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Defect-Induced Band Gap Narrowed CeO$_2$ Nanostructures for Visible Light Activities

Mohammad Mansoob Khan,† Sajid Ali Ansari,† Debabrata Pradhan,‡ Do Hung Han,† Jintae Lee,† and Moo Hwan Cho*†‡

†School of Chemical Engineering, Yeungnam University, Gyeongsan-si, Gyeongbuk 712-749, South Korea
‡Materials Science Centre, Indian Institute of Technology, Kharagpur, W. B. 721302, India

Supporting Information

ABSTRACT: This work reports an electron beam irradiation (30 kGy and 90 kGy) approach to narrow the band gap of the pristine CeO$_2$ nanostructure (p-CeO$_2$) to enhance their visible light activity through defect engineering. This was confirmed by diffuse reflectance spectroscopy, photoluminescence, Raman spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy (XPS), Brunauer−Emmett−Teller, electrochemical impedance spectroscopy, and linear scan voltammetry. XPS revealed changes in the surface states, composition, Ce$^{4+}$ to Ce$^{3+}$ ratio, and other defects in the modified CeO$_2$ nanostructures (m-CeO$_2$). The m-CeO$_2$ exhibits excellent photocatalytic activities by degrading 4-nitrophenol and methylene blue in the presence of visible light ($\lambda > 400$ nm) compared to the p-CeO$_2$. The optical, photocatalytic, and photoelectrochemical studies and proposed mechanism further support the enhanced visible light photocatalytic activities of the m-CeO$_2$. This study confirmed that defect-induced band gap engineered m-CeO$_2$ could be used effectively as photocatalyst and photoelectrodes owing to their enhanced visible light photocatalytic activities.

INTRODUCTION

The chemistry that occurs at the surfaces of metal oxides has attracted considerable attention for a range of industrial applications including catalysis, photocatalysis, optical display technology, solar energy devices, corrosion prevention, and three-way automotive catalytic converters.1−3 Among the metal oxides, CeO$_2$ is an important rare earth oxide that has attracted considerable attention for use in fuel cells, UV-blockers, sensors, oxygen storage capacitors, and biological applications.1−5 CeO$_2$ is a wide band gap semiconductor ($\sim$3.4 eV), which limits its use as an electronic material for logic operations and photocatalyst.4−6 The chemical functionalization of CeO$_2$ is a well-known method for tuning the band structure and majority carrier type for electronic and optical applications.1−3,4 Nevertheless, few studies have reported the extent to which the band gap can be tuned electrochemically. On the other hand, there are several reports on tuning the band gap energy of metal oxides by doping with nonmetals and metals.7−10

Few studies showed that the electron beam (EB) can be used for the synthesis of different metal nanoparticles and thin films of metal oxides with the desired properties.11−16 This approach has several advantages over other methods, such as scalability and an ability to interact effectively with all types of materials (including high band gap semiconductors, oxides, etc.) through coulomb interactions created by charged particles, i.e., electrons.11−16 Recently, it was reported that, as an alternative, chemical doping can be achieved by ionizing irradiation, such as EB or $\gamma$ radiation.17,18 Radiation-induced nanoparticles and supported catalysts exhibit particularly high efficiency and selectivity in catalysis due to their small size, monodisperse, and probably their strong adhesion to the support.18 Recent reports showed that an EB can be used to create defects in materials.13−19 Defects, such as oxygen vacancies and step edges, are the most reactive sites on the surface of metal oxides.13,15,19,20 Industrially, CeO$_2$ is one of the most interesting oxides because oxygen vacancy defects can be formed and eliminated rapidly, giving them high “oxygen storage capacity”.1,3 Control of the density and nature of oxygen vacancies can provide a means of tailoring the reactivity of ceria-based catalysts.1−3

Synthesizing CeO$_2$ with low band gap energy is a challenge. Recently, we used EB to substantially decrease the band gap of TiO$_2$ by creating different type of defects.19 Therefore, this approach was further extended to tune the wide band gap of commercially available CeO$_2$ to the desired (low) band gap energy without doping with any transition metals or nonmetals. To the best of the author’s knowledge, this is the first report of using EB to decrease the band gap energy of CeO$_2$ without doping. The modified CeO$_2$ showed outstanding photo-degradation of 4-nitrophenol (4-NP) and methylene blue (MB) under visible light ($\lambda > 400$ nm) irradiation. Electrochemical impedance spectroscopy (EIS) and linear scan voltammetry (LSV) studies in the dark and under visible light irradiation confirmed the substantial decrease in charge transfer resistance and minimizing the recombination of photo-generated electrons and holes, whereas LSV further confirms the enhancement in the photocurrent of the modified CeO$_2$ (30 kGy and 90 kGy) nanostructures, which support their enhanced photocatalytic activities, and potential use as a photocatalyst and photoelectrode. Hereafter, pure CeO$_2$ and
modified CeO\(_2\) (30 kGy and 90 kGy) are abbreviated as p-CeO\(_2\), 30 kGy-CeO\(_2\), and 90 kGy-CeO\(_2\), respectively.

