Synergistic Effects of Co-Doping on Photocatalytic Activity of Titanium Dioxide on Glucose Conversion to Value-Added Chemicals

Nopparat Suriyachai, Surawut Chuangchote,* Navadol Laosiripojana, Verawat Champreda, and Takashi Sagawa

ABSTRACT: Development of conversion of biomass derivatives in combination with utilization of solar energy by photocatalysts is a promising alternative strategy for biorefineries. The photocatalytic reaction could convert glucose to a mixture of value-added chemicals under UV irradiation. Modifications of titanium dioxide (TiO₂) nanoparticles by metal or metalloid (i.e., B and Ag) and nonmetal (i.e., N) dopants were carried out. The effects of co-doping (i.e., B/N and Ag/N) on physicochemical characteristics of the modified photocatalysts, photocatalytic glucose conversion, and the yields of the target chemical products (i.e., gluconic acid, xylitol, arabinose, and formic acid) were studied. The doping of the photocatalysts by different single dopants could improve the performance in terms of productivity and was further enhanced by the synergism from co-doping. The improvement in catalytic performances of the photocatalysts corresponded with the alterations in physicochemical characteristics of the catalysts resulting from the dopants.

INTRODUCTION

Photocatalysis is a clean, effective, and low-cost strategy for catalyzing chemical reactions under mild operational conditions. Photocatalytic processes can be applied for various chemical reactions, including oxidations and oxidative cleavages, reductions, isomerizations, substitutions, and condensations. It has been utilized in various applications, for example, wastewater or air treatment, pollutant degradation, and hydrogen production by water splitting. Research studies on designing new photocatalysts for extended applications have attracted increasing research interest as promising alternatives for waste treatment and chemical industry with advantages on energy saving compared with the conventional catalytic processes.

Conversion of sugars derived from renewable agricultural products and lignocellulosic wastes to biofuels and a range of commodity and value-added chemicals is a basis of the modern biorefinery industry, which can be performed by multi-disciplinary approaches using chemo-catalysis, thermo-catalysis, bio-catalysis, or fermentation routes. Implementation of these processes are, however, limited by their drawbacks such as intensive energy requirement of the chemical processes and cost of enzymes for bio-based conversion. Application of the photocatalytic reaction on conversion of sugars to value-added biochemicals is considered as an environmentally friendly alternative technology. A number of studies have been reported for conversion of sugars to several chemicals, for example, gluconic acid, formic acid, arabinose, and arabitol. In addition, xylitol was also found from photocatalytic glucose conversion.

Different heterogeneous photocatalysts are employed to catalyze the photocatalytic reactions with varying efficiencies and selectivities. Among them, titanium dioxide (TiO₂) is a most widely used material because of its chemical stability and nontoxic nature with high photocatalytic activity. As commonly known, a main drawback of TiO₂ is the need to perform the reactions under UV light irradiation (λ < 380 nm) because of its large energy band gap. The other featured property is the fast recombination of electron (e⁻) and hole (h⁺) on the active sites. To solve the problems, modification of TiO₂ with the addition of dopants has been investigated for improving their properties, aiming mainly on narrowing band gap, reducing recombination of electron and hole, and increasing highly active surface area, which resulted in enhancing performances of photocatalytic reactions. Effects of different dopants, including metals, metalloids, and nonmetals, have been widely studied on TiO₂. The presence of nonmetal dopant demonstrates advantages of improving the red shift of absorption edge and promoting more availability of active sites. Nitrogen doping...
has been studied because nitrogen could be substituted for oxygen in the p state to introduce band gap narrowing with a good performance on photocatalytic conversion. Also, the presence of nitrogen dopant provides the N surface state which enhances the photocatalytic activity. On the other hand, the metal or metalloid dopant has been effective on a smaller scale to become a center of charge recombination which resulted in enhancement of the photocatalytic activity of photocatalysts. Combination of nitrogen with other dopants was studied to modify photocatalysts for enhancement of visible light absorption and reduction of charge recombination and utilized in different applications such as antibacterial activity, dye degradation, gaseous adsorption, hydrogen production, dye-sensitized solar cells, and photoelectrochemistry. Increased performance of the co-doped photocatalysts is proposed to be due to the synergistic effects of the combined co-dopants on physicochemical properties of the photocatalysts.

So far, applications of TiO₂ on photocatalytic conversion of sugars have been reported in few works using commercial TiO₂ photocatalysts, with surfactant modification, with structure modification, and with different metal dopants (e.g., tungsten, chromium, and silver). However, no previous work has reported the use of co-doping on photocatalysts for sugar conversion to value-added chemicals. In this study, the modifications of TiO₂ nanoparticles by metal (or metalloid)/nonmetal dopants are reported. The effects of synthesis conditions, particularly, on the synergism of co-doing on physicochemical characteristics of the modified photocatalysts, photocatalytic glucose conversion, and the yields of the target biochemical products were studied.

