Surface modification of layered perovskite Sr$_2$TiO$_4$ for improved CO$_2$ photoreduction with H$_2$O to CH$_4$

Byeong Sub Kwak$^1$, Jeong Yeon Do$^1$, No-Kuk Park$^2$ & Misook Kang$^1$

Layered perovskite Sr$_2$TiO$_4$ photocatalyst was synthesized by using sol-gel method with citric acid. In order to increase the surface area of layered perovskite Sr$_2$TiO$_4$, and thus to improve its photocatalytic activity for CO$_2$ reduction, its surface was modified via hydrogen treatment or exfoliation. The physical and chemical properties of the prepared catalysts were characterized by X-ray diffraction, high-resolution transmission electron microscopy, elemental mapping analysis, energy-dispersive X-ray spectroscopy, N$_2$ adsorption-desorption, UV-Vis spectroscopy, X-ray photoelectron spectroscopy, photoluminescence, and electrophoretic light scattering. CO$_2$ photoreduction was performed in a closed reactor under 6 W/cm$^2$ UV irradiation. The gaseous products were analyzed using a gas chromatograph equipped with flame ionization and thermal conductivity detectors. The exfoliated Sr$_2$TiO$_4$ catalyst (E-Sr$_2$TiO$_4$) exhibited a narrow band gap, a large surface area, and high dispersion. Owing to these advantageous properties, E-Sr$_2$TiO$_4$ photocatalyst showed an excellent catalytic performance for CO$_2$ photoreduction reaction. The rate of CH$_4$ production from the photoreduction of CO$_2$ with H$_2$O using E-Sr$_2$TiO$_4$ was about 3431.77 μmol/g$_{cat}$ after 8 h.

As is well known, the temperature of Earth is increasing owing to greenhouse gas emissions, and CO$_2$ makes up the largest portion of these greenhouse gases. The United Nations Framework Convention on Climate Change (UNFCCC) has concluded that, to maintain a stable environmental, global warming since industrialization must not exceed 2°C. However, according to their investigation, the average ground temperature since industrialization has already increased by 0.75°C. When we consider the heat absorbed by the sea, this temperature increases by a further 0.6°C. Consequently, we have a temperature increase of only 0.65°C until the temperature change set by the UNFCCC is already reached. Because of the global warming, various natural disasters have been occurred$^1$. In order to avoid this problem, we must reduce CO$_2$ emissions. However, it is impossible to stop CO$_2$ emissions completely because of the current industrial systems are depending on the fossil fuels.

Carbon capture and storage (CCS) technology has been developed in order to reduce and/or control the CO$_2$ emissions$^{13}$. However, this CCS technology has several problems such as high cost, additional energy requirements, stability, and storage limitations. Therefore, carbon capture and utilization (CCU) technology is expected to replace it$^4$8, and is advantageous in economic and environmental view because it can prevent CO$_2$ emissions, and convert them into useful materials. There are various strategies for CO$_2$ utilization. One is the non-conversional use of CO$_2$, and the others involve its conversion using chemical, biochemical, photochemical, and electrochemical methods. Of these, the photochemical method is a more promising technology in environmental terms. CO$_2$ photoreduction using a photocatalyst can generate useful compounds such as CH$_4$, HCOOH, HCHO, and CH$_3$OH$^7$. Much research has been devoted to this field since the first report by Inoue$^{et al.}$ on the photoreduction of CO$_2$, and many different semiconductors have been developed and used as photocatalysts, such as TiO$_2$$^{9}$, WO$_3$$^{10}$, ZnO$^{11}$, GaP$^{12}$, CdS$^{13}$, and SiC$^{14}$. Of these, TiO$_2$ is one of the most well-known and widely used materials. In order to improve the optical properties of TiO$_2$, it has been combined with various metals to form hybridized composites such as Ag/TiO$_2$$^{15}$, Pt/TiO$_2$$^{16}$, Ru/TiO$_2$$^{17}$, Pd/TiO$_2$$^{18}$, Ni/TiO$_2$$^{19}$, Cu/TiO$_2$$^{20}$, TiO$_2$/Cu-TiO$_2$$^{21}$, CeO$_2$/TiO$_2$$^{22}$, MgO/TiO$_2$$^{23}$, NiO-In$_2$O$_3$/TiO$_2$$^{24}$, Cu$_2$O$_2$TiO$_2$$^{25}$, NiS-TiO$_2$$^{26}$, In$_2$O$_3$/TiO$_2$$^{27}$, TiO$_2$/Fe-TiO$_2$$^{28}$.

$^1$Department of Chemistry, College of Natural Sciences, Yeungnam University, Gyeongsan, Gyeongbuk, 38541, Republic of Korea. $^2$School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk, 38541, Republic of Korea. Correspondence and requests for materials should be addressed to M.K. (email: mskang@ynu.ac.kr)
and multi-walled carbon nanotube (MWCNT)@TiO$_2$\textsuperscript{29} in an attempt to reduce the band gap or suppress recombination of photogenerated charge carriers. Also, catalysts having a combination of an organic and metal material such as g-C$_3$N$_4$\textsuperscript{30}, Ni$_2$P/g-C$_3$N$_4$\textsuperscript{31}, Au cluster-NP/C$_3$N$_4$\textsuperscript{32}, AgX/g-C$_3$N$_4$ (X = Cl and Br)\textsuperscript{33}, RuRu’/Ag/NS-C$_3$N$_4$\textsuperscript{34–37} and Co-ZIF\textsuperscript{38–41} are being developed.

Recently, the development of TiO$_2$ photocatalysts with the perovskite structure ABO$_3$, has attracted due to the unique perovskite structure, their composition can be easily changed at the A, and B sites and the metal introduced can be quantitatively substituted into the skeleton. Among the perovskite semiconductors, SrTiO$_3$ is widely used as a photocatalyst. Much like TiO$_2$, SrTiO$_3$ has been combined with other species to form hybrid composites such as Mn/SrTiO$_3$\textsuperscript{42}, Cu/SrTiO$_3$\textsuperscript{43}, N-doped TiO$_2$/SrTiO$_3$\textsuperscript{44}, Fe$_2$O$_3$/SrTiO$_3$\textsuperscript{45}, SrTiO$_3$:Cr/Ta/F\textsuperscript{46}, SrTiO$_3$/HZSM-5\textsuperscript{47}, SrTiO$_3$/TiO$_2$/H-titanate nanofiber\textsuperscript{48}, SrTiO$_3$:Rh/Sb\textsuperscript{49}, La/Cr-doped SrTiO$_3$\textsuperscript{50}, Pt/SrTiO$_3$\textsuperscript{51}, Zn/SrTiO$_3$\textsuperscript{52}, Ag$_3$PO$_4$/Cr-SrTiO$_3$\textsuperscript{53}, and g-C$_3$N$_4$/SrTiO$_3$:Rh\textsuperscript{54} to improve its photocatalytic performance. Studies on other perovskite catalysts, including Ca$_x$Ti$_y$O$_3$\textsuperscript{55}, and basalt fiber/PbTiO$_3$\textsuperscript{56}, also have been recently reported.

