

Photocatalytic Activity of Erbium-doped CeO₂ Enhanced by Reduced Graphene Oxide/CuO Cocatalyst for the Reduction of CO₂ to Methanol

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Published online 31 July 2017 in Wiley Online Library (wileyonlinelibrary.com). DOI 10.1002/ep.12717

A series of erbium-doped CeO₂ composites loaded with reduced graphene oxide (rGO, denoted as Er-doped CeO₂/rGO) were prepared via a hydrothermal method. The crystal structures, morphological characteristics, and surface physicochemical properties of the as-prepared Er-doped CeO₂/rGO composites were characterized through X-ray diffraction, transmission electron microscopy, Raman spectroscopy, ultraviolet–visible diffuse reflection spectroscopy, and X-ray photoelectron spectroscopy. The photocatalytic activities of the composite samples were further evaluated by reducing CO₂ to methanol. Results show that erbium (III) doping caused a red shift of the response spectrum from 392 nm to 451 nm, and that rGO loading induced a response spectrum shift to 467.9 nm. The corresponding reduction yields of CO₂ to methanol approached 42.5 and 135.6 $\mu\text{mol g}^{-1}\text{cat h}^{-1}$ for Er-doped CeO₂/CuO and Er-doped CeO₂/rGO/CuO catalysts under similar conditions in 5 h, respectively. Accordingly, rGO enhances significantly the yield of the photocatalytic reduction of CO₂ to methanol. © 2017 American Institute of Chemical Engineers Environ Prog, 37: 655–662, 2018

Keywords: reduced graphene oxide, cocatalyst, erbium-doped CeO₂, carbon dioxide, photocatalytic reduction

INTRODUCTION

Carbon dioxide (CO₂) is a greenhouse gas whose emissions have resulted in global warming and climate deterioration. Thus, CO₂ capture, utilization and storage (CCUS) is an important carbon management strategy. To convert CO₂ to fuel, Halmann [1] exploited GaP semiconductor as the photocatalyst to reduce CO₂ to formic acid and formaldehyde. Inoue *et al.* [2] utilized TiO₂, CdS, and GaP semiconductors as photocatalysts for the reduction of CO₂ to formic acid, formaldehyde, methyl alcohol and methane. Photocatalytic CO₂ reduction [3–24], especially the photocatalytic reduction of CO₂ to methanol, has been extensively investigated since methanol is easily stored at ambient pressure and temperature and compatible with vehicles as a fuel [25–32].

CeO₂ is a semiconductor with oxygen vacancies related to the valence state of Ce³⁺ in CeO₂ [33], and oxygen vacancies can narrow the band gap of CeO₂, according to which band gaps can be adjusted by dominating the concentration of

oxygen vacancies or Ce³⁺ to improving the use of solar irradiation. Shieh *et al.* [34] reported the positions of conduction and valence bands for CeO₂ as $E_c = -1.02$ V (versus NHE) and $E_v = 1.53$ V (versus NHE). CeO₂ can catalyze the reduction of CO₂ to fuel molecules under light irradiation. Wang and coworkers utilized iron ions as a dopant to prepare Fe-doped CeO₂ catalysts, photocatalytically reducing CO₂ to CH₄ and CO [35]; Zhang *et al.* loaded CeO₂ onto g-C₃N₄, resulting in a CeO₂/g-C₃N₄ composite as a photocatalyst for the reduction of CO₂ to CH₄ and CO [36]. We previously reported the fabrication of an artificial photosynthesis system based on CeO₂ and N-doped graphene for the photocatalytic reduction of CO₂ to methanol [37]. However, the effects of reduced graphene oxide (rGO) on the photocatalytic reduction of CO₂ to methanol have yet to be investigated in the CeO₂/rGO composite system.