## EXPERIMENTAL SECTION

### Materials.

The CeO\(_2\) nanostructure and MB were purchased from Sigma-Aldrich, whereas sodium acetate, p-nitrophenol (4-NP), and sodium sulfate (Na\(_2\)SO\(_4\)) were obtained from Duksan Pure Chemicals Co. Ltd. South Korea and were used as received. Ethyl cellulose and \(\alpha\)-terpineol were purchased from KANTO Chemical Co., Japan. Fluorine doped transparent conducting oxide glass (FTO; F-doped SnO\(_2\) glass; 7 \(\Omega/\)sq) was obtained from Pilkington, U.S.A. All other chemicals used in this study were of analytical grade and used as received. All solutions were prepared from deionized water obtained using a PURE ROUP 30 water purification system.

### Methods.

An EB accelerator (ELV-0.5, BINP, Russia) with a maximum beam power, maximum beam current, and maximum beam energy of 28 kW, 40 mA, and \(\sim\)0.7 MeV, respectively, were used to modify p-CeO\(_2\). The UV–vis diffuse reflectance spectra (DRS) of the powdered samples were obtained using a UV–vis-NIR double beam spectrophotometer (VARIAN, Cary 5000, U.S.A.) equipped with a diffuse reflectance accessory. A He–Cd laser (Kimon, 1 K, Japan) with a wavelength of 325 nm and a power of 50 mW was used as an excitation source for the photoluminescence (PL) experiments (for photoelectrodes such as EIS and LSV) were conducted using a potentiostat (Versa STAT 3, Princeton Research, U.S.A.) with a standard three-electrode system, in which Ag/AgCl (saturated with KCl), a Pt gauge and Fluorine-doped tin oxide (FTO) glass coated with p-CeO\(_2\), 30 kGy-CeO\(_2\), or 90 kGy-CeO\(_2\) were used as the reference, counter and working electrodes, respectively, in a 0.2 M Na\(_2\)SO\(_4\) solution as the electrolyte. The working electrodes for EIS and LSV were prepared as follows: 100 mg of each sample was suspended thoroughly by adding ethyl cellulose as the binder and \(\alpha\)-terpineol as the solvent for the paste, and then coated on a FTO glass electrode using a doctor-blade and dried in oven.

### Modification of CeO\(_2\) Nanostructure by Electron Beam.

Commercial CeO\(_2\) nanostructure was modified using an EB accelerator in integral mode with an EB energy of 0.7 MeV and an initial EB current of 2 mA/sec in water at room temperature and atmospheric pressure. Two 75 mL aqueous dispersions of p-CeO\(_2\) (50 mM) were prepared. The initial pH of the aqueous dispersions was 4.40. The final pH of the aqueous dispersions was 3.93 and 4.08 after exposure to an EB dose of 30 kGy, (power 924 mA.sec and real time 8.8 min) and 90 kGy (power 2724 mA.sec and real time 23.40 min) respectively. The almost white p-CeO\(_2\) changed to a light yellow and pale yellow upon exposure to the 30 and 90 kGy EB dose, respectively. The resulting dispersions were centrifuged and a yellowish powder was obtained in both cases. The 30 kGy-CeO\(_2\) and 90 kGy-CeO\(_2\) nanostructures were dried in an oven at 90 °C, and used for different analyses, photocatalysis, and photoelectrodes.

### Photocatalytic Degradation of 4-NP and MB by p-CeO\(_2\), 30 kGy-CeO\(_2\) and 90 kGy-CeO\(_2\) Nanostructures.

The photocatalytic activities of the p-CeO\(_2\), 30 kGy-CeO\(_2\), and 90 kGy-CeO\(_2\) nanostructures were tested for the catalytic degradation of 4-NP (5 mg/L) as well as MB (10 mg/L) and estimated, as reported earlier.\(^{19,20}\) For the photodecomposition experiment, 2 mg of each photocatalyst was suspended in a 20 mL of the 4-NP and MB aqueous solutions. Each solution was sonicated for 5 min and later stirred in the dark for 30 min to complete the adsorption and desorption equilibrium of the specific substrate on the p-CeO\(_2\), 30 kGy-CeO\(_2\), and 90 kGy-CeO\(_2\) nanostructures. The solutions were irradiated using a 400 W lamp (\(\lambda \geq 400 \) nm). The two sets of experiments for 4-NP and MB degradation were observed for 5 and 6 h, respectively. The rate of 4-NP and MB degradation was examined by taking 2 mL of the samples from each set every 1 h, centrifuging them to remove the catalyst and recording the UV–vis spectra, from which the degradation of 4-NP and MB was calculated.