Another advantage of perovskite is that it forms a layered perovskite depending on the nature and contents of the A and B ions. Figure 1a shows the structure of a Ruddlesden-Popper A$_{j+1}$B$_j$O$_{3j+1}$ perovskite. Here, when the j value increases, the structure tends towards an ABO$_3$ perovskite. In particular, A$_3$BO$_4$, for which j = 1, shows a layered structure with a large gap between each BO$_6$ octahedron.

In this study, we have attempted to improve the photocatalytic performance of Sr$_2$TiO$_4$ layered perovskite by increasing its surface area (Fig. 1b). The surface of the synthesized catalyst was hydrogen treated or exfoliated to increase its interaction with the CO$_2$ feed material and thus amplify its CO$_2$ photoreduction activity. The characteristic properties of the synthesized catalysts were measured by using a variety of techniques such as X-ray
diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), N₂ adsorption-desorption isotherm analysis, UV-Vis spectroscopy, photoluminescence (PL), zeta potential analysis, and X-ray photoelectron spectroscopy (XPS). Furthermore, their photocatalytic activity for the reduction of CO₂ with H₂O under UV light was studied.

Results

X-ray diffraction (XRD) patterns. The XRD patterns for Sr₂TiO₄, H-Sr₂TiO₄, and E-Sr₂TiO₄ are given in Fig. 2. The peaks for Sr₂TiO₄ are observed at 2θ = 24.076, 28.386, 31.464, 32.656, 35.673, 42.899, 43.217, 43.852, 46.791, 55.049, 55.605, 56.319, 57.431, 65.452, and 68.390°, which are assigned to the (011), (004), (013), (110), (112), (015), (006), (114), (020), (116), (024), (017), (123), (026), and (220) planes of Sr₂TiO₄, respectively, identifying it as a layered perovskite-type tetragonal structure (JCPDS 00-039-1471)⁵⁷. The crystallite size of Sr₂TiO₄ calculated using Scherrer’s equation based on the (013) plane is 12.856 Å⁵⁸. After hydrogen treatment, an anatase TiO₂ peak is observed at 2θ = 25.429°. However, the other peaks for the Sr₂TiO₄ structure are maintained, and the crystallite sizes based on the Sr₂TiO₄ (013) plane and the TiO₂ anatase (011) plane are 9.371 and 3.024 Å, respectively. Conversely, the Sr₂TiO₄ sample exfoliated with HNO₃ and TPAOH presents a different XRD pattern. The peaks for E-Sr₂TiO₄ are found at 27.141, 36.070, 41.232, 54.414, 63.069, and 69.105°, which are assigned to the (110), (011), (111), (121), (130), and (031) planes of rutile TiO₂, respectively.⁵⁹ These structural changes are due to the fact that the Sr ions located between the Sr₂TiO₄ layers are removed by HNO₃ treatment, and only the TiO₆ octahedra (corresponding to BO₆) remain. The crystal structure analysis reveals that the Ti forms a rutile structure in the Sr₂TiO₄ and that the Sr is intercalated between the layers. The crystallite size of the catalysts was calculated using Scherrer’s equation. In the case of Sr₂TiO₄ and H-Sr₂TiO₄, 1013 plane and the TiO₂ anatase plane were selected, and 110 plane was selected for E-Sr₂TiO₄. As a result, the crystallite size of Sr₂TiO₄, H-Sr₂TiO₄, and E-Sr₂TiO₄ were found to be 11.568, 11.578, 1.165 Å, respectively.

High-resolution transmission electron microscopy (HR-TEM), element mapping and EDX analysis. The differences in the morphologies of Sr₂TiO₄ and E-Sr₂TiO₄ were investigated using HR-TEM and selected area electron diffraction (SAED) (Fig. 3). The larger particles are observed in Sr₂TiO₄, whereas E-Sr₂TiO₄ consists of the particles form a separate sheets or randomly folded sheets. The images show that the interplanar distance for E-Sr₂TiO₄ is larger than that for Sr₂TiO₄. The d-spacings for the Sr₂TiO₄ (013) plane and the E-Sr₂TiO₄ (110) plane are 2.84 and 3.25 Å, respectively. These results are in accordance with the values derived from XRD patterns.

The compositions of Sr₂TiO₄ and E-Sr₂TiO₄ were analyzed by HR-TEM element mapping analysis and EDX, and the results are shown in Fig. 4 and Table 1. In Sr₂TiO₄, Sr and Ti ions are uniformly distributed throughout the particles and Sr ions are more abundant than Ti ions. The atomic percent values for Sr and Ti are 16 and 11%, respectively. However, the Sr ion content of E-Sr₂TiO₄ is much lower than that of Sr₂TiO₄. Furthermore, EDX analysis showed that the Sr ion content, which is about 1.4-times that of Ti in Sr₂TiO₄, is reduced to just 0.07% that of Ti in E-Sr₂TiO₄. Thus, these results support the assertion that the layers are separated because Sr ions are removed from the interlayers by exfoliation.

Brunauer-Emmett-Teller (BET) surface area analysis. Figure 5 shows the N₂ adsorption-desorption isotherms at 77 K for P-25, which was used as a comparative sample, Sr₂TiO₄, H-Sr₂TiO₄, and E-Sr₂TiO₄. According to the IUPAC classification, the adsorption-desorption isotherm curves of all the catalysts belong to type III. Therefore, the synthesized catalysts are non-porous materials. However, the slight hysteresis in the curves is due to the bulk pores between the particles. The specific surface areas of Sr₂TiO₄ and H-Sr₂TiO₄ are 1.19 and 0.78 m²/g, respectively, which are very low. However, E-Sr₂TiO₄ has a specific surface area of 358.54 m²/g, which is much larger than those of Sr₂TiO₄ and H-Sr₂TiO₄. The increase in the specific surface area of E-Sr₂TiO₄ is due not only to the removal of Sr ions from between the layers, but also to the separation of the layers, as shown in the HR-TEM images. The increase in catalyst surface area leads to an increase in the number of active sites for CO₂
and H$_2$O to react, leading to an increase in reactivity. Therefore, E-Sr$_2$TiO$_4$ was expected to exhibit improved catalytic activity compared to those of Sr$_2$TiO$_4$ and H-Sr$_2$TiO$_4$. This specific surface area is considerably larger than that of the commercial catalyst P-25, which is 43.65 m$^2$/g.