rGO has been used as a substitute for noble metals, such as Pt, in the production of hydrogen fuels [38–43] because noble metals, including Pt and Au, are expensive and scarce. rGO is used to improve the photocatalytic reduction of CO₂ as a cocatalyst because this material can facilitate photocatalytic H₂ evolution. In addition to the loading of noble metals as cocatalysts, doping can improve catalytic activity. The cost of Er (III) salts is lower than that of noble metal compounds, such as H₂PtCl₆ and K₂PtCl₆. In this study, erbium (III) (Er³⁺) is utilized as a dopant to prepare erbium-doped cerium dioxide (Er-doped CeO₂) and to narrow the band gap. rGO is used as a noble metal-free cocatalyst to fabricate an Er-doped CeO₂/rGO/CuO system. Low-cost copper-based semiconductors abundantly available in the earth crust, are gaining great interest for photocatalytic reactions. The nanocomposites of Cu, Cu₂O and CuO with TiO₂ demonstrated excellent photocatalytic activities compared to the bare and noble metal loaded TiO₂ [26]. Copper-doped Titania catalysts and wedged N-doped CuO remarkably improved the yield of methanol [44,45]. Viswanathan *et al.* synthesized a La-modified sodium tantalite photocatalyst and investigated the effect of Pt, Ag, Au, CuO, NiO, and RuO₂ as cocatalysts to reduce CO₂ to methanol in alkaline medium. The results showed a maximum yield appearing in the case of CuO [46]. Therefore, to ameliorate the photocatalytic reduction of CO₂ to methanol, an Er-doped CeO₂/rGO/CuO system for photocatalytic CO₂ reduction was fabricated herein.

Chemicals

Graphite powder (average particle size = 30 μm) was purchased from Shanghai Colloid Chemical Plant (Shanghai, China). Cerium (III) trichloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) with erbium (III) nitrate pentahydrate ($\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) obtained from Sigma–Aldrich Co. LLC and Na_2SO_3 and NaOH procured from Tianjin Damao Chemical Factory, China. All of the reagents were of analytical grade and utilized as the received. All of the solutions were prepared with 18.2 $\text{M}\Omega \text{ cm}^{-1}$ deionized Milli-Q water.

Synthesis of Graphene Oxide

Graphene oxide (GO) was synthesized via a modified Hummers method as previously described [47,48]. First, graphitic oxide was prepared by adding powdered graphite flakes of 1.0 g and sodium nitrate of 0.5 g to 23 mL of 98% sulfuric acid while stirring. The ingredients were mixed in a 250-mL beaker that was cooled to 10°C in an ice bath. While maintaining vigorous agitation, potassium permanganate of 3.0 g was added to the suspension, with agitation maintained for 3 h. Then, the ice bath was removed, and the temperature of the suspension was increased to 35°C and maintained for 35 min. Afterwards, water of 45 mL was slowly dropped into the paste, causing violent effervescence and an increase in temperature to 98°C. The diluted suspension, now brown in color, was maintained at this temperature for 15 min. The suspension was further diluted to ~140 mL with warm water and then treated with 10% H_2O_2 to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate. Upon the treatment with H_2O_2 , the suspension turned bright yellow. The suspension was centrifuged, yielding a yellow-brown paste. Using a centrifuge, the paste was washed three times with 5% HCl solution, two times with 95% alcohol, and three times with deionized water in sequence, resulting in GO. The GO was dehydrated at 60°C in vacuo for 12 h. The as-synthesized GO (0.0050 g) was ultrasonically dispersed in deionized water of 10.0 mL to produce the GO solution.

Synthesis of Er-Doped $\text{CeO}_2/\text{rGO}/\text{CuO}$

$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (0.5587 g, 1.5 mmol) and $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.0160 g, 0.036 mmol) were separately dissolved in deionized water of 10.0 mL. Then, both solutions were mixed by stirring. Then, 1.0 mol L^{-1} NaOH of 15 mL was added dropwise to the mixed solution by stirring till a bright yellow color was achieved. Then, the GO dispersion solution was added dropwise to the $\text{Ce}(\text{OH})_3$ suspension solution by continuously stirring. Deionized water was added to the suspension solution to a final total volume of 60 mL. The suspension solution was then transferred into a Teflon-lined stainless steel autoclave of 100 mL that was sealed and maintained at 180°C for 6–8 h. The suspension was cooled to room temperature and filtered to collect the Er-doped CeO_2/rGO (the stoichiometric formula as $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}$) precipitates.

$\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}/\text{CuO}$ sample was prepared by adding Er-doped CeO_2/rGO in 0.005 mol L^{-1} CuSO_4 solution of 20.0 mL. The mixed system containing $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}$ and Cu^{2+} was vigorously stirred for 2 h. Then, 1.0 mol L^{-1} NaOH of 5 mL was dropped into the suspension solution. Finally, the suspension solution was transferred into a Teflon-lined stainless steel autoclave of 50 mL that was sealed and maintained at 180°C for 6–8 h. The suspension being cooled to room temperature, the precipitates were filtered, washed with deionized water and collected. A $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}/\text{CuO}$ (rGO = 4.0%, CuO = 4.0 wt%) composite photocatalyst was obtained.