As a control experiment, p-CeO\(_2\) nanoparticles (reference photocatalyst, Sigma-Aldrich) were used to degrade 4-NP and MB under same experimental conditions. Each degradation experiment was performed in triplicate to ensure the photocatalytic activity of the p-CeO\(_2\), 30 kGy-CeO\(_2\), and 90 kGy-CeO\(_2\) nanostructures. Another blank experiment was performed without any photocatalyst under visible light irradiation for 4-NP and MB under same experimental conditions. The degradation was observed for 5 and 6 h for 4-NP and MB respectively.

The stability and reusability of the 90 kGy-CeO\(_2\) nanostructures was tested after centrifuging the catalyst from 4-NP and MB degraded solutions and tested in a similar manner to that mentioned above. The isolated catalyst from the first and second runs were washed with DI water and dried in an oven at 90 °C and successively reused for the second and third runs to check their catalytic activity with a fresh 4-NP and MB solution under the same conditions.

### Photoelectrochemical Studies of the p-CeO\(_2\), 30 kGy-CeO\(_2\), and 90 kGy-CeO\(_2\) Nanostructures.

To examine the photoelectrode response of the p-CeO\(_2\), 30 kGy-CeO\(_2\), and 90 kGy-CeO\(_2\) nanostructures, photoelectrochemical experiments, such as EIS and LSV, were conducted under ambient conditions in the dark and under visible light irradiation in a 50 mL, 0.2 M Na\(_2\)SO\(_4\) aqueous solution at room temperature. For each electrode, EIS was first performed in dark conditions and later under visible light irradiation (\(\lambda \geq 400 \) nm) at 0.0 V and with a frequency ranging from 1 to 10\(^4\) Hz. The photocurrent response was obtained by LSV in the dark and under visible light irradiation at a scan rate of 50 mV/s over the potential range, –1.0 to 1.0 V.

## RESULTS AND DISCUSSION

An EB was used as a “defect engineer” because it can create different types of defects in the CeO\(_2\) crystal, thereby imparting

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novel characteristics, such as a reduced band gap and visible light photocatalytic activity. This protocol does not involve any expensive and toxic chemicals, which make this modification process quite useful and efficient in the field of nanoparticle modification. The entire process took place in water at room temperature and atmospheric pressure. Figure 1 shows the schematic model illustrating the defect induced band gap narrowing of commercially available CeO$_2$ nanostructure by EB, which is simple, easy, fast, and efficient. The high energy electrons generated by EB can either reduce some of the Ce$^{4+}$ ions to Ce$^{3+}$ or interact with molecules of H$_2$O as well as air and may form solvated electrons, H$_3^+$, OH$^-$, and strong oxidizing agents, such as ozone (O$_3$) and OH group. These species may modify the CeO$_2$ by forming Ce$^{3+}$, oxygen vacancies, or surface modifications. These Ce$^{3+}$, OH and other species generated in situ modify the commercial CeO$_2$ and impart enhanced visible light activities to the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures.

**Optical Properties.** Band gap measurements were carried out by DRS to determine the optical properties of the modified 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures that were caused by the EB treatment (Figure 2a). UV-vis DRS of both 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures showed the lower reflectance (%R) compared to p-CeO$_2$ (Figure 2a inset). This suggests that there are some changes in the EB-modified CeO$_2$ nanostructures at the molecular level. Figure S1 (Supporting Information) presents the UV-vis absorbance of these nanostructures, showing similar trends as well as color of the samples. A desirable band gap is very important for photocatalysis, photoelectrodes and photovoltaic applications. A plot of the Kubelka–Munk function as a function of energy is used to determine the band gap. The two 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures samples showed (Figure 2a) different band gaps compared to p-CeO$_2$, indicating changes in the optical properties of the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures. The 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures showed decrease in band gap energy ($E_g$) from 3.36 eV of p-CeO$_2$ to 3.15 and 3.12 eV, respectively. This shows that the changes in the %R and band gap of the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures caused by the 30 kGy EB and 90 kGy EB treatments were substantial in comparison to p-CeO$_2$. The red-shift in the band gap has been attributed to the presence of Ce$^{3+}$ at the grain boundaries, and the band gap decreases with increasing Ce$^{3+}$ concentration, which forms some localized gap states in the band gap. Tatar et al. reported that the red shift in the band gap is due to the formation of some localized band gap states caused by oxygen vacancies and Ce$^{3+}$. The band gap narrowing of the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures might be due to oxygen vacancies, defects and an increase in Ce$^{3+}$.

