and the transmittance of the peak related to C-H stretching vibration measured by Fourier-transform infrared (FT-IR) spectroscopy, resulting in that the decomposition efficiency in the presence of TM@CeO$_2$ NPs increased by approximately 1.7 times compared to that of CeO$_2$ NPs.

\textbf{2. Results And Discussion}
2.1 Characterization of TM@CeO$_2$ NPs

HRTEM images of CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs are shown in Fig. 1a–c. As shown in the HRTEM images and the inserted fast Fourier transform (FFT) forms, there is no principal structural change between the three NPs. In addition, on the basis of the STEM images and elemental distribution in the STEM-EDS data (Fig. S1), we confirm that the TM ions are homogeneously distributed in the TM@CeO$_2$ NPs. To obtain additional structural information on the particle regions by closer inspection, the line profiles were analyzed at regular intervals on the sub-nanometer scale for the three NPs, as shown in Fig. 1d. Compared with CeO$_2$ NPs, Cr@CeO$_2$ and Fe@CeO$_2$ NPs exhibited a decrease of 10.8 and 9.8 pm per lattice fringe in the interlayer d-spacing of the [111] plane, respectively. In general, compared to CeO$_2$ NPs, the smaller interlayer d-spacing in TM@CeO$_2$ NPs reflects the higher density of $V_o$, suggesting the successful fabrication of highly defective TM@CeO$_2$ NPs by Cr and Fe ion doping. Therefore, we can predict from the interlayer d-spacing values that the photocatalytic properties of the TM@CeO$_2$ NPs will be better than those of the CeO$_2$ NPs.

Next, XRD experiments were performed to investigate the changes in crystal structure of the TM@CeO$_2$ NPs by doping. In addition, the crystallite sizes and lattice parameters were determined through Pawley refinement of the obtained XRD spectra. As shown in Fig. 1e, all the XRD spectra correspond to the diffraction patterns associated with the cubic fluorite CeO$_2$ crystal structure with the space group Fm-3m, indicating that no principal structural change occurred by TM ion doping, in accordance with the HRTEM results. Moreover, peak broadening for TM@CeO$_2$ NPs compared to CeO$_2$ NPs is not clearly recognized in the XRD spectra, which indicates that their grain sizes are similar. The grains in nanoparticles are known to consist of crystallites. Therefore, if we estimate the crystallite size from the XRD data, we can infer the grain size from the crystallite size, which is defined as the coherent diffraction domain. As shown in Table 1, we can clearly confirm that the crystallite sizes of the TM@CeO$_2$ NPs are similar to those of the CeO$_2$ NPs within an error range, indicating that the effect of the size of the NPs does not need to be considered in our results. Furthermore, the $a$-axis lattice parameter of the cubic fluorite CeO$_2$ crystal structure for TM@CeO$_2$ NPs is slightly smaller than that for CeO$_2$ NPs, showing a trend similar to the results of the line profiles measured from the HRTEM images shown in Fig. 1d. It can be inferred that the shrinkage of the lattice constant for TM@CeO$_2$ NPs is due to the introduction of dopants into CeO$_2$ NPs, leading to an increase in $V_o$, as reported in the literature. Therefore, we expect that the photocatalytic abilities of the TM@CeO$_2$ NPs will be superior to those of the CeO$_2$ NPs, in agreement with the HRTEM data.
Table 1

Crystallite sizes and lattice constants of the cubic fluorite CeO$_2$ crystal structure estimated through Pawley refinement for XRD spectra acquired from CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs. The error rates indicate the 95% confidence interval.