**Optical properties of photocatalysts.** Figures 6 and 7 show the UV-Vis spectra and Tauc’s plots of P-25, Sr$_2$TiO$_4$, H-Sr$_2$TiO$_4$, and E-Sr$_2$TiO$_4$. The UV absorptions of Sr$_2$TiO$_4$ and H-Sr$_2$TiO$_4$ are blue-shifted compared to that of P-25 because of the influence of SrO, with its band gap of 5.71 eV$^{40}$. Conversely, the absorbance of E-Sr$_2$TiO$_4$ is shifted to a longer wavelength due to the removal of Sr ions. Most interestingly, it moved to longer wavelength than that of P-25. This is because E-Sr$_2$TiO$_4$ has a rutile TiO$_2$ structure (band gap: 3.0 eV), as

---

**Figure 3.** High resolution TEM and SAED images of catalysts: (a), (c) Sr$_2$TiO$_4$ and (b), (d) exfoliation Sr$_2$TiO$_4$. 

---

and H$_2$O to react, leading to an increase in reactivity. Therefore, E-Sr$_2$TiO$_4$ was expected to exhibit improved catalytic activity compared to those of Sr$_2$TiO$_4$ and H-Sr$_2$TiO$_4$. This specific surface area is considerably larger than that of the commercial catalyst P-25, which is 43.65 m$^2$/g.

**Optical properties of photocatalysts.** Figures 6 and 7 show the UV-Vis spectra and Tauc’s plots of P-25, Sr$_2$TiO$_4$, H-Sr$_2$TiO$_4$, and E-Sr$_2$TiO$_4$. The UV absorptions of Sr$_2$TiO$_4$ and H-Sr$_2$TiO$_4$ are blue-shifted compared to that of P-25 because of the influence of SrO, with its band gap of 5.71 eV$^{40}$. Conversely, the absorbance of E-Sr$_2$TiO$_4$ is shifted to a longer wavelength due to the removal of Sr ions. Most interestingly, it moved to longer wavelength than that of P-25. This is because E-Sr$_2$TiO$_4$ has a rutile TiO$_2$ structure (band gap: 3.0 eV), as
confirmed by the XRD analysis above. Therefore, the absorbance of E-Sr₂TiO₄ is shifted to longer wavelength than that of P-25, which composed mainly of anatase TiO₂ (band gap: 3.2 eV). The band gap was calculated using the Tauc equation:

$$E_g = \frac{1}{2} \left( \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)$$

Table 1. Atomic ratio by HR-TEM EDX analysis.

| Catalyst     | (Atomic %) |
|--------------|------------|
|              | Sr  | Ti  | O  |
| Sr₂TiO₄     | 16.16| 11.93| 71.89|
| E-Sr₂TiO₄   | 4.80 | 68.29| 26.90|

Figure 4. HR-TEM elemental mapping analysis of catalysts: (a) Sr₂TiO₄ and (b) exfoliation Sr₂TiO₄.

Figure 5. N₂ adsorption and desorption isotherms of catalysts; (a) P-25, (b) Sr₂TiO₄, (c) H-Sr₂TiO₄ and (d) E-Sr₂TiO₄.
where $\alpha$, $h$, $\nu$, $A$, and $E_{bg}$ represent the absorption coefficient, Planck’s constant, light frequency, a constant, and band gap energy, respectively. In a plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$), the intercept on the x axis gives the band gap. Using this method, the band gap of P-25, Sr$_2$TiO$_4$, H-Sr$_2$TiO$_4$ and E-Sr$_2$TiO$_4$ were calculated to be 3.16, 3.33, 3.34, and 3.03 eV, respectively. Therefore, E-Sr$_2$TiO$_4$ has the narrowest band gap, making it most suitable as a photocatalyst.

Photocatalysts with narrower band gaps have advantages in terms of photosensitization. However, in order to exhibit good performance in the current system, the band gap of a photocatalyst should also include the CO$_2$/CH$_4$ and H$_2$/O$_2$ reduction potentials. Figure 8 shows the XPS valence band spectra of the catalysts. Based on the data obtained, the valance band value of the catalysts was confirmed, and the values for P-25, Sr$_2$TiO$_4$, H-Sr$_2$TiO$_4$, and E-Sr$_2$TiO$_4$ are 2.46, 2.34, 1.60, and 2.06 eV, respectively. When the vacuum level of 4.5 eV is corrected to 0 V for a standard hydrogen electrode (SHE) and the work function of the XPS instrument is taken as 4.62 eV, 

$$\alpha h\nu = A(h\nu - E_{bg})^{1/2}$$

1
the valance band maximum values for P-25, SrTiO₃, H-Sr₂TiO₄ and E-Sr₂TiO₄ are 2.58, 2.46, 1.72 and 2.18 eV (vs. SHE), respectively. According to these valance band and band gap values, the conduction band minimum values for P-25, Sr₂TiO₃, H-Sr₂TiO₄, and E-Sr₂TiO₄ are -0.58, 0.87, -1.61, and -0.84 eV (vs. SHE), respectively. Figure 9 shows the energy diagrams obtained for the catalysts using the valance and conduction band values and the band gap. All catalysts contain the CO₂/CH₄ and H₂O/O₂ reduction potential. Therefore, the synthesized catalysts are suitable for the photoreduction of CO₂ with H₂O to CH₄.

In order to understand the recombination of excited electrons and holes, PL analysis was conducted, and the results are shown in Fig. 10. The PL spectra of the catalysts show a strong emission signal at 468.1 nm. The PL intensity of Sr₂TiO₃ is smaller than that of P-25. This is due to a decrease in the number of excited electrons because of the wide band gap of Sr₂TiO₃. The intensity for H-Sr₂TiO₄ is lower than that of Sr₂TiO₃. This is because the oxidation state of the exposed Ti on the surface is reduced to (4-δ)+, which is not +4, and the reduced Ti
suppresses the recombination of electrons and holes by trapping the excited electrons in the conduction band. The E-Sr$_2$TiO$_4$ also exhibits a PL intensity lower than that of Sr$_2$TiO$_4$ and much lower than that of P-25. Generally, excited electrons and holes move from the bulk of a particle to its surface where they react with reactants. The recombination of excited electrons and holes takes place in the bulk or on the surface of a particle during transport. When the particles are exfoliated, the internal area of the particles decreases and the distance to the surface for the electrons and holes decreases. Therefore, recombination inside the particles is also reduced. This is the reason that E-Sr$_2$TiO$_4$ has a lower PL intensity than that of P-25. Thus, the above analysis indicates that H-Sr$_2$TiO$_4$ and E-Sr$_2$TiO$_4$ will be better photocatalysts than Sr$_2$TiO$_4$.