## RESULTS AND DISCUSSION

Characterizations of Bare-TiO₂ and Doped TiO₂. The effects of doping on physicochemical properties and photocatalytic glucose conversion efficiency of the modified TiO₂ photocatalysts were studied. Scanning electron microscopy (SEM) images of the obtained photocatalysts in the presence of various dopants are illustrated in Figure 1. The morphological appearance of bare TiO₂, single-doped TiO₂ (B, Ag, and N), and co-doped TiO₂ (B/N and Ag/N) nanoparticles were compared. Nonospherical shapes of the agglomerated particles of bare and doped photocatalysts were observed. Self-agglomeration of the nanocrystalline particles during the hydrothermal step caused the heterogeneity of the sizes. The sizes of agglomerations were approximately in the size range of 10−30 μm with no substantial difference in the size among the bare and doped photocatalysts. However, no significant effect of agglomeration could be ascribed to the performance of photocatalytic activity. In addition, EDX spectrum clearly shows the presence of Ag/N dopants on the modified photocatalysts (Figure S1 and Table S1). It was found that the co-doping of Ag/N-doped TiO₂ demonstrates the intensity peaks of Ag and N with 2.44 and 2.13 wt %, respectively. For the B/N dopant, only N dopant was detected with an EDX intensity peak of 2.56 wt % (Figure S2 and Table S2). A low amount of dopant (2%) on the photocatalyst together with small atomic mass of B caused no detection of the dopant element. To prove the appearance of the B/N dopant in TiO₂, the catalyst was analyzed by X-ray photoelectron spectroscopy (XPS, Shimadzu, KRATOS/AXIS SUPRA). The appearances of B and N can be observed from the assigned peak energies in B 1s and N 1s regions, respectively (Figure S3).

The morphology of the photocatalysts was further determined by transmission electron microscopy (TEM) (Figure 2). According to the results, the dopant was shown to have effects on the grain boundary of the photocatalysts. ImageJ (Fiji software) program was used as a tool to measure grain and crystallite sizes from the TEM images. The TEM image of bare TiO₂ demonstrated the grain size about 9.6 nm with the crystal spacing of 0.351 nm. The presence of single doping led to a slight decrease in the crystallite size comparing with bare TiO₂, which revealed the grain size of B, Ag, and N-doped TiO₂ to approximately 8.4, 9.0, and 7.9 nm, respectively. However, no significant change in the lattice fringe of single doping was observed. In contrast, the expansion of crystallite size of co-dopants was found. Particularly, co-doping of Ag/N-doped TiO₂ revealed that the grain size was around 11.8 nm, with the crystal spacing of 0.350 nm. This could be ascribed to the fact that the substitution of co-dopants on photocatalysts led to the strain of crystallite structures.

Pore sizes, pore volume, and surface areas of TiO₂ modified with different dopants are shown in Table 1. The surface area is one of the main criteria which led to the improved activity of the photocatalytic conversion. It can be observed that the surface area of synthesized bare TiO₂ was 77.92 m²/g. The surface area was remarkably increased in the presence of all dopants. For single dopants, the presence of N-doped TiO₂ showed the most influence in the increasing of the surface area.
The specific pore volume of the single-doped TiO$_2$ was higher compared to that of the bare TiO$_2$ while pore size was found in the same range. Among the synthesized catalysts, the co-doping of B/N showed the obviously increased surface area of 227.69 m$^2$/g. The significant increase of the surface area of co-doping could be ascribed to the synergistic effect of the co-dopant on substitution in crystallite structures of photocatalysts when compared with the result of its single doping. According to a previous report,$^{29}$ the dopants (B and N) could substitute oxygen in the structure of TiO$_2$, resulting in expanding of the surface area. This corresponds with the TEM images (see Figure 2e). The notable increase in the pore size and pore volume of the co-doped sample was also observed. However, Ag/N doping only slightly changed the surface area compared with the result of its single doping. The atomic radius of Ag was not suitable for substitution in the TiO$_2$ lattice and could be the reason of this result. This is in line with the TEM result (see Figure 2f1), where the self-agglomeration of Ag particle on the surface of TiO$_2$ could be observed.

The photoluminescence (PL) technique was used to analyze all photocatalysts with the excitation wavelength of 270 nm (Figure 3). PL spectra of the synthesized photocatalysts show similar profiles. The decrease in intensity of all doped photocatalysts was observed. The change of PL intensity in the presence of single dopants is in the order of B, N, and Ag, respectively. The synergistic effect (i.e., the working together of two things to produce an effect greater than the sum of their individual effects) of co-doping (Ag/N and B/N) showed remarkably low PL intensity compared with the bare and single-doped TiO$_2$ and the sum of their single dopants. This indicated the quenching corresponding to the change in the surface state and the efficient charge trapping, immigration, and transfer in doped semiconductor nanoparticles.$^{47}$ The decreased PL intensity of the doped TiO$_2$ could be due to the inhibition of the recombination of electron and hole. This led to an enhanced generation of the oxidized and/or reduced radical, resulting in an improved photocatalytic performance of the process.$^1$