**PL Analysis.** PL is closely related to the surface states, oxygen vacancies, defects, and stoichiometry of any semiconductor material. This technique is used to determine the effectiveness of trapping, migration, transfer of charge carriers, as well as for better understanding the fate of the electron–hole pairs in semiconductors. In the cubic fluorite structure of CeO$_2$, oxygen ions are not closely packed, and CeO$_2$ may form many oxygen vacancies while maintaining the basic fluorite structure. The 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures show high PL intensities compared to p-CeO$_2$ (Figure 2b). This was attributed to the presence of a higher number of oxygen vacancies and/or defects in the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures, which leads to an enhancement of the optical properties. This observation is in accordance with the UV–vis reflectance spectra (Figure 2a). Liqiang et al. reported that oxygen vacancies and defects can easily bind the photoinduced electrons to form excitons so that the PL signal can occur easily, and the PL signal increases with increasing content of oxygen vacancies or defects. Therefore, high intensity PL spectra were observed for the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures compared to p-CeO$_2$ because of the high content of oxygen vacancies and an increase in Ce$^{3+}$ and other defects. On the other hand, the PL intensity observed in the case of the 90 kGy-CeO$_2$ nanostructure was higher than that of the 30 kGy-CeO$_2$ nanostructures, which suggests that in 90 kGy-CeO$_2$ nanostructures there is a higher separation rate of photoinduced charge carriers, higher
separation between the photoelectrons and holes, and higher number of different types of defects.\textsuperscript{19,25}

**XRD Analysis.** The phase purity of the modified nanostructures was examined by XRD (Figure 3) to identify the change in the phase and structure of the modified samples. All diffraction peaks from p-CeO\(_2\), 30 kGy-CeO\(_2\) and 90 kGy-CeO\(_2\) nanostructures could be indexed to the fluorite cubic phase of CeO\(_2\) (JCPDS 08-0792). The peaks at 28.54°, 33.08°, 47.48°, 56.33°, 59.08°, 69.40°, 76.69°, and 79.06° 2\(\theta\) were assigned to the CeO\(_2\) (111), (200), (220), (311), (222), (400), (331), and (420) planes, respectively. No obvious sign of crystalline Ce\(_2\)O\(_3\) or Ce(OH)\(_3\) were detected. The XRD patterns of the 30 kGy-CeO\(_2\) and 90 kGy-CeO\(_2\) nanostructures were similar to p-CeO\(_2\) except for a minor difference in the peak intensities and peak broadening. This shows that after EB irradiation, the basic structure (fluorite cubic phase) of CeO\(_2\) has not changed, even though the successive decrease in the intensities of 30 kGy-CeO\(_2\) and 90 kGy-CeO\(_2\) indicates a decrease in the crystallinity of the nanostructures. A very small

![Figure 3: XRD patterns of the p-CeO\(_2\), 30 kGy-CeO\(_2\), and 90 kGy-CeO\(_2\) nanostructures.](image)

![Figure 4: TEM and HRTEM images of the (a, b) p-CeO\(_2\), (c, d) 30 kGy-CeO\(_2\), and (e, f) 90 kGy-CeO\(_2\). The insets of (a), (c), and (e) show the SAED pattern of the corresponding sample.](image)
shift of the peaks were observed (Figure 3 inset), which could be due to oxygen vacancies, defects and Ce$^{3+}$ that contribute to the development of strain in the XRD pattern, which lead to a change in the particle size. The mean crystallite size of the p-CeO$_2$, 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures were calculated using the Scherrer’s formula, \( D = \frac{K \lambda}{\beta \cos \theta} \), where \( K \) is the shape factor and has a typical value of approximately 0.9, \( \lambda \) is the wavelength (Cu K\( \alpha \) = 0.15405 nm), \( \beta \) is the full width at half-maximum of the most intense peak, and \( \theta \) is the peak position. Using this equation, the calculated crystallite size of the p-CeO$_2$, 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures at \( \sim \)28.52° \( \theta \) were approximately 22.64 nm, 22.70 and 22.78 nm, respectively (Table 1), which were within the range of the particle sizes measured by TEM (Figure 4). After EB irradiation at 30 kGy and 90 kGy, the crystallite size had slightly increased compared to the p-CeO$_2$ nanostructure (Table 1). A small increase in the crystallite size upon EB irradiation indicates the formation of an amorphous phase and defects at the surface of CeO$_2$ crystals. This suggests that an EB could be a good tool for modifying the required XRD parameters without changing the basic structure (fluorite cubic phase) for defect induced band gap narrowing of different metal oxides for photocatalysis and photoelectrodes. Similar changes were observed by an EB treatment in the case of TiO$_2$.