X-ray photoelectron spectroscopy (XPS) analysis. The XPS spectra of the photocatalysts were obtained to confirm the oxidation state of the elements according to their chemical bonding, and the results are shown in Fig. 11. For Sr$_2$TiO$_4$, the peaks located at 133.38 and 134.88 eV are assigned to Sr-3d$_{5/2}$ and Sr-3d$_{3/2}$ core levels respectively. In H-Sr$_2$TiO$_4$, the Sr 3d peaks are shifted toward a slightly lower binding energy. In E-Sr$_2$TiO$_4$, the intensity of the 3d peaks is greatly reduced. This is due to the removal of Sr ions from the interlayer spaces, as described above. The Ti 2p$_{3/2}$ and 2p$_{1/2}$ peaks of Sr$_2$TiO$_4$ are observed at 457.88 and 463.78 eV, respectively. The Ti 2p peaks for H-Sr$_2$TiO$_4$ are shifted to a lower binding energy, similarly to the Sr 3d peaks. This is because some of the Sr$^{2+}$ and Ti$^{4+}$ ions are reduced by hydrogen to Sr($^{2-\delta}$)$^{+}$ and Ti($^{4-\delta}$)$^{+}$, respectively. The Ti 2p peaks for E-Sr$_2$TiO$_4$ have significantly different peak intensities to Sr$_2$TiO$_4$ or H-Sr$_2$TiO$_4$, and its Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ peaks are observed at 458.18 and 464.08 eV, respectively. This binding energy is shifted slightly lower compared to that of P-25. Therefore, the Ti ions of E-Sr$_2$TiO$_4$ are slightly more reduced ions than in P-25. It is believed that this can induce vacancies in the crystal framework and facilitate the movement of electrons and holes, which can be advantageous for photocatalytic activity.

There are two O 1s peaks in Sr$_2$TiO$_4$ and H-Sr$_2$TiO$_4$. The peak at ~529 eV is from oxygen bound to Ti, and the peak at ~531 eV corresponds to oxygen bound to Sr. For E-Sr$_2$TiO$_4$, only the peak corresponding to oxygen bonded to Ti is observed (at 529.48 eV), because the Sr is removed by exfoliation.

Zeta potential analysis of photocatalysts. Since the catalytic reaction takes place in H$_2$O, it is important to study the dispersion of the catalyst particles in H$_2$O. The zeta potentials were measured after dispersing the catalysts in distilled water or in bubbling-CO$_2$ solution (i.e., the reaction conditions), and the results are shown in Table 2. Generally, a larger absolute value for the measured zeta potential means that the particles are well dispersed in a solution. The zeta potentials for Sr$_2$TiO$_4$, H-Sr$_2$TiO$_4$, E-Sr$_2$TiO$_4$, and P-25 are $-11.99$, $-11.15$, $-42.39$, and $-15.61$ mV, respectively. Therefore, the degree of colloidal dispersion in H$_2$O follows the order E-Sr$_2$TiO$_4$ > P-25 > Sr$_2$TiO$_4$ > H-Sr$_2$TiO$_4$. Thus, all catalysts can be adequately dispersed in H$_2$O. However, the zeta potential shows a different pattern after CO$_2$ bubbling: all the negative potential values are changed to positive values. The zeta potentials for Sr$_2$TiO$_4$, H-Sr$_2$TiO$_4$, E-Sr$_2$TiO$_4$, and P-25 are 1.16, 16.29, 26.22, and 22.00 mV, respectively.

Figure 11. XPS spectra of catalysts; (a) Sr 3d spectra, (b) Ti 2p spectra, and (c) O 1s spectra.
Therefore, the degree of colloidal dispersion in the solution after CO₂ bubbling follows the order E-Sr₂TiO₄ > P-25 > H-Sr₂TiO₄ > Sr₂TiO₄. Thus, E-Sr₂TiO₄, P-25, and H-Sr₂TiO₄ show good dispersion under the reaction conditions, which is considered advantageous for CO₂ photoreduction performance. However, in the case of Sr₂TiO₄, the zeta potential is low, so it is likely to exhibit poor catalytic performance owing to it being more agglomerated than the other catalysts.

**Photocatalytic reduction of CO₂ with H₂O, property after reaction, and mechanism.** The products obtained though CO₂ reduction using the catalysts synthesized in this study are CH₄, H₂, C₂H₆, C₂H₄, and CO. Figure 12 shows the accumulation of the products according to irradiation time. The main product is CH₄ and the product amounts follow the order CH₄ > C₂H₆ > H₂ > C₂H₄ > CO. Overall, the reactivity of the surface-treated H-Sr₂TiO₄ and E-Sr₂TiO₄ is better than that of Sr₂TiO₄. After 8 h reaction, the rates of CH₄ production over Sr₂TiO₄, H-Sr₂TiO₄, and E-Sr₂TiO₄ are 844.94, 1353.46, and 3431.77 μmol/gcat, respectively. In

|                  | P-25 | Sr₂TiO₄ | H-Sr₂TiO₄ | E-Sr₂TiO₄ |
|------------------|------|---------|-----------|-----------|
| Band gap (eV)    | 3.16 | 3.33    | 3.34      | 3.03      |
| SBET (m²/g)      | 43.65| 1.19    | 0.78      | 358.54    |
| Zeta potential (mV) Before-CO₂ | −15.61 | −11.99 | −11.15 | −42.39 |
|                  | After-CO₂ | 22.00 | 1.16 | 16.29 | 26.22 |

Table 2. Summary of physical and chemical properties of catalysts.