![Figure 3. PL spectra of bare TiO$_2$ and doped TiO$_2$ with various dopants.](image-url)

(153.04 m$^2$/g). The specific pore volume of the single-doped TiO$_2$ was higher compared with that of the bare TiO$_2$ while pore size was found in the same range. Among the synthesized catalysts, the co-doping of B/N showed the obviously increased surface area of 227.69 m$^2$/g. The significant increase of the surface area of co-doping could be ascribed to the synergistic effect of the co-dopant on substitution in crystallite structures of photocatalysts when compared with the result of its single doping. According to a previous report,$^{29}$ the dopants (B and N) could substitute oxygen in the structure of TiO$_2$, resulting in expanding of the surface area. This corresponds with the TEM images (see Figure 2e). The notable increase in the pore size and pore volume of the co-doped sample was also observed. However, Ag/N doping only slightly changed the surface area compared with the result of its single doping. The atomic radius of Ag was not suitable for substitution in the TiO$_2$ lattice and could be the reason of this result. This is in line with the TEM result (see Figure 2f1), where the self-agglomeration of Ag particle on the surface of TiO$_2$ could be observed.

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UV–vis diffuse absorbance was studied to demonstrate the optical properties of the synthesized photocatalysts (Figure 4). It was found that the bare-TiO$_2$ showed the lowest light absorption in the visible region (400–700 nm). The presence of single dopants on TiO$_2$ led to a slight shift on light absorption in the visible region. The significant increase in absorbance of the single doping was found on Ag-doped TiO$_2$. It could be observed that the remarkable increase in absorbance reflected the synergism for the co-doped B/N on property of light absorption characteristics of TiO$_2$. This could be ascribed to the formation of dopants as the trapping state in the band gap.$^{19}$ Based on Tauc plots (Figure 5), the calculated

![Figure 2. TEM images of photocatalysts: (a) bare TiO$_2$, (b) B–TiO$_2$, (c) Ag–TiO$_2$, (d) N–TiO$_2$, (e) B/N–TiO$_2$, and (f) Ag/N–TiO$_2$. Number 1 and 2 refer to magnification of 400k and 800k, respectively.](image-url)

| samples          | pore size (nm) | pore volume (cm$^3$/g) | surface area (m$^2$/g) |
|------------------|----------------|------------------------|-------------------------|
| bare TiO$_2$     | 5.55           | 0.11                   | 77.92                   |
| B-doped TiO$_2$ | 3.99           | 0.15                   | 147.37                  |
| Ag-doped TiO$_2$| 3.76           | 0.11                   | 114.95                  |
| N-doped TiO$_2$ | 5.47           | 0.21                   | 153.04                  |
| B/N-doped TiO$_2$| 5.56           | 0.32                   | 227.69                  |
| Ag/N-doped TiO$_2$| 6.73           | 0.26                   | 152.42                  |
band gap energy of bare TiO$_2$ was $\sim 3.18$ eV which corresponded to the typical band gap of anatase TiO$_2$. Narrower band gap energies of B-, N-, Ag-, Ag/N-, and B/N-doped TiO$_2$ were approximately 3.18, 3.16, 3.09, 3.08, and 3.04, respectively. A wide absorption region led to the increase in the excited electron under light irradiation, resulting in improved performance of the photocatalysts.

Typically, the different crystal phases affect the photocatalytic activity of the catalysts. Among them, anatase TiO$_2$ has been reported for the high performance of photocatalysts. The phase characteristics of the photocatalysts were studied by X-ray diffraction (XRD), and the patterns are shown in Figure 6. It was found that all samples consisted of anatase as a unique phase. The strong peak at 2$\theta$ of 25.4° was observed with the (1 0 1) plane as anatase phase reflection. No change in the (1 0 1) plane was observed between the bare and doped TiO$_2$. The average crystalline sizes of all samples were calculated by the Scherrer formula, as shown in Table 2. The crystalline size of the single-doped TiO$_2$ was smaller compared with the bare TiO$_2$. On the other hand, co-doping showed a significant effect on the increasing crystallite size, which is in well agreement with the TEM results discussed above. This could be due to the substitution of the dopants, resulting in slight distortion in the crystalline structure.

Performances of Doped TiO$_2$ on Glucose Conversion. The glucose conversion efficiency of the synthesized photocatalysts is shown in Figure 7. According to the results, bare TiO$_2$ showed the glucose conversion of 24.9% under UV irradiation. The presence of a single dopant (B, Ag, or N) enhanced glucose conversion compared with the nondoped control. The highest glucose conversion with the single-doped samples was measured in the presence of Ag-doped TiO$_2$, which improved the conversion to 63.5%. Interestingly, the modified TiO$_2$ with co-doping of B/N and Ag/N showed remarkable increase in glucose conversion up to 93.1 and 97.7%, respectively. Synergistic effect of co-doping on TiO$_2$ led to alteration of the photocatalytic mechanism because of modification of the photocatalyst properties. In this study, the glucose conversion yield obtained using the co-doped photocatalyst was comparable with that reported in previous works that modified TiO$_2$ by surfactant-assisted technique or changed the photocatalyst form to nanofibers.