Structure Characterization

X-ray diffraction (XRD) measurements were performed using an X-ray diffractometer (Bruker D8, Germany). The $\text{Cu K}\alpha$ radiation with a wavelength of 0.15406 nm, tube voltage of 40 kV, and tube current of 40 mA was the X-ray source. The electron micrographs were obtained using a JEOL JEM-2000F transmission electron microscope operating at 200 kV. Powder samples were dispersed in water by using an ultrasonic device, placed on C-coated Cu grids, and dried under ambient conditions for morphological observations. The UV–visible (UV–vis) diffuse reflectance spectra were obtained under ambient conditions by using a Shimadzu model UV-2550 spectrophotometer equipped with an integrating sphere. BaSO_4 was used as a reference, with spectra recorded in the range of 200–800 nm. The Raman spectra were recorded on an HR800 micro-confocal Raman spectrometer with a laser of 633 nm, and the power of the laser line was maintained at ~3 mW to prevent a local heating effect. The resolution of the spectrometer was 1 cm^{-1} with a diameter of the analyzed spot of about 1 μm . The CeO_2 , $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2$, and $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}/\text{CuO}$ powder samples were placed on a clean SiO_2/Si substrate for the Raman measurement.

A gas chromatograph (Type 7890B, Agilent Technologies) equipped with a hydrogen flame detector with a 30-m-long Stabilwax with Integra-Guard column was used to detect methanol.

A model XSAM 800 X-ray photoelectron spectrometer (XPS) was used to characterize the valence state of Ce, C, and Er in the Er-doped $\text{CeO}_2/\text{rGO}/\text{CuO}$ samples. The binding energy (E_b) scale was calibrated with respect to the C 1s peak at 284.60 eV. The Al $\text{K}\alpha$ 1.2 line ($h\nu = 1486.60 \text{ eV}$) was used as the X-ray excitation source, with the instrument operated in a vacuum of 1×10^{-9} Torr in the analysis chamber.

Photocatalytic Reduction of CO_2 to Methanol

The photocatalytic reduction of CO_2 was carried out using a photoreactor (Type BL-GHX-V, Shanghai Bilon Instrument, China) in a 250 mL aqueous system under 250 W xenon lamp irradiation in the inner suspension solution. In distilled water of 250 mL containing NaHCO_3 (0.1 mol L^{-1}) and 0.1 mol L^{-1} Na_2SO_3 as electron donors, photocatalyst of 0.1 g was dispersed. The suspension solution was purged with CO_2 to remove oxygen for 20 min before the lamp was switched on. The suspension solution was magnetically stirred during irradiation. Control experiments were conducted in the dark or under irradiation without catalysts. Blank CH_3OH was also detected for all the tested catalysts before photoreaction occurred. The temperature inside the photoreactor was maintained at about 298 K by applying continuous water circulation driven by a 50-W freezer.

RESULTS AND DISCUSSION

Characterization by X-Ray Powder Diffraction

Figure 1 shows the XRD pattern of CeO_2 samples doped with erbium ions and loaded with rGO. The X-ray diffraction patterns of (a) CeO_2 , (b) Er-doped CeO_2 , (c) Er-doped CeO_2/rGO , and (d) Er-doped $\text{CeO}_2/\text{rGO}/\text{CuO}$ samples depict the expected peaks that are perfectly indexed as the face-centered cubic fluorite phase of well-crystallized CeO_2 materials (Fm $\bar{3}m$; JCPDS card No. 34–0394) with lattice constants $a = b = c = 5.4141 \text{ \AA}$. The diffraction peaks at $2\theta = 28.56^\circ$, 33.20° , 47.28° , 56.64° , 58.92° , 69.30° , and 76.89° are assigned to the Bragg reflections from the (111), (220), (220), (311), (222), (400), and (331) planes [49], respectively. The average diameters (D) of the as-synthesized CeO_2 particles were calculated using the Debye–Scherrer equation, $D = K\lambda/(\text{W}\cos\theta)$,

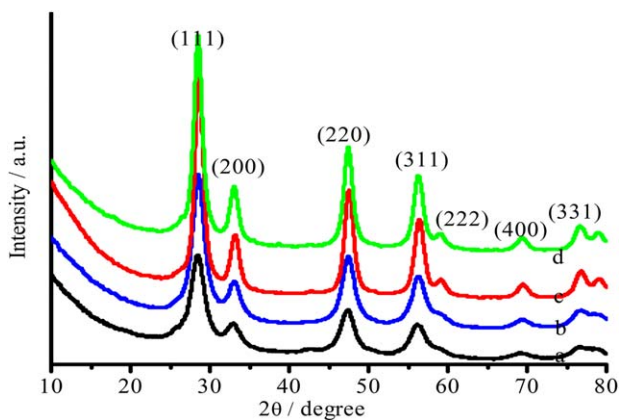


Figure 1. XRD patterns of the as-prepared samples. (a) CeO_2 ; (b) $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2$; (c) $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}$; (d) $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}/\text{CuO}$. [Color figure can be viewed at [wileyonlinelibrary.com](#)]