<table>
<thead>
<tr>
<th>Type of NPs</th>
<th>Crystallite size (nm)</th>
<th>a-Axis lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>19.1 ± 1.0</td>
<td>5.4150 ± 0.0008</td>
</tr>
<tr>
<td>Cr@CeO$_2$</td>
<td>18.3 ± 1.1</td>
<td>5.4123 ± 0.0004</td>
</tr>
<tr>
<td>Fe@CeO$_2$</td>
<td>19.2 ± 0.5</td>
<td>5.4136 ± 0.0008</td>
</tr>
</tbody>
</table>

Figure 1f shows the Raman spectra of CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs, where a strong band (F$_{2g}$) appears at approximately 467 cm$^{-1}$ due to the symmetric breathing mode of the oxygen ions coordinated with each Ce$^{4+}$ ion in the cubic fluorite CeO$_2$ structure. Through the Raman profiles, we also confirm that TM ion doping into the CeO$_2$ NPs barely influences the CeO$_2$ structure. The red shift of the prominent F$_{2g}$ band for Cr@CeO$_2$ (458 cm$^{-1}$) and Fe@CeO$_2$ (454 cm$^{-1}$) NPs indicates the incorporation of Cr and Fe ions into the CeO$_2$ NPs, in accordance with the HRTEM and XRD results. The width of the F$_{2g}$ mode for the TM@CeO$_2$ NPs is broader than that for the CeO$_2$ NPs, as shown in Fig. 1f. The increase in the peak broadening also signifies an increase in $V_0$ due to the introduction of dopants into the CeO$_2$ NPs, as described in a previous study. Therefore, from the red shift and peak broadening of the F$_{2g}$ peak, we can confirm that Cr and Fe ions were successfully integrated into the CeO$_2$ NPs without significant structural changes, resulting in an increase in the amount of $V_0$. In addition to the F$_{2g}$ peak, two weak bands related to the transverse acoustic mode and the non-degenerate longitudinal optical mode are observed at approximately 250 and 600 cm$^{-1}$ in Fig. 1f, respectively. These two peaks for the TM@CeO$_2$ NPs are stronger than those for the CeO$_2$ NPs. According to the literature, these bands can be attributed to the presence of defects dominantly created by $V_0$. In particular, the peak at approximately 600 cm$^{-1}$ arises from $V_0$ caused by the reduced Ce$^{3+}$ ions. Hence, we anticipate that TM@CeO$_2$ NPs will have better photocatalytic properties than those of CeO$_2$ NPs, owing to the increase in the number of defects attributed to $V_0$.

2.2 Electronic properties of TM@CeO$_2$ NPs

The doping of CeO$_2$ NPs with Cr or Fe ions changes the properties of the material at the nanoscale. To understand the implication of this process on the photocatalytic activity, a deeper understanding of the effect of the dopants on the change in electronic properties within the material is necessary. To obtain information on the electronic structure of the unoccupied state at the NP surface, we acquired the XAS profiles of the Ce $M$-edge, O $K$-edge, Cr $L$-edge, and Fe $L$-edge for the CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs, as shown in Fig. 2, where the spectra are normalized and overlaid vertically to identify changes in the electronic structure. In Fig. 2a, the peaks corresponding to M5 (marked as B) and M4 (marked as C) are
clearly observed, and additional satellite peaks are also found at higher photon energies for all NPs. The B/C intensity ratio for the two TM@CeO$_2$ NPs is slightly higher than that of the CeO$_2$ NPs. This indicates that more Ce$^{3+}$ states generated by the oxygen defect structure exist in TM@CeO$_2$ NPs. In addition, the pre-edge peak (marked as A) is directly related to the defect structure. As can be seen from the Ce M-edge spectra, the intensity of peak A for the two TM@CeO$_2$ NPs is slightly higher than that for the CeO$_2$ NPs. Therefore, the photocatalytic effects of the TM@CeO$_2$ NPs containing more defects are expected to be better than that of CeO$_2$ NPs. The peaks marked as D, E, and F in the O K-edge spectra (Fig. 2b) correspond to transition-induced O 2p-Ce 4f, Ce 5d-e$_g$, and Ce 5d-t$_{2g}$ states, respectively. Focusing on the relative intensity between peaks D and E, it can be seen that the D/E intensity ratio of the two TM@CeO$_2$ NPs is lower than that of the CeO$_2$ NPs. This indicates that the number of defects in TM@CeO$_2$ NPs is greater than in the CeO$_2$ NPs. To confirm the oxidation state and electronic structure of the TMs formed on the surface of the TM@CeO$_2$ NPs, we measured the Cr L-edge spectrum for Cr@CeO$_2$ NPs and the Fe L-edge spectrum for Fe@CeO$_2$ NPs (Fig. 2c–d). From these spectra, we confirm that the Cr and Fe L-edge profiles show the shapes of typical Cr$_2$O$_3$ and Fe$_2$O$_3$ composition, respectively. Note that because XAS is a surface-sensitive technique, Cr$_2$O$_3$ and Fe$_2$O$_3$ constituents on the surface of TM@CeO$_2$ NPs were not detected by the other techniques. From the XAS data, we envision that the formation of chromium or iron oxides on the surface of the TM@CeO$_2$ NPs can give rise to oxygen deficiencies, leading to the promotion of conversion of Ce$^{4+}$ to Ce$^{3+}$ ions to compensate for the charge valence. As a result, we propose that the concentration of $V_0$ in the TM@CeO$_2$ NPs is higher than that in the CeO$_2$ NPs, resulting in an increase in photocatalytic performance.