Figure 12. Photocatalytic CO₂ reduction with H₂O on catalysts. (a) yield of CH₄, (b) yield of H₂, (c) yield of C₂H₆, (d) yield of C₂H₄, and (e) yield of CO.
particular, E-Sr$_2$TiO$_4$ shows excellent reactivity and produces more CH$_4$ than P-25 catalyst, and. Figure 12b shows the amounts of H$_2$ produced. H$_2$ is a necessary substance for reducing CO$_2$. Therefore, the greater the amount of H$_2$ generated, the easier the CO$_2$ reduction. The amounts of H$_2$ generated over Sr$_2$TiO$_4$, H-Sr$_2$TiO$_4$, and E-Sr$_2$TiO$_4$ are 267.73, 373.65, and 640.71 $\mu$mol/g$_{cat}$, respectively. Therefore, the CO$_2$ reduction reaction is promoted over E-Sr$_2$TiO$_4$ is higher than the other catalysts. Furthermore, the C$_2$H$_6$ production over E-Sr$_2$TiO$_4$ is higher than that over the other catalysts. When E-Sr$_2$TiO$_4$ is used, the amount of C$_2$H$_6$ produced after 8 h is 150.8 $\mu$mol/g$_{cat}$. If the C$_2$H$_6$ reacts with H$_2$ on the catalysts surface it can be further converted to CH$_4$. The amounts of C$_2$H$_4$ and CO produced over the catalysts are similar. After 8 h, the production of C$_2$H$_4$ and CO is 457.63–573.33 and 69.35–81.30 $\mu$mol/g$_{cat}$, respectively. Figure 13 shows the product distribution on the catalysts. P-25 showed the highest CH$_4$ selectivity, which was 80 to 90%. Next, when E-Sr$_2$TiO$_4$ was used, the CH$_4$ selectivity was high and its value was about 70%. Table 3 shows the apparent quantum yield of catalysts.

![Product distribution on catalysts. (a) P-25, (b) Sr$_2$TiO$_4$, (c) H-Sr$_2$TiO$_4$ and (d) E-Sr$_2$TiO$_4$.](image)

| Catalysts     | Quantum yield (%) | CH$_4$ | H$_2$ | C$_2$H$_6$ | C$_2$H$_4$ | CO   | Total |
|---------------|-------------------|--------|-------|------------|------------|------|-------|
| P-25          | 2.693             | 0.120  | 0.000 | 0.000      | 0.016      | 2.829|
| Sr$_2$TiO$_4$  | 1.283             | 0.102  | 0.019 | 0.527      | 0.030      | 1.961|
| H-Sr$_2$TiO$_4$| 2.055             | 0.142  | 0.053 | 0.653      | 0.031      | 2.934|
| E-Sr$_2$TiO$_4$| 5.211             | 0.243  | 0.200 | 0.321      | 0.026      | 6.201|

Table 3. The apparent quantum yield of catalysts.

The XRD analysis of the catalysts after the reaction was carried out to confirm the structural stability and displayed in Fig. 14. From the XRD analysis results, it was observed that the catalysts structure was remained stable before and after the reaction. Therefore, the catalysts structure was stable during the reaction conditions. The photoreaction of E-Sr$_2$TiO$_4$ showing the best activity was repeated three times. The results for CH$_4$ production, the main product, are shown in Fig. 15. A slight amount of difference was observed in the results but
similar performance was maintained without deactivation in all three times. Therefore, it was confirmed that the E-Sr$_2$TiO$_4$ was excellent in not only structural stability but also reusability during the reaction.

Based on these results, a plausible reaction pathway over E-Sr$_2$TiO$_4$, which has the best performance is proposed in Fig. 16. The excited electrons on the exfoliated improved catalyst surface react with CO$_2$ to produce ∙CO$_2$ radicals, and the holes react with H$_2$O to produce OH$^-$ and H$^+$. Hydrogen radicals (∙H) are formed by the reaction of H$^+$ with excited electrons, and then CO is produced by the reaction of ∙H and ∙CO$_2$ radicals. CH$_4$, C$_2$H$_6$, and C$_2$H$_4$ are produced finally as the CO and ∙H radicals continuously react.

**Conclusion**

In this study, nanosized layered perovskite Sr$_2$TiO$_4$ photocatalyst was successfully synthesized using sol-gel technique with the assistance of citric acid. The surface of layered perovskite Sr$_2$TiO$_4$ photocatalyst was treated to improve the CO$_2$ photoreduction activity. The particles were treated with HNO$_3$ to remove the Sr ions present between the layers, and the layers were exfoliated by treatment with TPAOH. The catalyst, E-Sr$_2$TiO$_4$ showed the rutile TiO$_2$ structure after exfoliation because the Sr$_2$TiO$_4$ structure was collapsed. The shape of the exfoliated thin film was confirmed by TEM. In comparison to Sr$_2$TiO$_4$ and H-Sr$_2$TiO$_4$ photocatalysts, the exfoliated catalyst E-Sr$_2$TiO$_4$ showed an excellent performance in CO$_2$ photoreduction to CH$_4$, and after 8 h, 3431.77 $\mu$mol/g$_{cat}$ of CH$_4$ was generated. The reason for the excellent performance of E-Sr$_2$TiO$_4$ can be explained by the following factors.

First, it has a narrow band gap compared to the other two catalysts, and exhibits reduced electron-hole recombination. Therefore, a relatively larger number of electrons and holes transferred to CO$_2$ and H$_2$O. Next, a large amount of CO$_2$ and H$_2$O can interact with the active sites on the surface because it has a large surface area and is well dispersed in the solution. Based on the excellent physical and photochemical properties of the exfoliated layered perovskite catalyst, it may be employed for different photocatalytic applications as well as the CO$_2$ photoreduction reactions.
Methods

Synthesis of photocatalysts. The synthesis of layered perovskite Sr₂TiO₄ was performed as follows: Strontium nitrate (Sr(NO₃)₂, 97.0%, Junsei Chemical, Japan) and titanium isopropoxide (Ti(OCH(CH₃)₂)₄, TTIP, 98.0%, Junsei Chemical, Japan) were used as precursors. First, 0.1 mol of Sr(NO₃)₂ was dissolved in double distilled water (100 mL) with continuous stirring. Then, 10 mL of HNO₃ (60%, OCI company Ltd., Republic of Korea) was added with stirring to prevent hydrolysis. This solution was labeled A. In a separate vessel, 0.05 mol of TTIP was dissolved in EtOH (99.9%, OCI company Ltd., Republic of Korea), and then glacial acetic acid (CH₃COOH, 99.0%, Ducsan, Republic of Korea) was added with stirring to prevent hydrolysis. This solution was labeled as B. The solutions A and B were then mixed with stirring, and citric acid monohydrate (C₆H₈O₇·H₂O, 99.5%, Daejung Chemicals and Metals Co Ltd., Republic of Korea), which is a complexing agent for the gel, was added, and the mixture was stirred until it became homogeneous. Then, the solvent was removed without the temperature exceeding 323.15 K to obtain a sol gel, which was subsequently pretreated at 493.15 K. Finally, a white powder was obtained by thermal treatment at 1323.15 K for 6 h. In some cases, hydrogen treatment was then performed at 1123.15 K for 3 h in H₂ atmosphere. In other cases, exfoliation was achieved by a three-step process, as shown in Fig. 17. Ion exchange of Sr for H cations was carried out in 1 M HNO₃ for 5 days using ultrasonication. The powder obtained was treated in tetrapropylammonium hydroxide (TPAOH, 25.0%, in water, ACROS, Belgium) for 3 weeks using ultrasonication. The final white precipitate was washed several times with distilled water and ethanol and dried at 343 K for 24 h. The hydrogen-treated and exfoliated Sr₂TiO₄ samples were labeled H-Sr₂TiO₄ and E-Sr₂TiO₄, respectively.