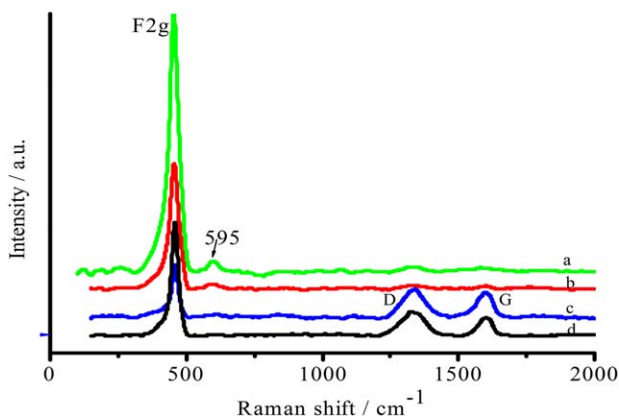


Figure 2. Raman spectra of samples. (a) CeO_2 ; (b) $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2$; (c) $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}$; (d) $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}/\text{CuO}$. [Color figure can be viewed at [wileyonlinelibrary.com](#)]

in a diffraction angle of 28.56° (2θ) as 3.1 nm for CeO_2 sample, 4.8 nm for Er-doped CeO_2 sample, and 5.1 nm for Er-doped CeO_2/rGO sample. No peaks were observed from erbium oxide in Figure 1, showing erbium ions at lattices of CeO_2 crystal [50].

Raman Characterization

Figure 2 shows the Raman spectra of (a) CeO_2 , (b) $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2$, (c) $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}$, and (d) $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}/\text{CuO}$ samples. The observed peaks at approximately 465 cm^{-1} were assigned to the characteristic F_{2g} mode of the face-centered cubic fluorite phase of CeO_2 materials ($\text{Fm}\bar{3}\text{m}$ group). The peak at $\sim 595\text{ cm}^{-1}$ was attributed to the O vacancies due to the presence of Ce^{3+} in the CeO_2 lattice and defects caused by small size effects [51]. Interestingly, the peak became small when Er (III) ions were doped in the CeO_2 lattices as shown by Curve *b* in Figure 2. Finally, the peak disappeared when rGO was introduced to CeO_2 , as shown by Curves *c* and *d*. As a consequence, the Er (III) ions were doped into the CeO_2 lattices.

The Raman spectra of graphene have two main features, namely, G and D modes, each presenting different physical origins. The peak at $\sim 1598\text{ cm}^{-1}$ (G band) arising from the

emission of zone-centered optical phonons corresponds with the doubly degenerated E_{2g} mode of graphite and it is related to the coplanar vibration of sp^2 -bonded C atoms. The peak at 1335 cm^{-1} (D band) is related to the occurrence of defects and disorders. The intensity ratio of D to G bands ($I_D/I_G = 1.26$) is extremely low, displaying the lowered defect density of rGO when linked to Er-doped CeO_2 .

TEM Observation

The Er-doped CeO_2 loaded with rGO and rGO samples were placed in the vacuum chamber for transmission electron microscopy (TEM) observations. The rGO sheets are clearly visible in Figure 3a, with Figure 3b–d indicating the different-scale micrographs of Er-doped CeO_2 nanoparticles distributed on rGO sheets. Figure 3d shows a high-resolution TEM image, from which the polycrystalline nature and crystal size of Er-doped CeO_2 can be clearly observed. The TEM image reveals that Er-doped CeO_2 is crystalline with the crystal size of $\sim 3\text{--}7\text{ nm}$. This result is in good agreement with the XRD observations. Lattice fringes can be observed in the magnified images of different crystallites with the d-spacing value measured as 0.30 nm, which corresponds to the inter-plane distance between the (111) lattice planes of cubic CeO_2 .