Table 2. Crystalline Size of Bare TiO$_2$ and Doped TiO$_2$

| photocatalyst | crystal phase (%) | anatase | rutile | degree | fwhm | crystallite size (nm) |
|---------------|-------------------|---------|--------|--------|------|----------------------|
| bare TiO$_2$  | 100               | 25.32   | 1.04   | 9.05   |
| B-doped TiO$_2$ | 100             | 25.33   | 1.18   | 7.68   |
| Ag-doped TiO$_2$ | 100             | 25.35   | 1.13   | 7.99   |
| N-doped TiO$_2$ | 100             | 25.32   | 1.03   | 8.76   |
| B/N-doped TiO$_2$ | 100             | 25.33   | 0.99   | 9.11   |
| Ag/N-doped TiO$_2$ | 100             | 25.33   | 0.78   | 11.6   |

Figure 7. Photocatalytic conversion of glucose under UV irradiation for 180 min in the presence of bare TiO$_2$ and doped TiO$_2$ with various dopants.
conversion yield obtained was higher than that in a previous report using rutile TiO$_2$-based photocatalysts with different selectivity of the derived products in the solvent systems.

In addition, the glucose conversion with a short reaction time in this study was relatively high compared with the previous work using heteropolyacid-TiO$_2$ composites. This suggested that the synergistic effect of the co-dopants on the photocatalysts has a significance. Time-course profiles of the products from the photocatalytic reactions are shown in Figure 8. No change in product distribution was observed for the bare and doped photocatalysts. The product yield of all modified photocatalysts was in line based on the order of glucose conversion. Formic acid and arabinose were presented as the major products from glucose conversion. High yields of xylitol and gluconic acid were obtained at the beginning and then slightly decreased afterward. The trend of xylitol and gluconic yield was in good agreement with the oxidation-reduction pathway of photocatalytic glucose conversion because both products were revealed as intermediates in the photoreaction. The use of synergistic Ag/N-doped TiO$_2$ led to the highest yield of gluconic acid (12.3%) at 60 min of irradiation time, while the yield of xylitol (10.8%) was obtained at 90 min, which were higher than those obtained using the single-doped and bare TiO$_2$. The highest yields of formic acid and arabinose could be observed with longer irradiation times. In comparison, the product distribution was similar to the previous reports based on the oxidation pathway. However, the difference on selectivity of the derived products was observed in the presence of the Cr–TiO$_2$-supported photocatalyst. In addition, the use of rutile TiO$_2$-based photocatalysts also resulted in different selective oxidation patterns.

**Rates of Reactions on Photocatalytic Glucose Conversion.** Figure 9 shows the reaction rate of photocatalytic glucose conversion. It could be seen that the reaction using bare TiO$_2$ showed a slight increase in the glucose consumable rate until a retention time of 90 min which gave the highest rate of 0.9 mmol L$^{-1}$ h$^{-1}$. Particularly, the doped photocatalyst could enhance the performance of glucose conversion at the beginning of the reaction time. It was observed that the product rates depended on the rate of glucose consumed. The rapid reaction of all doped photocatalysts occurred within 30 min and then slightly decreased until the end of the reaction. Among the synthesized catalysts, co-doping demonstrated the synergistic effect to improve photocatalytic performance, including glucose consumption and product generation rates. Obviously, Ag/N-doped TiO$_2$ led to the highest glucose consumption rate with 4.6 mmol L$^{-1}$ h$^{-1}$ within 30 min of the irradiation time. This result corresponded to the highest rate of all products generated which were formic acid (7.31 mmol L$^{-1}$ h$^{-1}$), arabinose (3.11 mmol L$^{-1}$ h$^{-1}$), gluconic acid (1.11 mmol L$^{-1}$ h$^{-1}$), and xylitol (0.93 mmol L$^{-1}$ h$^{-1}$). It could suggest that the co-doping could improve the yield of xylitol and gluconic acid with shorter irradiation time. This indicates the benefit in terms of processing design for further economic feasibility. In terms of selectivity, the photocatalytic reaction in batch processing showed the same product selectivity for all photocatalysts according to the reaction pathway of glucose conversion as previously proposed.