Characterization of photocatalysts. The structures and crystallinities of the as-prepared Sr₂TiO₄, H-Sr₂TiO₄, and E-Sr₂TiO₄ samples were confirmed with XRD (model MPD from PANalytical) using nickel-filtered CuKα radiation (40.0 kV, 30.0 mA). The morphologies were investigated using HR-TEM (Tecnal G2 F20 S-TWIN, FEI, Netherlands) operated at 200 kV. The presence of different elements was confirmed using the elemental mapping and energy dispersive X-ray spectroscopy (EDS) attached to the TEM setup. The specific surface areas (SBET) were calculated according to the Brunauer-Emmett-Teller theory using a Belsorp II mini (BEL, Japan Inc.). The UV-Vis absorption spectra were obtained using a SCINCO Neosys-2000 spectrometer fitted with a reflectance sphere. PL profiles were obtained using a SCINCO FluoroMate FS-2 at room temperature using a He-Cd laser source at a wavelength of 325 nm. XPS measurements were performed on a K-alpha (Thermo Scientific, UK) using Al Kα X-rays as the excitation source. The zeta potential of the material was determined by electrophoretic mobility using an electrophoresis measurement apparatus (ELS 8000, Otsuka Electronics, Japan) with a plate sample cell. Electrophoretic light scattering (ELS) determination was performed in reference beam mode with a 670 nm laser light source at a modular frequency of 250 Hz and a scattering angle of 15°. The standard error of the zeta potential, converted from the experimentally determined electrophoretic mobility, was typically <1.5% with 5% error. To measure the zeta potentials, the samples were dispersed in deionized water or bubbling-CO₂ water at 0.1 wt%. The final zeta potentials were obtained by averaging 2 or 3 measurements.

Photocatalytic activity measurements. The photocatalytic tests for the reduction of CO₂ with H₂O were performed in a photoreactor comprising a quartz chamber with a total volume of 150.0 cm³ (Fig. 18). To photoreduce CO₂, 0.01 g of the catalyst was placed in the reactor chamber with 50 mL of double distilled water, and the reactor was closed. A UV lamp (6 W/cm², 20 cm length × 2.0 cm diameter, Shinan, Republic of Korea) emitting light at 365 nm was used to irradiate the reaction mixture. Supercritical-fluid-grade CO₂ with a certified maximum hydrocarbon content of <1 ppm was used as the reactant. Before the reaction was initiated by illumination, the reactor was purged with CO₂ gas for 5 min. The lamp was then switched on to start the experiment. The reaction temperature and pressure were maintained at 303 K and 1 atm, respectively. The gas products were
analyzed using a gas chromatograph (iGC7200, DS Science, Republic of Korea) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The product yield and quantum yield during reaction was calculated using following equation (2–3).

Figure 17. Preparation of Sr$_2$TiO$_4$, Exfoliation Sr$_2$TiO$_4$ and H-Sr$_2$TiO$_4$ catalysts.

Figure 18. The Schematic diagram of experimental set up of a circulated photo reactor for CO$_2$ reduction.
Product yield = Total of product (μmol)/Amount of photocatalyst used (g<sub>cat</sub>)

(2)

Quantum yield = Number of reacted electrons/Number of incident photons × 100%

(3)