**TEM Analysis.** Figure 4a, c and e shows TEM images of the p-CeO$_2$, 30 kGy-CeO$_2$, and 90 kGy-CeO$_2$ samples. The shapes of the CeO$_2$ particles are nonuniform with a majority observed as cubes. Triangular and diamond shaped particles were also clearly visible in the TEM images. The size of the particles was measured to be in the range of 10 to 100 nm. The ring selected area electron diffraction (SAED) pattern confirmed the polycrystalline nature of the CeO$_2$ samples (Figure 4 insets). Figure 4b, d and f shows the corresponding HRTEM images with a continuous lattice, indicating the high crystalline nature of CeO$_2$ nanostructures. A lattice spacing of 0.31 nm, which corresponds to the (111) plane, was measured from the HRTEM images. This is in accordance with the prominent (111) XRD peak. Amorphous regions are also observed (see Figure 4f) around the crystalline particles, suggesting the presence of amorphous Ce$_2$O$_3$ in the samples. The amorphous regions appear to be higher for the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures than p-CeO$_2$.

**Raman Analysis.** Figure 5 shows the Raman spectra of the p-CeO$_2$, 30 kGy-CeO$_2$, and 90 kGy-CeO$_2$ nanostructures. A lattice spacing of 0.31 nm, which corresponds to the (111) plane, was measured from the HRTEM images. This is in accordance with the prominent (111) XRD peak. Amorphous regions are also observed (see Figure 4f) around the crystalline particles, suggesting the presence of amorphous Ce$_2$O$_3$ in the samples. The amorphous regions appear to be higher for the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures than p-CeO$_2$.

**Table 1. Structural Parameters Measured from the XRD Patterns of the p-CeO$_2$, 30 kGy-CeO$_2$, and 90 kGy-CeO$_2$ Powder**

<table>
<thead>
<tr>
<th>samples</th>
<th>2θ</th>
<th>d-spacing (Å)</th>
<th>lattice parameters (Å)</th>
<th>volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-CeO$_2$</td>
<td>28.52</td>
<td>3.11</td>
<td>( a = b = c = 5.408 )</td>
<td>158.22</td>
</tr>
<tr>
<td>30 kGy-CeO$_2$</td>
<td>28.53</td>
<td>3.12</td>
<td>( a = b = c = 5.409 )</td>
<td>158.27</td>
</tr>
<tr>
<td>90 kGy-CeO$_2$</td>
<td>28.51</td>
<td>3.12</td>
<td>( a = b = c = 5.409 )</td>
<td>158.25</td>
</tr>
</tbody>
</table>

The peak broadening in the case of 90 kGy-CeO$_2$ was slightly more than that of the 30 kGy-CeO$_2$, which shows a higher concentration of defects, Ce$^{3+}$, and strain in 90 kGy-CeO$_2$ than 30 kGy-CeO$_2$. These observations are similar to those of DRS, PL and XRD, which further confirms the larger number of defects and strain in the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures compared to p-CeO$_2$. Several factors might have affected the changes in the main Raman peak position and line width, including phonon confinement, strain, broadening associated with the size distribution, defects, and variations in phonon relaxation with particle sizes. Oxygen vacancies and Ce$^{3+}$ ions in the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures are believed to be responsible for the changes in the Raman spectra, which is further supported by DRS, PL and XPS.