**Proposed Photocatalytic Activity of the Synergized Co-Doped Photocatalyst.** Typically, the photocatalytic process is activated by light energy in an appropriate wavelength corresponding to the band gap of each material. This induces the moving of electron from the valence band into the conduction band. Generally, the leaving holes then react with water molecules to generate hydroxyl radicals (*OH), while electrons react with oxygen species to produce superoxide ions (O$_2^−$). Accordingly, we propose the different mechanisms for the two co-doped photocatalysts (B/N-doped TiO$_2$ and Ag/N-doped TiO$_2$), as shown in Scheme 1. For B/N-doped TiO$_2$ photocatalyst, the B and N dopants are introduced in the band gap of the modified TiO$_2$ photocatalyst, which are located as the defect state. B is assigned as a p-type doping, while N is presented as an n-type doping. The dopants would act as shallow traps on charge separation, resulting in the inhibition of the recombination of electrons and holes. For the Ag/N-doped TiO$_2$ photocatalyst,
N is also introduced in the lattice of TiO₂ similar to that explained for the B/N-doped TiO₂, while the Ag dopant acts as nanoparticles on the surface of the photocatalyst. N acts as a shallow traps to induce charge separation, while Ag acts as an electron acceptor. Accordingly, the mechanisms for the two synergized co-doped photocatalysts are the keys to improve the photocatalytic activity. Increasing charge separation and active surface area could lead to enhanced generation of the hydroxyl radical, which can oxidize glucose into the derived products. Appropriate species of combined dopants could induce the synergistic effect on the mechanisms of the photocatalyst, which lead to improve the performance of the photocatalytic process.

**CONCLUSIONS**

Modifications of TiO₂ nanoparticles by single-metal (or metalloid) and nonmetal doping (i.e., B, Ag, and N) and co-doping (i.e., B/N and Ag/N) were carried out. Physicochemical properties of the modified photocatalysts were characterized, and the synthesized photocatalysts were used for photocatalytic glucose conversion to produce the value-added chemicals, that is, gluconic acid, xylitol, arabinose, and formic acid. The doping of the photocatalysts by different single dopants could improve the performance in terms of productivity and was further enhanced by the synergistic effects from the co-doping. The highest glucose conversion of the single doping was Ag-doped TiO₂ which improved the conversion to 63.5%, while the modified TiO₂ with co-doping of Ag/N showed the highest glucose conversion of 97.7%. The Ag/N-doped TiO₂ photocatalysts also showed the highest yield of gluconic acid (12.3%) at 60 min of irradiation time, while the yield of xylitol 10.8% was obtained at 90 min, which were higher than those obtained using the single-doped and bare TiO₂. The improvement in catalytic performances of the photocatalysts corresponded with the alterations in physicochemical characteristics of the catalysts, resulting from the dopants.

**EXPERIMENTAL SECTION**

**Materials.** Titanium (IV) butoxide (TiBu), acetylacetone (ACA), and isopropyl alcohol used to prepare titanium dioxide (TiO₂) sol were purchased from Sigma-Aldrich (USA). Boric acid (H₃BO₃), silver nitrate (AgNO₃), and ammonia (NH₃) used as boron (B), silver (Ag), and nitrogen (N) dopants were of analytical grades obtained from Wako (Japan). Glucose monohydrate (analytical grade) used as the substrate in photocatalytic reactions was obtained from Carlo Erba Reagents Co. (France).

**Synthesis of Bare TiO₂ and Modified TiO₂ Photocatalysts.** Bare, metal-doped, metalloid-doped, nonmetal-doped, and co-doped TiO₂ nanoparticles were prepared using a sol–gel method. In details, a pure titanium precursor solution was prepared by mixing titanium butoxide (4.36 mL) with acetylacetone (1.26 mL) at room temperature (25 °C) with continuous stirring (so called solution A). Solution B was prepared by mixing 2-propanol (20 mL) and deionized water (15 mL). The obtained solution B was dropwise added to solution A with continuous stirring. The resultant mixture was stirred for 3 h at room temperature, followed by aging at 80 °C in an oil bath for 12 h. The obtained gel was dried at 100 °C on a hot plate for 8 h. Finally, the dry particles were grounded and calcined at 400 °C in a muffle furnace for 3 h to obtain...
TiO₂ powders. Modification of TiO₂ was performed by addition of different dopants (with a mixing ratio of 2% mole of dopant to a mole of Ti) in solution B and followed the procedure mentioned above. It should be noted that the mixing ratio of 2% mole of the dopant was selected from an experiment, and the result is shown in Figure S4.