References
1. Dewi, M.S., Hartono, D.M., Moersidik, S.S. & Kustawan, I. Green housing evaluation through carbon footprint dynamic model: questioned the urban policy sustainability. Procedia Soc. Behav. Sci. 227, 317–324 (2016).
2. Najaft-Marghamaleki, A., Barati-Harooni, A. & Mohammad, A. Impact of gas impurities on CO2 mole fraction: Application in carbon capture and storage (CCS) processes. Int. J. Greenhouse Gas Control, 57, 173–184 (2017).
3. Mechleri, E., Brown, S., Fennell, J.P. & Dowell, N.M. CO2 capture and storage (CCS) cost reduction viainfrastrutecture right-sizing. Chem. Eng. Res. Des. 119, 130–139 (2017).
4. Oh, S.T. & Martin, A. Thermodynamic efficiency of carbon capture and utilisation in anaerobic batch digestion process. J. CO2 Util. 16, 182–193 (2016).
5. Kang, D. et al. Carbon capture and utilization using industrial wastewater under ambient conditions. Chem. Eng. J. 308, 1073–1080 (2017).
6. Pan, S.-Y., LaFuente, A.M. & Chiang, P.-C. Engineering, environmental and economic evaluation of high-gravity carbon capture and utilization. Appl. Energy 170, 269–277 (2016).
7. Li, X. et al. Engineering heterogeneous semiconductors for solar water splitting. J. Mater. Chem. A 3, 2485–2534 (2015).
8. Enoue, T., Fujishima, A., Konishi, S. & Honda, K. Photocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. Nature 277, 637–638 (1979).
9. Chen, L. et al. Photoreduction of CO2 by TiO2 nanocomposites synthesized through reactive direct current magnetron sputter deposition. Thin Solid Films 517, 5641–5645 (2009).
10. Wang, P.-Q., Bai, Y., Luo, P.-Y. & Liu, J.-Y. Graphene–WO3 nanobelt composite: Elevated conduction band toward photocatalytic reduction of CO2 into hydrocarbon fuels. Catal. Commun. 38, 82–85 (2013).
11. Li, X. et al. Green synthesis and photo-catalytic performances for ZnO-reduced graphene oxide nanocomposites. J. Colloid Interface Sci. 411, 69–75 (2013).
12. Marci, G., Garcia-Lopez, E.I. & Palmisano, L. Photocatalytic CO2 reduction in gas-solid regime in the presence of H2O by using GaP/TiO2 composite as photocatalyst under simulated solar light. Catal. Commun. 53, 38–41 (2014).
13. Beigi, A.A., Fatemi, S. & Salehi, Z. Synthesis of nanocomposite CdS/TiO2 and investigation of its photocatalytic activity for CO2 reduction to CO and CH4 under visible light irradiation. J. CO2 Util. 7, 23–29 (2014).
14. Li, H. et al. Photocatalytic reduction of carbon dioxide to methanol by Cu2O/SC nanocrystallite under visible light irradiation. J. Nat. Gas Chem. 20, 145–150 (2011).
15. Zhao, C., Krall, A., Zhao, H., Zhang, Q. & Li, Y. Ultrasonic spray pyrolysis synthesis of Ag/TiO2 nanocomposite photocatalysts for simultaneous H2 production and CO2 reduction. Int. J. Hydrogen Energy 37, 9967–9976 (2012).
16. Wang, W.-N. et al. Size and Structure Matter: Enhanced CO2 Photoreduction Efficiency by Size-Resolved Ultrafine Pt Nanoparticles on TiO2 Single Crystals. J. Am. Chem. Soc. 134, 11276–11281 (2012).
17. Lee, C.-W. et al. Photocatalytic conversion of CO2 to hydrocarbons by light-harvesting complex assisted Rh-doped TiO2 photocatalyst. J. CO2 Util. 5, 33–40 (2014).
18. Zbudińiewski, K., Góralski, J. & Rynkowski, J. Studies on TiO2/SiO2 and Pt/TiO2/SiO2 Catalysts in Photoreduction of CO2 with H2O to Methanol. Russ. J. Phys. Chem. A 86, 2057–2062 (2012).
19. Kwak, B. S. et al. Methane formation from photoreduction of CO2 with water using TiO2 cladding Ni ingredient. Fuel 143, 570–576 (2015).
20. Tseng, I.-H., Wu, J. C. S. & Chou, H.-Y. Effects of sol–gel procedures on the photocatalysis of Cu/TiO2 in CO2 photoreduction. J. Catal. 221, 432–440 (2004).
21. Park, M., Kwak, B. S., Jo, S. W. & Kang, M. Effective CH3 production from CO2 photoreduction using TiO2-x mol% Cu-TiO2 double-layered films. Energy Convers. Manage. 103, 431–438 (2015).
22. Abdullah, H., Khan, M. R., Pudukudy, M., Yaakob, Z. & Ismail, N. A. CeO2-TiO2 as a visible light active catalyst for the photoreduction of CO2 to methanol. J. Rare Earths 33, 1155–1161 (2015).
23. Wang, F., Zhou, Y., Li, P., Kuai, L. & Zou, Z. Synthesis of bimicro/macromanor=microporous MgO-modified TiO2 for enhanced CO2 photoreduction into hydrocarbon fuels. Chin. J. Catal. 37, 863–868 (2016).
24. Tahir, M. & Amin, N. S. Performance analysis of nanostructured NiO–In2O3/TiO2 catalyst for CO2 photoreduction with H2 in a monolith photocreactor. Chem. Eng. J. 285, 635–649 (2015).
25. Lee, H. et al. Assembly of a check-patterned Cu2S–TiO2 film with an electron-rich rich film and its application for the photoreduction of carbon dioxide to methane. Appl. Surf. Sci. 393, 385–396 (2017).
26. Lee, J. H., Kim, S.-I., Park, S.-M. & Kang, M. A p-n heterojunction NiS-sensitized TiO2 photocatalyst system for efficient photoreduction of carbon dioxide to methane. Ceram. Int. 43, 1768–1774 (2017).
27. Tahir, M., Tahar, A., Amin, N. S. & Elias, H. Selective photocatalytic reduction of CO2 by H2O/H2 to CH4 and CH2OH over Cu-promoted In2O3/TiO2 nanocrystal catalyst. Appl. Surf. Sci. 389, 46–55 (2016).
28. Do, Y. J., Im, Y., Kwak, B. S., Kim, J.-Y. & Kang, M. Dramatic CO2 photoreduction with H2O vapors for CH4 production using the TiO2 (bottom)/Fe–TiO2 (top) double-layered films. Chem. Eng. J. 275, 288–297 (2015).
29. Mohamed, M., Chai, S.-P. & Mohamed, A. R. Modification of MWCNT@TiO2 core–shell nanocomposites with transition metal oxides for photoreduction of carbon dioxide into methane. Appl. Surf. Sci. 319, 37–43 (2014).
30. Zhou, M., Hou, Z. & Chen, X. The Effects of Hydrogenation on Graphitic C3N4 Nanosheets for Enhanced Photocatalytic Activity. Part. Part. Syst. Charact. 2017, 1700038–1700046 (2017).
31. Zeng, D. et al. Nb3P nanomaterials embedded into porous g-C3N4 nanosheets as a noble-metal-free hetero-structure photocatalyst for efficient H2 production under visible light. J. Mater. Chem. A, https://doi.org/10.1039/C7TA04816E (2017).
32. Chen, W. et al. Synergic enhancement of plasmonic hot-electron injection in Au cluster-nanoparticle/g-C3N4 for photocatalytic hydrogen evolution. J. Mater. Chem. A, https://doi.org/10.1039/C7TA03808A (2017).
33. Ong, W.-J., Putri, L.K., Tan, L.-I., Chai, S.-P. & Yong, S.-T. Heterostructured AgX/g-C3N4 (X = Cl and Br) nanocomposites via a sonication-assisted deposition-precipitation approach: Emerging role of halide ions in the synergistic photocatalytic reduction of carbon dioxide. Appl. Catal. B 180, 530–543 (2016).
34. Kuriki, R. et al. Robust Binding between Carbon Nitride Nanosheets and a binuclear Ruthenium (II) Complex Enabling Durable, Selective CO2 Reduction under Visible Light in Aqueous Solution. Angew. Chem. Int. Ed. 56, 4867–4871 (2017).