2.3 Selective production of HMFCA and high conversion efficiency to FDCA by photolysis of HMF in the presence of TM@CeO$_2$ NPs

Maximizing the amount of $V_0$ by doping without altering the principal structure of CeO$_2$ NPs is one of the easiest and most effective strategies for improving the efficiency of the photocatalyst. To verify this, we investigated the photocatalytic activity of CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs in the PCD reaction of HMF. As shown in Fig. 3a, the PCD reaction rates of HMF in the presence of the two TM@CeO$_2$ NPs are higher than that of the CeO$_2$ NPs. Table 2 presents the photocatalytic efficiency of the three NPs for the PCD reaction of HMF for 24 h, and the PCD rates with the TM@CeO$_2$ NPs are approximately 1.6 times faster than that with CeO$_2$ NPs. We speculate that this is due to the enhanced photocatalytic performance of the TM@CeO$_2$ NPs compared to that of the CeO$_2$ NPs. As mentioned above, HMF, which contains aldehyde and alcohol groups, is converted to FDCA via pathways that produce HMFCA and/or DFF (Scheme 1). To trace the exact reaction mechanism of the photolysis of HMF, we performed a quantitative analysis of the HMFCA, DFF, and FDCA products formed over time using HPLC-MS during the photolysis of HMF with CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs, dividing it into two distinct phases as a function of the reaction time (Fig. 3b). As shown, in Phase A (0–6 h) only HMFCA is produced from the selective oxidation of HMF in all three NPs. Interestingly, DFF is not produced, which clearly suggests that only the aldehyde functional
group within HMF is preferentially oxidized to the carboxyl functional group. From these results, we confirmed that only HMFCA, a suitable alternative to furanic polyesters obtained from fossil resources,\textsuperscript{19–21} is selectively produced from HMF. In Phase B (6–24 h), FDCA starts to form gradually over time with simultaneous decreases in the concentrations of HMF and HMFCA. This definitely demonstrates that the conversion reaction from HMF to FDCA occurs only through the formation of HMFCA and not through that of DFF, suggesting that selective extraction of HMFCA from HMF is possible. Furthermore, from the initial concentration of 25 mM HMF, 9.8 and 10.1 mM FDCA were obtained over 24 h for Cr@CeO\textsubscript{2} and Fe@CeO\textsubscript{2} NPs, respectively, which corresponds to approximately a 40\% conversion yield, approximately 3.7 times better efficiency than the CeO\textsubscript{2} NPs (Table 2). As a result, we found that FDCA, a sustainable replacement for petrochemicals,\textsuperscript{19–21} is produced from HMF with a high conversion yield in TM@CeO\textsubscript{2} NPs prepared by the simple method of doping Cr and Fe ions into CeO\textsubscript{2} NPs.