Characterizations of Photocatalysts. The physicochemical properties of synthesized TiO₂ and its modified forms were characterized. The morphology of the photocatalysts was determined by a scanning electron microscope (SU-8030, Hitachi, Tokyo, Japan) with energy-dispersive X-ray spectroscopy and a high-resolution transmission electron microscope (JEM-2100Plus, JEOL, Tokyo, Japan). The specific surface area, pore size, and pore volume of the photocatalysts were determined by the Brunauer–Emmett–Teller method, according to N₂ adsorption–desorption isotherm (BELSORP 18, MicrotracBEL Corp., Osaka, Japan) at 77 K. The optical properties were analyzed using diffuse reflectance UV–vis absorption spectrophotometry (UV–vis DRS; Jasco V-550, Jasco Int., Tokyo, Japan). The UV–vis absorption spectra were determined using the dry-pressed vessel of the photocatalysts (P25). The crystal structure and phase analysis were determined by XRD (D8 advance, Bruker, USA) using Cu Kα radiation with the angle scanning (2θ) of 20°–80° at 40 kV and 40 mA. The approximate crystallite size of samples was calculated using the Scherrer equation (eq 2).

\[ D = \frac{Kl}{\beta \cos \theta} \]  

where \( D \) is the crystallite size, \( K \) is the coefficient (0.94), \( \beta \) is the full width at half-maximum (fwhm) of the diffraction peak of anatase phase [101], \( \theta \) is diffraction angle, and \( \lambda \) is the wavelength of X-ray corresponding to the Cu Kα irradiation (1.5406 Å).

Photocatalytic Reaction of Glucose under UV Irradiation. Glucose solution (1 g/L) was prepared in a mixture of distilled water and acetonitrile (10:90 v/v).\(^{15,46} \) Noted that the solvent mixture at 10:90 v/v was selected from a preliminary experiment (Figure S5). The prepared solution (400 mL) was transferred into a Pyrex cylindrical double-walled reactor. The photocatalysts (1 g/L) were loaded under dark condition and incubated with continuous stirring for 30 min to reach an absorption–desorption equilibrium. A mercury lamp of 450 W (250–365 nm, UM-452, USHIO, Osaka, Japan) was located inside the reactor as a light source to irradiate the samples. The reaction temperature was maintained by a cooling water system at 25 °C. The samples were taken from the photoreactor at the specified times for analysis. The responses of photocatalytic process were defined, as described below in eqs 3–5.

\[ \text{Glucose conversion} = \frac{\text{C}_i - \text{C}_f}{\text{C}_i} \times 100 \]  

\[ \text{Yield of product} = \frac{\text{C}_p}{\text{C}_i} \times 100 \]  

\[ \text{Product rate} (\text{mmol L}^{-1} \text{h}^{-1}) = \int_{t_0}^{t_f} \text{r}_p \text{dt} \]  

where \( \text{C}_i \) is the initial concentration of glucose, \( \text{C}_f \) is the concentration of glucose at specific time, \( \text{C}_p \) is the concentration of products at specific time, and \( \text{r}_p \) is the volumetric production rate in terms of mmol of target product per liter (L) of reaction volume per hour (h).

Product Analysis. The amounts of organic products in the reactions were quantified by high-performance liquid chromatography (LC-10AD, Shimadzu, Kyoto, Japan) equipped with a refractive index detector (Shimadzu RID-10A). The liquid products taken from the photoreactor at the specified times were filtered by a 0.22 μm nylon filter before analysis. Product separation was performed on an Aminex HPX-87H column (300 × 7.8 mm) (Bio-Rad, Hercules, CA, USA). The mobile phase was 5 mM sulfuric acid at a flow rate of 0.5 mL/min with an injection volume of 20 μL.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02334.

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Notes

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REFERENCES

(1) Srisaswimon, N.; Chuangchote, S.; Laosiripojana, N.; Sagawa, T. TiO2/Lignin-Based Carbon Composites Photocatalysts for Enhanced Photocatalytic Conversion of Lignin to High Value Chemicals. ACS Sustain. Chem. Eng. 2018, 6, 13968–13976.

(2) Xie, R.; Lei, D.; Zhan, Y.; Liu, B.; Tsang, C. H. A.; Zeng, Y.; Li, K.; Leung, D. Y. C.; Huang, H. Efficient photocatalytic oxidation of glucose (Pt)-TiO2 suspension. J. Mol. Catal. A: Chem. 2016, 121025.

(3) Olowoyo, J. O.; Kumar, M.; Jain, S. L.; Shen, S.; Zhou, Z.; Mao, S. S.; Vorontsov, A. V.; Kumar, U. Reinforced photocatalytic reduction of CO2 to fuel by efficient S-TiO2: Significance of sulfur doping. Int. J. Hydrogen Energy 2018, 43, 17682–17695.

(4) Zou, J.-J.; Zhu, B.; Wang, L.; Zhang, X.; Mi, Z. Zn- and La-doped TiO2 photocatalysts for the isomerization of norbornadiene to quadricyclane. J. Mol. Catal. A: Chem. 2008, 286, 63–69.

(5) Honeker, R.; Garza-Sanchez, R. A.; Hopkinson, M. N.; Glorius, F. Visible-Light-Promoted Trifluoromethylthiolation of Styrenes by Codoped TiO2 Hollow Spheres with Enhanced Visible-Light Photocatalytic Activity. ACS Catal. 2013, 3, 4088–4097.