UV–Vis Diffuse Reflectance Spectra

The UV–vis absorption spectra of the CeO_2 , Er-doped CeO_2 , and Er-doped CeO_2/rGO samples are shown in Figure 4. The direct band-gap energy (E_g) is determined by fitting absorption data to the direct transition, as shown in Tauc–Mott equation [52], $(\alpha h\nu)^2 = A(h\nu - E_g)$, where α is the optical absorption coefficient, $h\nu$ is the photon energy, E_g is the direct band-gap energy, and A is a constant. The linear portions of curves toward absorption equaling zero ($y = 0$) were extrapolated to yield E_g for direct transitions (Figure 5). The estimated direct band gaps for CeO_2 , Er-doped CeO_2 , and Er-doped CeO_2/rGO samples were equal to 3.15, 2.75, and 2.65 eV, respectively. The band gap of Er-doped CeO_2 was narrower than that of CeO_2 because of the doping of erbium (III) ions in CeO_2 , leading to enhanced oxygen vacancies. The Er-doped CeO_2/rGO sample possesses the smallest band gap of 2.65 eV, which corresponds to 468 nm. The red shift of the absorption edge of Er-doped CeO_2/rGO benefited the absorption of solar energy.

XPS Characterization

The wide-scan XPS spectrum of the as-synthesized Er-doped $\text{CeO}_2/\text{rGO}/\text{CuO}$ sample is shown in Figure 6a. C 1s, O 1s, and Ce 3d peaks appear at ~ 284.6 , 534, and 900 eV, respectively [37], evidently proving the existence of Ce, C, and O elements in the sample. Figure 6b,c display the high-resolution XPS spectra of the sample. The peak at 167.7 eV is attributed to the binding energy of Er 4d [53]. Therefore, the results reveal that the erbium element was doped in the CeO_2 cell lattices. The Cu peaks appeared at 934.88 and 955.59 eV, which were assigned to Cu $2p^{3/2}$ and Cu $2p^{1/2}$ binding energy in CuO particles, revealing that CuO were linked to the Er-doped CeO_2/rGO catalyst [54,55].

Photocatalytic Reduction of CO_2

The reactivity of CeO_2 , Er-doped CeO_2 , CeO_2/rGO , and Er-doped $\text{CeO}_2/\text{rGO}/\text{CuO}$ catalysts was examined by means of the photocatalytic reduction of CO_2 to methanol with Na_2SO_3 as sacrificial donor and water as solvent. During photocatalytic reduction, liquid of 1 mL was withdrawn at intervals and analyzed by a gas chromatograph equipped with a hydrogen flame detector with a Stabilwax w/Integra-Guard column of 30-m long. Methanol yields are presented in Figure 7. At 5 h, the methanol yields approached 0.2, 6.2,

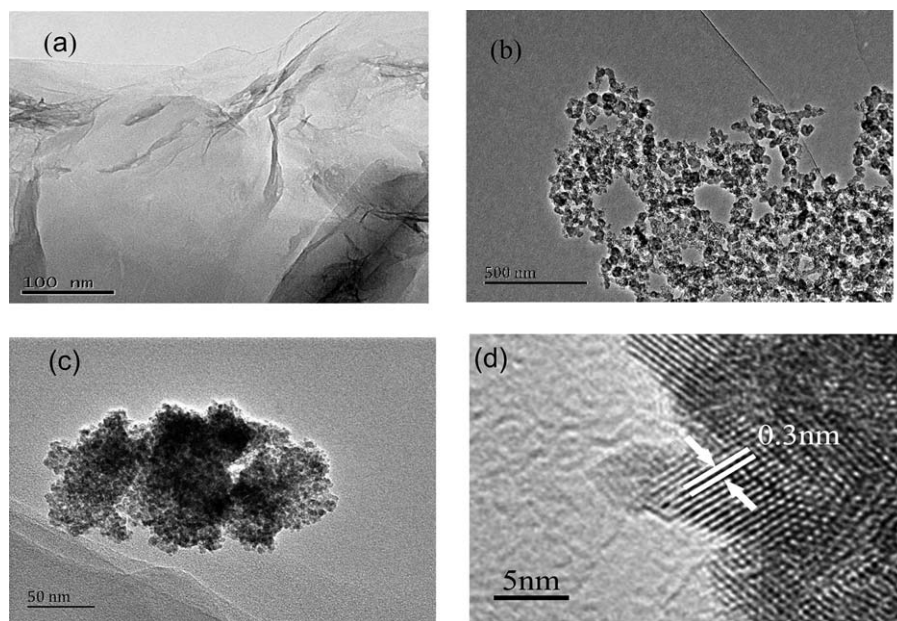


Figure 3. TEM images of samples. (a), rGO; (b,c), $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}$; (d), High resolution image of $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}$.