**XPS Analysis.** The chemical state and composition of the p-CeO$_2$, 30 kGy-CeO$_2$, and 90 kGy-CeO$_2$ nanostructures were characterized by XPS. Carbon, oxygen and cerium were detected in the XPS survey spectra (Figure S2a, Supporting Information). The C 1s photoelectron peak at 284.5 eV binding energy (BE) was stronger for p-CeO$_2$ and the intensity of the C 1s feature was reduced for the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures, which was attributed to the removal of surface carbon impurities by EB irradiation (Figure S2b, Supporting Information). Figure 6a, c and e and Figure 6b, d and f show the Ce 3d and O 1s photoelectron peaks of p-CeO$_2$, 30 kGy-CeO$_2$, and 90 kGy-CeO$_2$ nanostructures, respectively. The broad Ce 3d photoelectron peaks were deconvoluted to assign precisely and allow an estimation of the composition of different chemical states present in the samples. The major Ce$^{4+}$ 3d$_{5/2}$ (Ce$^{4+}$ 3d$_{3/2}$) photoelectron peaks for the p-CeO$_2$, 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures was observed at a BE of 898.94 eV (916.43 eV), 898.23 eV (916.12 eV), and 898.8 eV (916.32 eV), respectively. Similarly, the main Ce$^{3+}$ 3d$_{3/2}$ (Ce$^{3+}$ 3d$_{5/2}$) photoelectron peaks for the p-CeO$_2$, 30 kGy-CeO$_2$, and 90 kGy-CeO$_2$ nanostructures was observed at a binding energy of 882.96 eV (901.98 eV), 882.03 eV (900.97 eV), and 882.81 eV (901.73 eV), respectively. The less intense deconvoluted Ce 3d peaks were assigned to the “shake-up” peaks normally observed in the case of CeO$_2$. The broad O 1s feature in Figure 6d, and f was deconvoluted into four oxygen peaks for all the samples. The XPS BE position at 528.37, 530.29, 531.48, and 533.49 eV for the p-CeO$_2$ sample was assigned to surface adsorbed oxygen, oxygen from CeO$_2$, oxygen from Ce$_2$O$_3$, and Ce(OH)$_3$ and/or Ce(OH)$_4$, respectively. The 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ samples...
showed similar O 1s XP spectra. The Ce\(^{3+}\) to Ce\(^{4+}\) ratios in the p-CeO\(_2\), 30 kGy-CeO\(_2\) and 90 kGy-CeO\(_2\) samples were estimated from the deconvoluted peak area (Figure 6a, c, and e).\(^{32}\) The detailed procedure of the estimation is reported elsewhere.\(^{32}\) The Ce\(^{3+}\) concentration increased with increasing the EB irradiation energy. The presence of trivalent Ce\(^{3+}\) can be due either to the formation of Ce\(_2\)O\(_3\) or oxygen vacancies. To confirm this, the [O]/[Ce] and [O 1s]/[Ce 3d] ratios were measured from their photoelectron peak area considering their sensitivity factor and are tabulated in Table 2.\(^{32,33}\) The sensitivity factor for Ce and O is 7.399 and 0.711, respectively. Semiquantitative analysis of the integrated peak areas can provide the concentrations of Ce\(^{3+}\) and Ce\(^{4+}\) ions in the p-CeO\(_2\), 30 kGy-CeO\(_2\), and 90 kGy-CeO\(_2\) nanostructures, as listed in Table 2, using the reported methods and formulas.\(^{32}\) XPS analysis confirmed the presence of both Ce\(^{4+}\) and Ce\(^{3+}\) in all samples and an increase in the Ce\(^{3+}\) concentration with EB irradiation, which is due to the formation of more defects and/or an amorphous phase of Ce\(_2\)O\(_3\).

As indicated by XPS and Raman spectroscopy, the 30 kGy-CeO\(_2\) and 90 kGy-CeO\(_2\) nanostructures contained large number of defects and Ce\(^{3+}\). These defects might lead to the formation of a surface state energy band of oxygen. The oxygen adsorption, desorption and diffusion processes may occur easily on the surface of the 30 kGy-CeO\(_2\) and 90 kGy-CeO\(_2\).
nanostructures, that can greatly enhance their optical properties and imparts visible light photocatalytic activity.\textsuperscript{6,23}