<table>
<thead>
<tr>
<th>Type of NPs</th>
<th>PCD efficiency of HMF (C/C\textsubscript{0})</th>
<th>Conversion efficiency from HMF to FDCA(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO\textsubscript{2}</td>
<td>0.41 ± 0.05</td>
<td>10.8 ± 0.51</td>
</tr>
<tr>
<td>Cr@CeO\textsubscript{2}</td>
<td>0.08 ± 0.01</td>
<td>39.2 ± 0.78</td>
</tr>
<tr>
<td>Fe@CeO\textsubscript{2}</td>
<td>0.03 ± 0.01</td>
<td>40.4 ± 0.82</td>
</tr>
</tbody>
</table>

2.4 High decomposition rate of HDPE microplastics in TM@CeO\textsubscript{2} NPs

We next investigated the capability of the CeO\textsubscript{2}, Cr@CeO\textsubscript{2}, and Fe@CeO\textsubscript{2} NPs to decompose HDPE microplastics. Before examining the degradation efficiency of HDPE with the three photocatalytic NPs, we evaluated the decomposition of HDPE under ultraviolet (UV) irradiation without NPs (Fig. S2a–b). We observed that HDPE is slightly degraded under UV light even in the absence of the NPs. To evaluate whether the decrease in the particle size of HDPE was accompanied by any change in the chemical bonding of the HDPE polymer, FT-IR measurements were performed under these conditions (Fig. S3). As shown in Fig. S3, the FT-IR spectra of HDPE show four main peaks corresponding to the stretching vibrations of the C-H group of the main chain at approximately 2915 and 2845 cm\textsuperscript{-1} (marked as A and B, respectively) and the bending and rocking vibrations of methylene (-CH\textsubscript{2}) group at 1472–1462 cm\textsuperscript{-1} and 730–717 cm\textsuperscript{-1} (marked as C and D, respectively).\textsuperscript{61,62} In comparing the changes in the two C-H stretching modes at peaks A and B (Fig. S3), we determined that HDPE was slightly decomposed with C-H bond scission under UV irradiation even without the NPs.
When HDPE was irradiated by UV light in the presence of CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs, a decrease in the particle size of HDPE was more evident (Fig. S2c–e). The average particle size of HDPE degraded by CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs were calculated as 14.0, 10.0, and 10.4 µm, respectively, indicating that the HDPE decomposition efficiency of the TM@CeO$_2$ NPs is more than 1.8 times better compared than that of the CeO$_2$ NPs. These results suggest that the photocatalytic degradation of HDPE is accelerated in the presence of TM@CeO$_2$ NPs under UV illumination, leading to a significant reduction in HDPE particle size. In addition to the SEM images, we measured the FT-IR spectra to revalidate the decomposition of HDPE under these conditions (Fig. 4). Peak A in the FT-IR spectra shows transmittances of 66.0, 81.0, and 83.6% for the CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs, respectively, indicating that HDPE is considerably decomposed with significant degradation of C-H bonds under UV irradiation in the presence of the TM@CeO$_2$ NPs. These data signify that the ability of TM@CeO$_2$ NPs to decompose HDPE is more than 1.7 times better than that of CeO$_2$ NPs, in agreement with the SEM results. The FT-IR results along with SEM images suggest that a photocatalytic reaction with TM@CeO$_2$ NPs triggers C–H bond breakage in the polymer backbone of the HDPE microplastics, leading to the generation of smaller-sized HDPE particles. In other words, TM@CeO$_2$ NPs are more efficient in promoting C-H bond cleavage than CeO$_2$ NPs. As a result, we concluded that TM@CeO$_2$ NPs as a photocatalyst are more effective for HDPE decomposition than CeO$_2$ NPs.