35. Kuriki, R. et al. Nature-Inspired, Highly Durable CO2 Reduction System Consisting of a Binuclear Ruthenium (II) Complex and an Organic Semiconductor Using Visible Light. J. Am. Chem. Soc. 138, 5159–5170 (2016).
36. Ong, W.-J. et al. Unraveling charge carrier dynamics in protonated g-C3N4 interfaced with carbon nano dots as co-catalysts toward enhanced photocatalytic CO2 reduction: A combined experimental and first-principles DFT study. Nano Res. 10, 1673–1676 (2017).
37. Ong, W.-J., Tan, L.-L., Ng, Y. H., Yong, S. T. & Chai, S.-P. Graphitic Carbon Nitride (g-C3N4)-Based Photocatalysts for Artificial Photosynthesis and Environmental Remediation: Are We a Step Closer To Achieving Sustainability? Chem. Rev. 116, 7159–7192 (2016).
38. Wang, S., Yao, W., Lin, J., Ding, Z. & Wang, X. Cobalt Imidazolate Metal-Organic Frameworks Photosplit CO2 under Mild Reaction Conditions. Angew. Chem. Int. Ed. 53, 1034–1038 (2014).
39. Wang, S. & Wang, X. Imidazolium Ionic Liquids. Imidazolylhendene Heterocyclic Carbenes, and Zeolitic Imidazolate Frameworks for CO2 Capture and Photochemical Reduction. Angew. Chem. Int. Ed. 55, 2308–2320 (2016).
40. Wang, S. & Wang, X. Multifunctional Metal-Organic Frameworks for Photocatalysis. Small 11, 3097–3112 (2015).
41. Wang, S. & Wang, X. Photocatalytic CO2 reduction by CdS promoted with a zeolitic imidazolate framework. Appl. Catal., B 162, 494–500 (2015).
42. Wu, G. et al. Hydrothermal synthesis and visible-light-driven photocatalytic degradation for tetracycline of Mn-doped SrTiO3 nanocubes. Appl. Surf. Sci. 333, 39–47 (2015).
43. Bui, D.-N., Mu, J., Wang, L., Kang, S.-Z. & Li, X. Preparation of Cu-loaded SrTiO3 nanoparticles and their photocatalytic activity for hydrogen evolution from methanol aqueous solution. Appl. Surf. Sci. 274, 328–333 (2013).
44. Ruzimuradov, O. et al. A facile preparation of dual-phase nitrogen-doped TiO2–SrTiO3 macroporous monolithic photocatalyst for organic dye photodegradation under visible light. J. Eur. Ceram. Soc. 35, 1815–1821 (2015).
45. Zhang, Z., Liu, G. & Mao, Y. Improved separation efficiency of photogenerated carriers for Fe2O3/SrTiO3 heterojunction Semiconductor. Int. J. Hydrogen Energy 38, 9349–9354 (2013).
46. Kang, H. W., Park, S. B., Kim, J. G. & Kim, I. T. Effects of F for enhancement of H2 evolution on visible-light-driven photocatalyst of SrTiO3/Cr/Ta/F prepared by spray pyrolysis. Int. J. Hydrogen Energy 39, 5537–5545 (2014).
47. Zhang, W., Du, L., Bi, F. & He, H. A novel SrTiO3/HZSM-5 photocatalyst prepared by sol–gel method. Mater. Lett. 157, 103–105 (2015).
48. Li, Y. et al. Sandwich SrTiO3/TiO2/H-Titane nanofiber composite photocatalysts for efficient photocatalytic hydrogen evolution. Appl. Surf. Sci. 315, 314–322 (2014).
49. Nishiro, R., Tanaka, S. & Kudo, A. Hydrothermal-synthesized SrTiO3 photocatalyst codoped with rhodium and antimony with visible-light response for sacrificial H2 and O2 evolution and application to overall water splitting. Appl. Catal. B 150–151, 187–196 (2014).
50. Shen, S., Jia, Y., Fan, F., Peng, Z. & Li, C. Time-resolved infrared spectroscopic investigation of roles of valence states of Cr in (La,Cr)-doped SrTiO3 photocatalysts. Chin. J. Catal. 34, 2036–2040 (2013).
51. Hirayama, I., Abe, R. & Kamiya, Y. Combinational effect of Pt/SrTiO3–Rh photocatalyst and SnPd/Al2O3 non-photocatalyst for photocatalytic reduction of nitrate to nitrogen in water under visible light irradiation. Appl. Catal. B 144, 721–729 (2014).
52. Zou, J.-P. et al. Preparation and photocatalytic activities of two new Zn-doped SrTiO3 and BaTiO3 photocatalysts for hydrogen production from water without photocatalysts loading. Int. J. Hydrogen Energy 37, 17068–17077 (2012).
53. Guo, J. et al. A new heterojunction Ag2PO4/Cr/SrTiO3 photocatalyst towards efficient elimination of gaseous organic pollutants under visible light irradiation. Appl. Catal. B 134–135, 286–292 (2013).
54. Kang, H. W., Lim, S. N., Song, D. & Park, S. B. Organic-inorganic composite of g-C3N4–SrTiO3:Rhz photocatalyst for improved H2 evolution under visible light Irradiation. Int. J. Hydrogen Energy 37, 11602–11610 (2012).
55. Kwak, B. S. & Kang, M. Photocatalytic reduction of CO with H2O using perovskite CaTiO3, Appl. Surf. Sci. 337, 138–144 (2015).
56. Do, J. Y., Im, Y., Kwak, B. S., Park, S. –M. & Kang, M. Preparation of basal fiber/perovskite PtBiO3 core–shell composites and their electrocatalytic production from CO2 photoreduction. Ceram. Int. 42, 5942–5951 (2016).
57. Sun, X. & Xu, X. Efficient photocatalytic hydrogen production over La/Rh co-doped Ruddlesden-Popper compound Sr2TiO4. Appl. Catal. B 210, 149–159 (2017).
58. Zak, A. K., Majid, W. H. A., Abrishami, M. E., Yousefi, R. & Parvizi, R. Synthesis, magnetic properties and X-ray analysis of Zn1-xMgxO nanoparticles (X = Mn, Ni, and Co) using Scherrer and size-strain plot methods. Solid State Sci. 14, 488–494 (2012).
59. Yu, Q. et al. Different toxicity of anatase and rutile TiO2 nanoparticles on macrophages: Involvement of difference in affinity to proteins and phospholipids. J. Hazard. Mater. 335, 125–134 (2017).
60. Khan, I., Ahmad, I., Amin, B., Murtaza, G. & Ali, Z. Bandgap engineering of Cd1-xSrxO. Chin. J. Catal. 22, 274–280 (2013).
61. Do, J. Y., Im, Y., Kwak, B. S., Park, S. –M. & Kang, M. Preparation of basal fiber/perovskite PtBiO3 core–shell composites and their electrocatalytic production from CO2 photoreduction. Ceram. Int. 42, 5942–5951 (2016).
62. Huang, Y. et al. Preparation of 2D hydroxyl-rich carbon nitride nanosheets for photocatalytic reduction of CO2. RSC Adv. 5, 33254–33261 (2015).
63. Park, H.-A., Choi, J. H., Choi, K. M., Lee, D. K. & Kang, J. K. Highly porous gallium oxide with a high CO2 affinity for the photocatalytic conversion of carbon dioxide into methane. J. Mater. Chem. 22, 5304–5307 (2012).

Acknowledgements
This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of the Science ICT & Future Planning (NRF-2015R1A1A3A04001268).

Author Contributions
B.S.K. and M.K. designed the study, performed experiments, analyzed data and wrote the manuscript. J.Y.D. carried out catalytic stability test, N.-K. Park performed XRD analysis of the catalyst after reaction. All authors discussed the results and reviewed the manuscript.

Additional Information
Competing Interests: The authors declare that they have no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s) 2017