(6) Panagiotopoulou, P.; Antoniadou, M.; Kondarides, D. I.; Lianos, V. K.; Zetty, A. Preparation and characterization of nano silver-doped mesoporous titania photocatalysts for dye degradation. Catal. Today 2009, 147, 576–580.

(7) Das, S.; Mahalingam, H. Dye degradation studies using immobilized pristine and waste polystyrene-TiO2/rGO/g-C3N4 nanocomposite photocatalytic film in a novel airlift reactor under visible light Irradiation. J. Phys. Chem. C 2011, 115, 4507–4515.

(8) Gong, Y.; Fu, C.; Ting, L.; Chen, J.; Zhao, Q.; Li, C. Exploring the effect of boron and tantalum codoping on the enhanced photocatalytic activity of TiO2. Appl. Surf. Sci. 2015, 351, 746–752.

(9) Binitha, N. N.; Yaakob, Z.; Reshmi, M. R.; Sugunan, S.; Ambili, V. K.; Emeline, A. V.; Bahmann, D. W. Influence of the Dopant Concentration on the Photocatalytic Activity: Al-Doped TiO2. J. Phys. Chem. C 2015, 119, 24695–24703.

(10) Di Valentino, C.; Pacchioni, G.; Selloni, A.; Livraghi, S.; Gianello, E. Characterization of Paramagnetic Species in N-Doped TiO2 Powders by EPR Spectroscopy and DFT Calculations. J. Phys. Chem. B 2005, 109, 11414–11419.

(11) Lin, X.; Fu, D. Facile one-pot hydrothermal synthesis of B/N-codoped TiO2 hollow spheres with enhanced visible-light photocatalytic activity and photoelectrochemical property. Solid State Sci. 2014, 34, 73–77.

(12) Barolo, G.; Livraghi, S.; Chiesa, M.; Paganini, M. C.; Gianello, E. Mechanism of the Photoactivity under Visible Light of N-Doped Titanium Dioxide. Charge Carriers Migration in Irradiated N-TiO2 Investigated by Electron Paramagnetic Resonance. J. Phys. Chem. C 2016, 117, 20887–20894.

(13) Asahi, R.; Morikawa, T.; Irie, H.; Ohwaki, T. Nitrogen-Doped Titanium Dioxide as Visible-Light-Sensitive Photocatalyst: Designs, Developments, and Prospects. Chem. Rev. 2014, 114, 9824–9852.

(14) Wang, Y.; Zhu, L.; Ba, N.; Gao, F.; Xie, H. Effects of NH4F quantity on N-doping level, photodegradation and photocatalytic H2 production activities of N-doped TiO2 nanotube array films. Mater. Res. Bull. 2017, 86, 266–276.

(15) Kumar, A.; Patel, A. S.; Mohanty, T. Correlation of Photo degradation Efficiency with Surface Potential of Silver-TiO2 Nanocomposite Thin Films. J. Phys. Chem. C 2012, 116, 20404–20408.

(16) Ilie, M.; Cojocaru, B.; Parvu, V. I.; Garcia, H. Improving TiO2 activity in photo-production of hydrogen from sugar industry wastewaters. Int. J. Hydrogen Energy 2011, 36, 15509–15518.
(29) Feng, N.; Zheng, A.; Wang, Q.; Ren, P.; Gao, X.; Liu, S.-B.; Shen, Z.; Chen, T.; Deng, F. Boron Energy of Doped and (B, N)-Codoped TiO2 Photocatalysts: A Combined Solid-State NMR and Theoretical Calculation Study. J. Phys. Chem. C 2011, 115, 2709−2719.

(30) Kuvarega, A. T.; Krause, R. W. M.; Mamba, B. B. Nitrogen/Palladium-Codoped TiO2 for Efficient Visible Light Photocatalytic Dye Degradation. J. Phys. Chem. C 2011, 115, 22110−22120.

(31) Nasir, M.; Lei, J.; Iqbal, W.; Zhang, J. Study of synergistic effect of Sc and C co-doping on the enhancement of visible light photocatalytic activity of TiO2. Appl. Surf. Sci. 2016, 364, 446−454.

(32) Sanitnon, P.; Chiarakorn, S.; Chawengkijwanich, C.; Chuanchothe, S.; Pongprayoon, T. Synergistic effects of zirconium and silver co-dopants in TiO2 nanoparticles for photocatalytic degradation of an organic dye and antibacterial activity. J. Aust. Ceram. Soc. 2020, 56, S79.

(33) Yang, G.; Yin, H.; Liu, W.; Yang, Y.; Zou, Q.; Luo, L.; Li, H.; Hoo, Y.; Li, H. Synergistic Ag/TiO2-N photocatalytic system and its enhanced antibacterial activity towards Acinetobacter baumannii. Appl. Catal., B 2018, 224, 175−182.

(34) Nasir, M.; Xi, Z.; Xing, M.; Zhang, J.; Chen, F.; Tian, B.; Bagwasi, S. Study of Synergistic Effect of Ce- and S-Codoping on the Enhancement of Visible-Light Photocatalytic Activity of TiO2. J. Phys. Chem. C 2013, 117, 9520−9528.