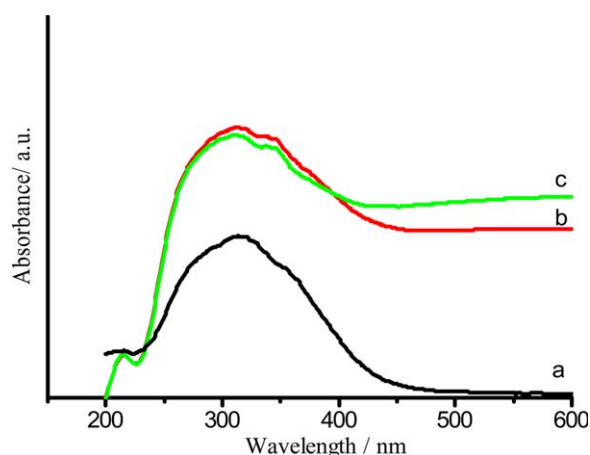


Figure 4. UV-vis diffuse reflectance spectra of the samples. (a) CeO_2 ; (b) Er-doped CeO_2 ; (c) Er-doped CeO_2/rGO . [Color figure can be viewed at wileyonlinelibrary.com]

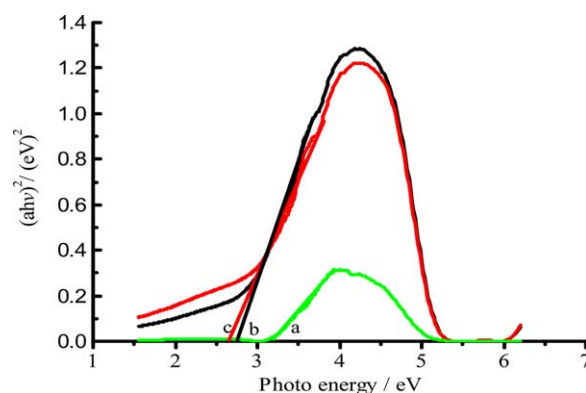


Figure 5. Plot of $(\alpha h\nu)^2$ as a function of photon energy for the samples. (a) CeO_2 ; (b) Er-doped CeO_2 ; (c) Er-doped CeO_2/rGO . [Color figure can be viewed at wileyonlinelibrary.com]

42.5, 33.8, 66.8, and $135.6 \mu\text{mol g}^{-1} \text{cat h}^{-1}$ for CeO_2 , Er-doped CeO_2 , Er-doped CeO_2/CuO , CeO_2/rGO , Er-doped CeO_2/rGO and Er-doped $\text{CeO}_2/\text{rGO}/\text{CuO}$ catalysts. The yield of methanol for Er-doped CeO_2 catalyst is 31-fold that of the bare CeO_2 catalyst, showing the enhanced effect of Er-doping. Moreover, the yields of methanol for Er-doped $\text{CeO}_2/\text{rGO}/\text{CuO}$, Er-doped CeO_2/rGO and CeO_2/rGO catalysts were 3.2-fold, 10.8-fold, and 169-fold those of the corresponding Er-doped CeO_2/CuO , Er-doped CeO_2 , and CeO_2 catalysts without rGO, respectively. These results reveal profoundly that rGO significantly enhances the photocatalytic activity of CeO_2 as a cocatalyst for the reduction of carbon dioxide to methanol. The significantly enhanced effect is possibly attributed to the separation of the photogenerated electron-hole pairs by rGO and the absorption of light irradiation by rGO. The material shows the high catalytic activity compared with TiO_2 [56].

A series of tests with various ratios of erbium mass comparing to that of cerium dioxide were conducted to

determine the optimal methanol yield. The results are listed in Table 1.

By comparison, the doping of erbium in cerium dioxide enhanced the activity of the catalyst. In the initial stage, the yield of methanol increased with erbium doping, approaching a maximum value of $6.4 \mu\text{mol g}^{-1} \text{cat h}^{-1}$ at 2.0 wt% erbium of cerium dioxide. However, the activity of the catalyst decreases when the 2.0 wt% erbium point is exceeded. Therefore, the optimal percentage of erbium mass in Er-doped CeO_2 catalyst is 2.0%, with the formula denoted as $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2$. The enhanced effect of Er doping is possibly attributed to the red shift absorption of light irradiation.

