Electrospun Ag-TiO₂ Nanofibers for Photocatalytic Glucose Conversion to High-Value Chemicals

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ABSTRACT: TiO₂ nanofibers were fabricated by combination of sol–gel and electrospinning techniques. Ag-doped TiO₂ nanofibers with different Ag contents were prepared by two different methods (in situ electrospinning or wetness impregnation of Ag on TiO₂ nanofibers) and heat treated at 500 °C for 2 h under an air or N₂ atmosphere. The obtained catalysts were characterized by field emission scanning electron microscopy, X-ray diffraction, photoluminescence, and N₂ adsorption analyzed by the Brunauer–Emmett–Teller (BET) method. Photocatalytic glucose conversions with electrospun TiO₂ and Ag-doped TiO₂ nanofibers for production of high-value products were carried out. From different doping methods, the results indicated that 1 wt % Ag-TiO₂ nanofibers prepared by an in situ method with calcination under N₂ achieved the highest glucose conversion (85.49%). From several Ag loading contents (i.e., 0, 1, 2, and 4 wt %) in Ag-doped TiO₂ nanofibers, the nanofibers exhibited different glucose conversions [in order of 2 wt % (99.65%) > 1 wt % (85.49%) > 4 wt % (77.72%) > 0 wt % (29.64%)]. Arabinose, xylitol, gluconic acid, and formic acid were found as the high-value chemicals with the photocatalytic reaction of TiO₂ and Ag-doped TiO₂ nanofibers under UVA irradiation. Product yields of each converted chemicals from diacid, and formic acid were found as the high-value chemicals with the photocatalytic reaction of TiO₂ and Ag-doped TiO₂ nanofibers for production of high-value products were carried out. From all results, it can be concluded that the good characteristics of 2 wt % Ag-TiO₂ nanofibers such as the smallest anatase crystallite size (8.25 nm) and the highest specific surface area (S_BET = 53.69 m²/g) promoted the highest photocatalytic activity. Additionally, TiO₂ and Ag-doped TiO₂ nanofibers exhibited higher photocatalytic performance for glucose conversion than commercial TiO₂ (P25) and synthesized TiO₂ nanoparticles. Finally, Ag-doped TiO₂ nanofibers showed recycling ability with high photocatalytic glucose conversion after four-time use.

INTRODUCTION

Biomass is one of important feedstock for various utilizations instead of fossil fuels. Normally, biomass has been converted into fuels and chemicals using various technologies, such as steam gasification,¹ fast pyrolysis,² and supercritical conversion.³ These processes, however, have limitations such as requiring high temperature, high pressure, high-energy consumption, and high system cost to produce chemicals and fuels. Moreover, there are many steps to produce chemicals in these processes. Alternative processes that can solve these limitations and produce chemicals in one step should be developed. In this sense, photocatalysis is one of the most promising technologies because it represents an easy way to utilize the energy from UV lamps or natural sunlight by catalysis at room temperature and mild conditions.⁴

Photocatalysis is the acceleration of a photoreaction due to the presence of a catalyst.⁵ Recently, photocatalysis is one of technologies that have been used in environmental and energy fields, such as degradation of organic compounds in wastewater,⁶ air purification,⁷ and water splitting.⁸ Titanium dioxide (TiO₂) is a white solid inorganic substance that occurs naturally in several kinds of rock and mineral sands. There are three different crystalline modifications, i.e., anatase, rutile, and brookite. It is a semiconducting material that can be chemically activated by light with a band gap energy (E_g) of about 3.2 eV.⁹ It is the most important photocatalyst for many applications because TiO₂ is a nontoxic, cheap, and versatile material with attractive applications not only in photocatalysis but also in the production of electrodes, capacitors, and solar cells. TiO₂ has various structures, such as nanoparticles, nanosheets, nanowires, nanotubes, and nanofibers.¹⁰

Nanofibers are one-dimensional nanostructures with diameters ranging from 10 to 100 nm with aspect ratios larger than 1000. The TiO₂ nanofiber is an outstanding form because it can solve some limitations of TiO₂, for example, reduction of TiO₂ agglomeration and low interfacial charge transfer.
Moreover, it was reported that TiO₂ nanofibers could perform much better than the nanoparticles in various applications, such as photodegradation and hydrogen production.

