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# Selective methane production from visible-light-driven photocatalytic carbon dioxide reduction using the surface plasmon resonance effect of superfine silver nanoparticles anchored on lithium titanium dioxide nanocubes ($Ag@Li_xTiO_2$)

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ABSTRACT

This study focused on the results of applying the strong surface plasmon resonance (SPR) effect of silver (Ag) particles anchored on cubic phase $Li_xTiO_2$ to the carbon dioxide ($CO_2$) photoreduction reaction. The study demonstrated the importance of three aspects: First, the cubic $TiO_2$, which activated the [101] facet, was successfully produced. Secondly, $Li^+$ ions were introduced as Frenkel defects in some lattices to create oxygen defects. These vacancies increased the adsorption of carbon dioxide and sped up the rate-determining step in the $CO_2$ reduction reaction. In other words, they induced the easy conversion of $CO_2$ to CO, which is the first reduction product. Finally, the loading of Ag nanoparticles onto the $Li_xTiO_2$ cubic surface the improved photocatalytic activity through SPR effects, and in particular led to selective conversion of $CO_2$ to methane ($CH_4$). Quantitatively, the yield of $CH_4$ from $CO_2$ using the $Ag@Li_{0.075}TiO_2$ particles was 49 μmol/g after 10 h of reaction, which was 8.2 and 1.5 times higher than that of cubic $TiO_2$ (6 μmol/g) and $Li_{0.075}TiO_2$ (33 μmol/g) under UV-light. Additionally, its activity did not decrease under visible lights of 420 and 620 nm with the similar $CH_4$ yields of 42 and 34 μmol/g after 10 h, respectively. In particular, the production ratio of $CH_4$ and CO using cubic $TiO_2$ and $Li_xTiO_2$ were about 1:1, with no selectivity for either product. However, after metallic Ag nanoparticles were loaded, the product selectivity shifted towards $CH_4$, and the product ratio of $CH_4$ to CO was about 3:1. Furthermore, the $Ag@Li_{0.075}TiO_2$ particles exhibited a strong SPR effect (in particular, direct electron transfer), which contributed to maintaining the charge separation and the lifetime of the catalyst over a long period. Catalytic deactivation was not observed during five cycles of recycling tests.

## 1. Introduction

Even ten years ago, carbon dioxide was regarded as the culprit of global warming, and a great deal of money is spent worldwide on carbon capture and storage (CCS) technology to reduce or eliminate $CO_2$. In recent years, however, most countries have begun to utilize carbon dioxide as a carbon energy source, and have focused on the use of carbon capture and utility (CCU) as the main method of $CO_2$ reduction. One attractive CCU technology is biomimetic artificial photosynthesis, which uses a photocatalyst and sunlight to decompose carbon dioxide and water to produce hydrocarbons, which could replace existing fossil fuels [1]. However, great barriers remain to be overcome in the commercialization of this technology, namely, the efficiency and lifetime of the photocatalyst. In general, a photocatalyst should have both a semiconductor band structure for absorbing light and converting it into energy, and a catalytic surface for inducing a chemical reaction. The photocatalyst absorbs photons from sunlight, which excites the electrons of the valence band to the conduction band, thereby forming electron-hole pairs. In the valence band, oxygen is produced, and in the conduction band, hydrogen is produced. This hydrogen serves to reduce the carbon dioxide. For artificial photosynthesis, the minimum energy required for water decomposition is 1.23 eV (although practically,

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1.8 eV or more is required), and thus the size of the band gap is very important. Furthermore, there must be a redox potential between the valence band and the conduction band of the band-gap that corresponds to the hydrogen and oxygen evolution reaction [2]. When all these conditions are satisfied, the photocatalyst can be used for artificial photosynthesis. $TiO_2$, $Fe_2O_3$, $BiVO_4$, ZnO, and $WO_3$ are typical photocatalysts that meet these conditions [3–7]. $TiO_2$ is chemically stable and is the only commercially available catalyst for artificial photosynthesis, and is also used in sterilization, air purification, water treatment, and organic matter decomposition applications. However, in many studies, inefficient light absorption, rapid recombination of the charges generated by light, and the possibility of a reverse reaction have been reported, due to its wide band gap (2.8 to 3.2 eV). Therefore, catalysts such as $BiVO_4$, $WO_3$, and $Fe_2O_3$ have been attracting attention as chemically stable materials with smaller band-gaps of 2.2 to 2.6 eV. However, with the exception of $TiO_2$, no material with a lifetime of more than 10,000 h, which is required for commercialization, have been identified.