**Photocatalytic Degradation of 4-NP and MB by the p-CeO\textsubscript{2}, 30 kGy-CeO\textsubscript{2}, and 90 kGy-CeO\textsubscript{2} Nanostructures.** 4-NP is an important reagent used in the drugs and chemical industries, whereas MB is a hetero polyaromatic model dye used in the textile industry. 4-NP is highly toxic, whereas MB is mildly toxic. The photocatalytic activities were examined as reported earlier for the p-CeO\textsubscript{2}, 30 kGy-CeO\textsubscript{2}, and 90 kGy-CeO\textsubscript{2} nanostructures in the degradation of 4-NP and MB under visible light (\(\lambda > 400\) nm) illumination.\textsuperscript{19,20} Both the 30 kGy-CeO\textsubscript{2} and 90 kGy-CeO\textsubscript{2} nanostructures showed better degradation than p-CeO\textsubscript{2}. The degradation was estimated from the decrease in the absorption intensity of 4-NP and MB at a fixed wavelength, \(\lambda_{\text{max}} = 400\) and 665 nm respectively, during the course of the visible light photocatalytic degradation reaction. The degradation was calculated using \(C/C_0\), where \(C_0\) is the initial concentration and \(C\) is the concentration after photoirradiation (Figure 7).\textsuperscript{14} The blank experiment (Figure 7) did not show any degradation under visible light irradiation for 4-NP and MB. 90 kGy-CeO\textsubscript{2} showed better catalytic activity than 30 kGy-CeO\textsubscript{2}. The probable reasons for the enhanced photocatalytic activities compared to p-CeO\textsubscript{2} are the surface concentration of surface donor defects, such as oxygen vacancies and Ce\textsuperscript{3+} centers.\textsuperscript{21,23,35} When commercially available CeO\textsubscript{2} (Sigma) was irradiated with EB, 90 kGy EB irradiation produced more defects or surface modification in CeO\textsubscript{2} than 30 kGy EB irradiation to make CeO\textsubscript{2} photoactive in visible light. 90 kGy-CeO\textsubscript{2} showed higher photocatalytic activity than 30 kGy-CeO\textsubscript{2}, even though the difference in band gap was not significant. The increase in the photocatalytic activities might be due to surface modification and oxygen vacancy which minimizes the recombination of photogenerated electrons and holes. Photocatalytic activity is supported by DRS, PL, and XPS.

**Stability and Reusability of the 90 kGy-CeO\textsubscript{2} Nanostructure.** The stability and reusability of the 90 kGy-CeO\textsubscript{2} nanostructure was tested by centrifuging the catalyst from the dye solutions (4-NP and MB), washing with DI water and drying in an oven at 100 °C. The reused catalyst showed \(~95%\) and \(~90%\) response for the second and third runs, respectively, in each case to that of the fresh catalyst (Figure S3, Supporting Information), which highlights the stability and reusability of the 90 kGy-CeO\textsubscript{2} nanostructure.

**Photoelectrochemical Studies of the p-CeO\textsubscript{2}, 30 kGy-CeO\textsubscript{2}, and 90 kGy-CeO\textsubscript{2} for Photoelectrodes.** The photoelectrochemical activity of the nanomaterials is determined by both the light-harvesting capacity and the separation of electron–hole pairs.\textsuperscript{6} Therefore, photoelectrochemical impedance spectroscopy (EIS) and linear scan voltammetry (LSV) under
dark and visible light irradiation were performed to know the visible light activity and efficiency of charge separation of the 30 kGy-CeO2 and 90 kGy-CeO2 photoelectrodes.

**Electrochemical Impedance Spectroscopy.** EIS measurements were performed on p-CeO2, 30 kGy-CeO2, and 90 kGy-CeO2 photocatalysts to examine the charge transfer resistance and separation efficiency between the photogenerated electrons and holes because the charge separation efficiency of photogenerated electrons and holes is a critical factor for the photocatalytic activity and photoelectrodes.38-41

Figure 9a shows the typical EIS Nyquist plots of the p-CeO2, 30 kGy-CeO2, and 90 kGy-CeO2 photocatalysts in the dark and under visible light irradiation.40-42 The arc radius of the EIS spectra reflects the interface layer resistance arising at the surface of the electrode.42 A smaller arc radius indicates higher charge transfer efficiency.19,39,43 The arc radius of the EIS spectrum for the 30 kGy-CeO2 and 90 kGy-CeO2 photocatalysts were smaller than that of p-CeO2 in the cases of dark and visible light irradiation. This suggests that the 30 kGy-CeO2 and 90 kGy-CeO2 photocatalysts has lower resistance than p-CeO2, which can accelerate the interfacial charge-transfer process. The arc radius of the 90 kGy-CeO2 photocatalyst was smaller than that of the 30 kGy-CeO2 in dark and under visible light irradiation. This suggests that the 90 kGy-CeO2 photocatalyst has the lowest charge transfer resistance and is most suitable for photocatalytic applications. These observations are supported by the PL results and the visible light photocatalytic degradation of 4-NP and MB. The EIS results further support the important role of Ce3+ and different types of defects and oxygen vacancies, which facilitate the charge separation (electrons and holes) and transfer efficiency of photogenerated electrons and holes on the surface of the 30 kGy-CeO2 and 90 kGy-CeO2 photocatalysts.