The optimal yield of methanol can be achieved by loading various masses of rGO. Table 2 displays the yields of Er-doped CeO_2 distributed in various masses of GO. The methanol yield increased with the GO mass reaching to the maximum of $66.8 \mu\text{mol g}^{-1} \text{cat h}^{-1}$ at 4.0% of GO, whereas only $6.4 \mu\text{mol g}^{-1} \text{cat h}^{-1}$ was reached at 0.0% of GO. Further addition of GO did not increase the methanol yield, thus the optimal percentage of GO in the Er-doped CeO_2 catalyst

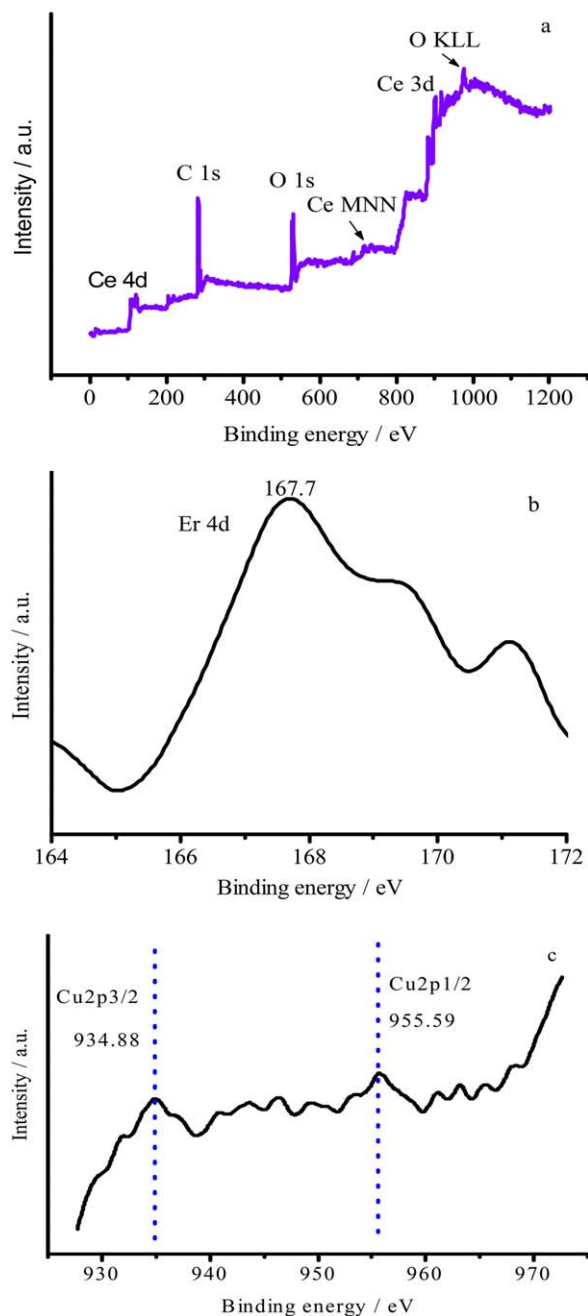


Figure 6. Wide-scan XPS spectrum of the as-synthesized $\text{Ce}_{0.9766}\text{Er}_{0.0234}\text{O}_2/\text{rGO}/\text{CuO}$ sample (a); High-resolution XPS spectrum of Er 4d (b) and Cu 2p (c). [Color figure can be viewed at [wileyonlinelibrary.com](#)]

being ~ 4.0 wt%. CuO works as a cocatalyst together with rGO to synergistically promote the separation of photogenerated electron-hole pairs, to effectively transfer photogenerated electrons, and to increase the photo-reduced activity of the catalytic system.

Table 3 displays the effects of various CuO amounts on methanol yield. At the initial stage, the yield of methanol increased with the CuO weight reaching $135.6 \mu\text{mol g}^{-1}\text{cat h}^{-1}$ at 4.0% of CuO, amounting up to a maximum value. The yield shows the photocatalytic activity of the Er-doped CeO_2/rGO catalyst is higher than that of TiO_2 catalyst [56]. Beyond that point, a continuous addition of CuO led to the decline in methanol yield instead of an