Recently, $TiO_2$-related research has focused on adjusting the band gap or improving the adsorption of reactants by controlling the morphology or defects in crystals [8,9]. For example, one method involves making a non-uniform junction on the surface by adjusting the crystal planes. In the case of anatase $TiO_2$, the order of the surface energies of the low index facets is [101] < [010] < [001], which results in different catalytic activities for the facets. Researchers have reported that the photochemical carbon dioxide reductive activity increased on a 2D-$TiO_2$ nanosheet whose exposed facets were almost exclusively of the [101] type [10]. In particular, Li et al. reported [11] that loading Ag onto brookite $TiO_2$ quasi-nanocubes with exposed [210] and [001] facets increased the activity and selectivity of the photoreduction of $CO_2$ to $CO/CH_4$. They concluded that when the Ag-loading level is $\leq 0.5\%$, the small Ag nanoparticles are mainly dispersed on the [210] facets of the brookite nanocubes, resulting in an enhancement in the selectivity of CO generation; while > 0.5% Ag-loading could lead to the formation of Ag nanoparticles aggregated on the [210] facets with some Ag nanoparticles dispersed on the [001] facets, causing greater selectivity for $CH_4$ generation. Another strategy is to create defect sites on the $TiO_2$ surface or to create a surface state that enhances the adhesion of $CO_2$ to the surface to promote the reduction reaction. Typically, hydrogen plasma treatment is used to create oxygen vacancies [12], or to treat surfaces with non-noble metals, inorganic bases, or organic amines [13–15]. In recent years, the use of surface plasmon resonance (SPR) has been popular for improving the efficiency and lifetime of artificial photosynthetic catalysts. Plasmons are similar particles that vibrate in metal. They are attracting attention as a light absorption phenomenon in the visible region of metal particles or metamaterials, and they form a strong local electric field [16]. Plasmons have been studied in various fields such as optical waveguides, sensors, and light emitting devices, because they allow particles to collect light with a wavelength larger than the particle size. In particular, the use of plasmons is attracting attention due to the improved light absorptivity and photocurrent generation that can be achieved using this photoelectric phenomenon [17]. Recently, studies have been reported in which the efficiency of artificial photosynthesis was increased using the quantum phenomenon caused by SPR, which occurs when metal is exposed to light, allowing photocatalysts that are not normally sensitive to visible light to operate in visible light [18]. When SPR occurs, two important properties arise: the phenomenon of light trapping on the metal surface, and the phenomenon of excited electrons moving into the photocatalyst, resulting in large photocurrents. Initially, the enhancement of photocurrent by the SPR effect was reported mainly due to the light trapping effect of Au [19], Ag [20], and Cu [21] nanoparticles. Recently, however, SPR effects have also been reported in various metals and metal/metal oxide mixtures such as Al [22], Fe [23], Co [24], $Ag/Ag_2O$ [25], and $Cu/Cu_2O$ [26]. In particular, reports of the SPR of silver loaded $TiO_2$ ($Ag/TiO_2$) catalysts have been increasing rapidly, and these catalysts have shown fairly good visible light activity in water splitting and organic decomposition [27,28]. However, the published reports did not completely reveal the evidence for SPR. In particular, an in-depth study of the effect of SPR on the photocatalytic reduction of $CO_2$ is needed, as well as further investigation of the improvement in product selectivity, which one of the most important aspects of this catalytic reaction. Additionally, an in-depth investigation into the correlation between SPR and charge separation is required.