(35) Wang, C.; Zhang, X.; Mei, J.; Hu, Q.; Yang, S. Novel Synergistic Effect of Fe and Mo in FeMoSx/TiO2 for Recovering High Concentrations of Gaseous Hg²⁺ from Smelting Flue Gas: Reaction Mechanism and Kinetics. Environ. Sci. Technol. 2020, 54, 586−594.

(36) Yang, S.; Wang, H.; Yu, H.; Zhang, S.; Fang, Y.; Zhang, S.; Peng, F. A facile fabrication of hierarchical Ag nanoparticles-decorated N-TiO2 with enhanced photocatalytic hydrogen production under solar light. Int. J. Hydrogen Energy 2016, 41, 3446−3455.

(37) Bellardita, M.; Garcia-Lopez, E. I.; Marci, G.; Nasillo, G.; Palmisano, L. Photocatalytic Solar Light H₂ Production by Aqueous Glucose Reforming. Eur. J. Inorg. Chem. 2018, 4522−4532.

(38) Iervolino, G.; Vaiano, V.; Muccia, J. J.; Rizzo, L.; Ventre, G.; Pepe, G.; Campiglia, P.; Hidalgo, M. C.; Navio, J. A.; Sannino, D. Photocatalytic hydrogen production from degradation of glucose over fluorinated and platinum TiO₂ catalysts. J. Catal. 2016, 339, 47−56.

(39) Dhomde, K. S.; Dhonde, M.; Murty, V. V. S. Novel synergistic combination of Al/N Co-doped TiO₂ nanoparticles for highly efficient dye-sensitized solar cells. Sol. Energy 2018, 173, 551−557.

(40) Nada, A. A.; El Rouby, W. M. A.; Bekheet, M. F.; Antuch, M.; Weber, M.; Miele, P.; Viter, R.; Roualdis, S.; Millet, P.; Bechelany, M. Highly textured boron/nitrogen co-doped TiO₂ with honeycomb structure showing enhanced visible-light photoelectrocatalytic activity. Appl. Surf. Sci. 2020, 505, 144419.

(41) Colmenares, J. C.; Magdziarz, A.; Bielejewska, A. High-value chemicals obtained from selective photo-oxidation of glucose in the presence of nanostructured titanium photocatalysts. Bioresour. Technol. 2011, 102, 11254−11257.

(42) Payormhorm, J.; Chuanchothe, S.; Kiatkittipong, K.; Chiarakorn, S.; Laosiripojana, N. Xylitol and gluconic acid productions via photocatalytic-glucose conversion using TiO₂ fabricated by surfactant-assisted techniques: Effects of structural and textural properties. Mater. Chem. Phys. 2017, 196, 29−36.

(43) Chong, R.; Li, J.; Ma, Y.; Zhang, B.; Han, H.; Li, C. Selective conversion of aqueous glucose to value-added sugar aldehyde on TiO₂-based photocatalysts. J. Catal. 2014, 314, 101−108.

(44) Bellardita, M.; Garcia-Lopez, E. I.; Marci, G.; Megna, B.; Pomilla, F. R.; Palmisano, L. Photocatalytic conversion of glucose in aqueous suspensions of heteropolyacid-TiO₂ composites. RSC Adv. 2015, 5, 59037−59047.

(45) Chuanchothe, S.; Jitputti, J.; Sagawa, T.; Yoshihikawa, S. Photocatalytic Activity for Hydrogen Evolution of Electrospun TiO₂ Nanofibers. ACS Appl. Mater. Interfaces 2009, 1, 1140−1143.

(46) Roongraung, K.; Chuanchothe, S.; Laosiripojana, N. Enhancement of Photocatalytic Oxidation of Glucose to Value-Added Chemicals on TiO₂ Photocatalysts by A Zeolite (Type Y) Support and Metal Loading. Catalysts 2020, 10, 423.

(47) Liqiang, J.; Yichun, Q.; Baiqi, W.; Shudan, L.; Baojiang, J.; Libin, Y.; Wei, F.; Hongsang, F.; Jiazhong, S. Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity. Sol. Energy Mater. Sol. Cells 2006, 90, 1773−1787.

(48) Fu, C.; Gong, Y.; Wu, Y.; Liu, J.; Zhang, Z.; Li, C.; Niu, L. Photocatalytic enhancement of TiO₂ by B and Zr co-doping and modulation of microstructure. Appl. Surf. Sci. 2016, 379, 83−90.

(49) Payormhorm, J.; Chuanchothe, S.; Laosiripojana, N. CTAB-assisted sol-microwave method for fast synthesis of mesoporous TiO₂ photocatalysts for photocatalytic conversion of glucose to value-added sugars. Mater. Res. Bull. 2017, 95, 546−555.

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