### 3. Conclusions

Cr@CeO$_2$ and Fe@CeO$_2$ NPs were developed by introducing a simple method of doping Cr and Fe ions into CeO$_2$ NPs. Based on a thorough analysis of the structural and electronic variation in CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs, we confirmed that the density of $V_o$ in the two TM@CeO$_2$ NPs was greater than that in the CeO$_2$ NPs, suggesting an improvement in their photocatalytic performance. To prove this, we demonstrated the photocatalytic activity of CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs toward HMF oxidation and HDPE decomposition. As expected, the PCD rates of HMF with TM@CeO$_2$ NPs were approximately 1.6 times faster than that with CeO$_2$ NPs. More importantly, a high conversion efficiency of 40% to FDCA through a selective pathway to produce HMFCA was achieved from the photolysis of HMF in the presence of TM@CeO$_2$ NPs, where HMFCA and FDCA are known to be possible starting materials for the production of sustainable alternatives to petrochemical substances. Furthermore, we observed that the degradation efficiency of HDPE microplastics with TM@CeO$_2$ NPs was more than 1.7 times higher than that with CeO$_2$ NPs, indicating that TM@CeO$_2$ NPs can be used as a photocatalyst to solve the issue of microplastics under abundant solar light.

### 4. Material And Methods

#### 4.1 Chemicals and NP preparation
CeO₂ NPs were synthesized using a modified thermal method.⁶³ CeCl₃•7H₂O (0.2 g) and PVP (0.3 g) were dissolved in 40 mL of deionized water under vigorous magnetic stirring. Then, 1 mL of formamide and 0.2 mL of H₂O₂ were added to the solution under continuous stirring at 90 rpm for 1 h. The as-formed yellow solution was treated by adding KOH until the pH was 13.0 and then held at that pH for 3 h. Next, the solution was transferred into a Teflon-lined autoclave and heated for 9 h at 220°C. The resulting CeO₂ NPs were filtered and washed with double-distilled water (DDW) to remove any impurities. The products (CeO₂ NPs) were then washed with absolute ethanol and dried for 48 h at 95°C. After fabricating the CeO₂ NPs,⁶³,⁶⁴ two different TM ions (TM nitrate n-hydrate: Cr(NO₃)₃•9H₂O and Fe(NO₃)₃•6H₂O, Sigma-Aldrich, 99%) were added to the CeO₂ NPs at 90°C with moderate stirring until a homogeneous and transparent mixture was formed (approximately 3 h). The obtained solution was then heated at 220°C for 9 h. The resulting TM@CeO₂ NPs were filtered and washed with DDW to remove any impurities, resulting in TM@CeO₂ NPs with 5 wt% Cr³⁺ or Fe³⁺ ions. The photocatalytic properties of CeO₂, Cr@CeO₂, and Fe@CeO₂ NPs were determined using HMF (Sigma-Aldrich, 99%) and HDPE (Sigma Aldrich, 95%). HDPE was ground into a fine powder, and the resulting powder was filtered through a mesh sieve (20 µm size) to prepare HDPE microplastics with a size of ≤ 20 µm.

### 4.2 Characterization

The morphology of CeO₂, Cr@CeO₂, and Fe@CeO₂ NPs was analyzed by HRTEM (JEM-ARM200CF, JEOL Ltd., Japan) using an accelerating voltage of 200 kV. In addition, the distribution of the constituent elements within the NPs at the nanoscale was mapped using STEM-EDS (JED-2300T, JEOL Ltd, Japan). The XRD data were recorded in the range 20–100° in a scanning step of 0.02° for 0.3 s using a MiniFlex600 system (Rigaku, Japan) with Cu Kα radiation operated at 15 mA and 40 kV. Crystallite sizes and lattice parameters were calculated by Pawley refinement of the corresponding diffraction patterns using TOPAS software (Version 4.2, Bruker, Germany). Raman spectra were obtained using an XploRA Raman spectrometer (HORIBA, Japan) with a helium-neon laser of 532 nm wavelength operating at 10 mW at Core Research Support Center for Natural Products and Medical Materials at Yeungnam University. To compare the electronic structure of CeO₂ and TM@CeO₂ NPs, we obtained Ce M-edge, O K-edge, Cr L-edge, and Fe L-edge spectra using XAS in the 8A1 beamline at the Pohang Accelerator Laboratory.