Thus, in this study, we tried to improve the $CO_2$ photoreduction performance using all three of the methods described above: in order to activate the [101] facet having the smallest surface activation energy, tetra ethyl ammonium hydroxide was added as a capping agent to obtain nanocube-shaped $TiO_2$. In order to simultaneously introduce oxygen defects into the $TiO_2$ lattice (so-called Frenkel defects), x moles of the organic base $Li_2O$ were incorporated into the $TiO_2$ crystal structure to form anatase $Li_xTiO_2$ cubes. The addition of Li anions creates oxygen anion defect sites in the lattice, which can increase $CO_2$ gas adsorption. In addition, we tried to induce the SPR effect by loading 1.0 wt.% of Ag nanoparticles onto $Li_xTiO_2$, expecting an improvement of the photocatalytic efficiency by the optical trap effect. In particular, we hoped to induce the selective production of $CH_4$ by enhancing the hydrogen production capability of Ag ions that was reported in a previous study [29]. Four types of cubic $Li_xTiO_2$ were synthesized in this study using a hydrothermal method by the addition of 2.5, 5.0, 7.5, and 10.0 mol.% of Li. The synthesis of $Ag@Li_xTiO_2$ with an Ag loading of 1.0 wt.% Ag using the most optimal $Li_xTiO_2$ particle was then carried out. The surface properties of the synthesized particles were characterized using various analytical techniques, and the particles were applied in the photoreduction of $CO_2$. Furthermore, the expected mechanisms for $CO_2$ photoreduction by the SPR effect over the $Ag@Li_xTiO_2$ particles under UV and visible radiation were described.

## 2. Experimental

### 2.1. Synthesis of anatase structured $TiO_2$, $Li_xTiO_2$, and $Ag@Li_xTiO_2$ cubic particles

The $TiO_2$, $Li_xTiO_2$, and $Ag@Li_xTiO_2$ particles were prepared by a typical hydrothermal method. To prepare the sol-mixtures, titanium tetraisopropoxide (TTIP, 99.99%, Junsei Chemical, Japan), lithium hydroxide (LiOH, 99.99%, Junsei Chemical, Japan), and silver nitrate ($AgNO_3$, 99.99%, Junsei Chemical, Japan) were used as the Ti, Li, and Ag precursors, respectively. In the first step of the $TiO_2$ synthesis, 1.0 mol of TTIP was dissolved in distilled water, and 2.0 mol of the capping agent tetra ethyl ammonium hydroxide were added slowly to the solution, and then stirred to homogeneity for 2 h. The final solution was transferred to an autoclave for thermal treatment at 200 °C at 10 atm for 1 h in a nitrogen environment. After thermal treatment, the resulting precipitate was collected, washed with acetic acid, and then dried at 80 °C for 24 h. In the second step, the synthesis of $Li_xTiO_2$ particles was carried out similarly to the synthesis of $TiO_2$, but the molar percentage of Li ions in the starting materials was adjusted to 2.5, 5.0, 7.5, and 10.0 mol.%, corresponding to 1.0 mol of Ti ions. Consequently, four kinds of particles, which were named $Li_{0.025}TiO_2$, $Li_{0.05}TiO_2$, $Li_{0.075}TiO_2$, and $Li_{0.1}TiO_2$, were synthesized in this study. In final step, an amount of $AgNO_3$ corresponding to 1.0 wt.% of the amount of $Li_xTiO_2$ was dissolved in a beaker containing an ethanol solution in which the $Li_xTiO_2$ catalyst was dispersed. After being dispersed well by stirring, a $NaBH_4$ solution was slowly added over 2 h to reduce the Ag ions. The product was dried at 80 °C for 3 h and then further dried in a dry oven at 70 °C for 24 h. The obtained sample was named $Ag@Li_xTiO_2$.

### 2.2. Characterization of the $TiO_2$, $Li_xTiO_2$, and $Ag@Li_xTiO_2$ cubic particles

The XRD diffraction patterns of the synthesized $TiO_2$, $Li_xTiO_2$, and