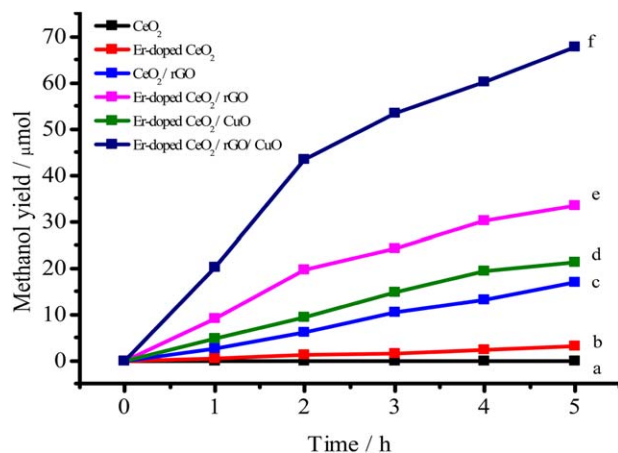


Figure 7. Photocatalytic reduction of CO_2 to methanol in 250.0 mL solution of $0.1 \text{ mol L}^{-1} \text{NaHCO}_3$ with 0.1 g photocatalysts. A 250 W Xe lamp was used as irradiation source in the inner reactor. (a) CeO_2 ; (b) Er-doped CeO_2 ; (c) CeO_2/rGO ; (d) Er-doped CeO_2/CuO ; (e) Er-doped CeO_2/rGO ; (f) Er-doped $\text{CeO}_2/\text{rGO}/\text{CuO}$. [Color figure can be viewed at [wileyonlinelibrary.com](#)]

Table 1. Effects of Er(III) doping in CeO_2 catalyst on methanol yield.

Er-doped (percent/%)	0.0	1.0	2.0	3.0	4.0
Yield ($\mu\text{mol g}^{-1} \text{cat h}^{-1}$)	0.2	4.2	6.4	5.4	3.1

Table 2. Effect of various mass of GO on the activity of Er-doped CeO_2 .

GO (percent/%)	0.0	1.0	3.0	4.0	5.0
Yield ($\mu\text{mol g}^{-1} \text{cat h}^{-1}$)	6.4	44.1	50.3	66.8	52.0

Table 3. Effect of various weights of CuO on the activity of Er-doped CeO_2/rGO .

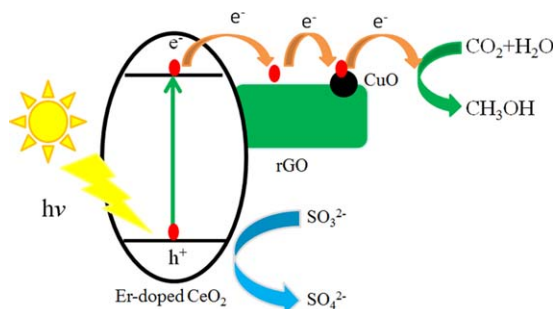
CuO (percent/%)	0.0	1.0	3.0	4.0	5.0
Yield ($\mu\text{mol g}^{-1} \text{cat h}^{-1}$)	66.8	88.8	103.1	135.6	99.5

increase. As a result, the optimal percentage of CuO in Er-doped CeO_2/rGO catalyst is ~ 4.0 wt%.

Reaction Mechanism

To verify the origin of methanol, we conducted a blank test on $0.1 \text{ mol L}^{-1} \text{Na}_2\text{SO}_3$ solution containing Er-doped $\text{CeO}_2/\text{rGO}/\text{CuO}$ catalyst of 0.10 g in the absence of NaHCO_3 . The analytical result revealed that methanol was not detected in the absence of the NaHCO_3 system even if this system was irradiated for 5 h. This finding confirmed that methanol did not originate from the catalyst.

The conduction band (E_c) for CeO_2 is -1.02 V (versus NHE) and the valence band (E_v) is 1.53 V (versus NHE), with the reduction potential for CO_2 to methanol being $E^0_{\text{CO}_2/\text{CH}_3\text{OH}} = -0.38 \text{ V}$ [57]. Thus, the Er-doped $\text{CeO}_2/\text{rGO}/\text{CuO}$ catalyst reduced CO_2 to methanol under light irradiation. The photocatalytic reduction is shown in Scheme 1, in



Scheme 1. Photocatalytic reduction of CO₂ to methanol via Er-doped CeO₂/rGO/CuO photocatalyst. [Color figure can be viewed at wileyonlinelibrary.com]

which rGO facilitates the separation of photogenerated electron–hole pairs.

CONCLUSIONS

CeO₂ is a rare-earth semiconductor with the tunable band gap. The band gap can be tuned by doping erbium (III) ions into CeO₂ lattices, which narrows the band gap. The photocatalytic reduction of CO₂ to methanol can be significantly enhanced by loading reduced GO as a cocatalyst, which functions by separating the photogenerated pairs of electrons and holes. The loaded CuO acts as a selective cocatalyst, which determines the main product of CO₂ reduction to fuel.

ACKNOWLEDGMENT

The work was financially supported by the National Natural Science Foundation of China (Nos. 21576175, 21277094), the Natural Science Foundation of the Jiangsu Higher School of China (No. 12KJA430005), the Natural Science Foundation of Jiangsu Province of China (No. BK20141178, BE2015190), Collaborative Innovation Center of Technology and Material of Water Treatment, the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions, China.

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