**Linear Scan Voltammetry.** To investigate the possible mechanisms for the enhanced visible light photoactivity (i.e., photocurrent), LSV for p-CeO2, 30 kGy-CeO2, and 90 kGy-CeO2 nanostructures were performed under the dark and visible light irradiation.19,40,42 Figure 9b shows the improvement in the photocurrent response of 30 kGy-CeO2 and 90 kGy-CeO2 nanostructures which is attributed to the increase of light harvesting ability due to defects which gives narrowed band gap to 30 kGy- and 90 kGy-CeO2. Due to the narrow band gap the valence electrons can be excited to the conduction band by absorbing visible light. It is known that the photoelectrochemical activity is determined by both the capacity of light-harvesting and the separation of electron–hole pairs. Therefore, electron–hole pairs are generated by absorbing the incident photons with energies larger than the Eg and they will recombine unless they are separated quickly.31-44

Generally, a high value of the photocurrent indicates that the sample holds strong ability to generate and transfer the photoexcited charge carrier under irradiation.40-47 The 30 kGy-CeO2 and 90 kGy-CeO2 nanostructures show higher photocurrent than p-CeO2 under the same condition, suggesting that the 30 kGy-CeO2 and 90 kGy-CeO2 nanostructures exhibits stronger ability in separation of electron–hole pairs than p-CeO2 as proven by the PL. However, the 90 kGy-CeO2 nanostructures shows higher photocurrent than the 30 kGy-CeO2 nanostructures. The significant improvement in the photocurrent for 90 kGy-CeO2 nanostructures shows that it can be easily motivated by visible light, and produce more photoinduced carriers, thus possessing high visible photocatalytic activity. The EIS and LSV results show that the 90 kGy-CeO2 nanostructures can be used effectively as photocatalysts and photoelectrode materials.

The difference in the appearance (Figure 2a) of the p-CeO2 (white), 30 kGy-CeO2 (light yellow), and 90 kGy-CeO2 (pale yellow) photocatalysts suggests that there is a change in either the quantum state or energy absorbed by the nanostructures. DRS (Figure 2a) revealed a change in the band gap energy because the state change is quite difficult in CeO2 without additional impurities, whereas energy absorption by the 30 kGy-CeO2 and 90 kGy-CeO2 nanostructures might be possible. A range of characterizations techniques, such as DRS, PL, XPS, Raman spectroscopy, and photoelectrochemical studies (EIS and LSV), highlighted the importance of Ce3+ and different types of oxygen species in the 30 kGy-CeO2 and 90 kGy-CeO2 nanostructures relative to p-CeO2 for visible light photocatalytic degradation reactions and photoelectrodes. The EB produces solvated electrons and other radicals, such as *OH, which might alter the ratio of Ce3+/Ce4+ and oxygen species.19,21,23 Moreover, Ce sites cannot be replaced because there is no other dopant in the system. Therefore, CeO2 modification by an EB leads to either the addition of electrons or radicals to the CeO2, which makes the CeO2 have different ratios of Ce3+/Ce4+ and oxygen deficient/rich either by the addition of electrons or the replacement of oxygen from the CeO2 matrix, in such a way that oxygen species residing at the surface of CeO2 makes the matrix either oxygen deficient or rich.
CONCLUSION

EB irradiation of two different doses (30 kGy and 90 kGy) was used for defect-induced band gap narrowing of CeO$_2$ for visible light photocatalytic activities and photoelectrodes. Defect-induced band gap narrowing of CeO$_2$ nanostructure was confirmed by DRS, PL, XRD, Raman, XPS, and TEM. The p-CeO$_2$, 30 kGy-CeO$_2$, and 90 kGy-CeO$_2$ nanostructures were used to photodecompose 4-NP and MB. The 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures showed much higher photocatalytic activity than p-CeO$_2$. EIS confirmed the defect-induced band gap narrowing of CeO$_2$ by showing higher electron transfer and minimizing the recombination of photogenerated electrons and holes for the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures under visible light irradiation. LSV further confirmed the enhanced visible light activity of the 30 kGy-CeO$_2$ and 90 kGy-CeO$_2$ nanostructures. This shows that EB can be used as an effective tool to reduce the band gap of metal oxides (semiconductors) for the enhanced visible light photocatalytic activities and photoelectrodes.

ASSOCIATED CONTENT

Supporting Information

Further additional information about UV−vis and XPS surveys and C 1s spectra of CeO$_2$ nanostructures modified by Electron beam. C/C$_0$ plots of 4-NP and MB photodegradation by 90 kGy CeO$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Tel: +82 53 810 2517. Fax: +82 53 810 4631. E-mail: mhcho@ynu.ac.kr.

Notes

The authors declare no competing financial interest.

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