### 4.3 Photocatalytic experiments

To evaluate the photocatalytic degradation (PCD) activity, suspensions of CeO₂, Cr@CeO₂, and Fe@CeO₂ NPs (0.5 g/L) containing HMF (25 mM) were stirred in the dark for 2 h until adsorption equilibrium was attained. A reactor with a solution containing each NP was placed in front of a blue light-emitting diode (LED) (λ = 365 nm, output power = 6 W; Thorlabs, USA) at a distance of 10 cm and magnetically stirred at 80 rpm. The HMF oxidation products were analyzed using HPLC-MS (ULTIMATE 3000 RSLC SYSTEM, Thermo Fisher Scientific and Q-EXACTIVE ORBITRAP PLUS MS, Thermo Fisher Scientific).

For the analysis of HDPE decomposition, suspensions were prepared by mixing 0.15 g of HDPE powder and 0.015 g each of CeO₂, Cr@CeO₂, and Fe@CeO₂ NPs in 29 mL of deionized water. The three different
suspensions (HDPE/CeO$_2$, HDPE/Cr@CeO$_2$, and HDPE/Fe@CeO$_2$ NPs) were magnetically stirred in the dark for 10 min. The stirred solutions were then irradiated for 3 h using a 300 W Xe arc lamp (Newport, USA) with a cutoff filter ($\lambda = 365$ nm). After irradiation, HDPE was collected from each of the three suspensions and dried for 24 h at 90°C for postmortem analysis. The SEM images were obtained using a field-emission scanning electron microscopy (JSM-7600F, JEOL, Japan) operated at an acceleration voltage of 15 kV. The FT-IR spectra were obtained using a Nicolet IS50 spectrometer (Thermo Fisher Scientific, USA).

**Declarations**

**Acknowledgements**

This research was supported by the National Research Foundation of Korea (NRF) funded by the Korean government (MSIP) (Grant Nos. 2021R1A2C2007992 and 2021R1G1A109336111). This work also supported by the 2022 Yeungnam University Research Grant.

**Author contributions**

M.S., H.L., and Y.-S.Y. conceived and designed the experiments. V.N.P. fabricated the nanoparticles. J.-W.N., V.N.P., and J.M.H. performed the experiments. J.-W.N. and Y.-S.Y. analyzed the XRD and Raman data. V.N.P. and H.L. analyzed the other data. H.L. and Y.-S.Y. wrote the manuscript. All the authors reviewed and approved the final manuscript.

**Competing interests**

The authors declare no competing interests.

**Data availability**

All data generated or analyzed during this study are included in this published article and its supplementary information files.

**References**


Schemes

Scheme 1 is available in the Supplementary Files section

Figures
Figure 1

HRTEM images of (a) CeO$_2$, (b) Cr@CeO$_2$, and (c) Fe@CeO$_2$ NPs. Insets: The corresponding FFT data. (d) Line profile of the red line shown in (a–c) for the corresponding NPs. The decrease in the interlayer d-spacings of the [111] plane for Cr@CeO$_2$ and Fe@CeO$_2$ NPs is measured as 65 and 59 pm on the six lattice fringes compared to that for CeO$_2$ NPs, indicating 10.8 and 9.8 pm less per lattice fringe, respectively. (e) XRD and (f) Raman spectra of CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs. Bottom panel in (e): Diffraction pattern of cubic fluorite CeO$_2$ (PDF#34-0394) with Miller indices extracted from the PDF-2 database.
Figure 2

XAS profiles of (a) Ce $M$-edge, (b) O $K$-edge, (c) Cr $L$-edge, and (d) Fe $L$-edge for CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs.
Figure 3

(a) PCD data for the change in the relative amount of HMF and (b) quantitative analysis of products by photolysis of HMF under UV irradiation of 365 nm wavelength in the presence of CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs. $C_0$ and C indicate the initial concentration and post-reaction concentration of HMF, respectively.
Figure 4

FT-IR spectra acquired from the HDPE with the CeO$_2$, Cr@CeO$_2$, and Fe@CeO$_2$ NPs under UV illumination.

**Supplementary Files**

This is a list of supplementary files associated with this preprint. Click to download.

- Scheme1.jpg
- SupplementaryInformation.docx