Electrospinning or electrostatic spinning is a basic method to produce nanofibers with extreme lengths and high ratios of surface area to volume through a process using a high-voltage electric field. There are many advantages of electrospinning such as low cost, simplicity, and high reproducibility. Electrospinning has been first reported by Rayleigh in 1897 and then was developed as a patent in 1934 by Formhals. It was described in the patent the experimental setup for the production of polymer filaments using electrostatic force. Since then, this technique has received much attention. Li et al. synthesized TiO₂ nanofibers by electrospinning a TiO₂ precursor with polyvinylpyrrolidone (PVP) at different solution concentrations. They found that the ultrafine nanofibers were obtained at high viscosity. Li et al. synthesized mesoporous TiO₂ nanofibers via electrospinning and studied the effect of the calcination process on the activity of TiO₂ in a photocatalytic application. They found that the TiO₂ nanofibers obtained at 500 °C presented the best photocatalytic activity.

Recently, TiO₂ nanofibers were modified by several dopants, e.g., metals, for lower band gap and lower electron–hole recombination rate than pristine TiO₂. Inexpensive metals, e.g., silver (Ag), have been of great interest to be used in modification of TiO₂ because they could decrease recombination of electron (e⁻)–hole (h⁺) pairs by acting as an electron sink. In addition, Ag has the ability to generate surface plasmon resonance with TiO₂ by visible light. This causes Ag to enhance the performance of photocatalytic activity of TiO₂ and quantum yield of photocatalytic processes.

TiO₂ nanofibers are widely used in various applications such as solar cells, sensors, and photocatalysts. Photocatalysis has important functions in disinfection, air cleaning, and water treatment applications. However, there is no report about utilization of TiO₂ nanofibers in glucose conversion. In this work, we report, for the first time, applications of TiO₂ nanofibers for glucose conversion by photocatalysis.

Glucose is a monosaccharide that is attractive as a feedstock for producing value-added chemicals such as gluconic and glucaric acids. Photocatalytic conversion of glucose first drew great attention to produce hydrogen (H₂). After that, some works were focused in the liquid-phase products and some value-added chemicals were found in that phase. Colmenares et al. reported photocatalytic conversion of glucose using TiO₂ as a photocatalyst. Gluconic acid, glucaric acid, and arabitol were found as the main products after the reaction. The highest selectivity of products (70%) was achieved in a mixed solvent of acetonitrile and water. Recently, Payormhom et al. first reported that, in addition to the reported chemicals, xylitol was also found as a product after the photocatalytic conversion of glucose. Moreover, increasing the surface area of TiO₂ was found to increase the glucose conversion and product yields. In this sense, it is interesting to use the unique properties of nanofibers for enhancement of photocatalytic activity in glucose conversion. Therefore, TiO₂ nanofibers were fabricated in this work by combination of sol–gel and electrospinning followed by calcination. Effects of several conditions in modifications of TiO₂ photocatalysts by Ag doping, i.e., preparation methods (in situ and wetness impregnation), atmospheres during calcination (air and N₂), and contents of Ag, were studied. Photocatalytic activities of the obtained photocatalysts in the conversion processes of glucose to high-value products were studied.

### RESULTS AND DISCUSSION

#### Variation of Photocatalyst Preparation Techniques.

TiO₂ nanofibers were fabricated by combination of sol–gel and electrospinning methods. The TiO₂ nanofibers were then doped by Ag. Calcination conditions (i.e., under air and N₂ atmospheres) and methods of Ag doping (i.e., in situ and wetness impregnation methods) were studied. As-spun TiO₂/PVP nanofibers have a smooth surface with an average diameter of 320 nm (not shown here). Figure 1 shows the SEM images of mechanically broken nanofibers of (A) TiO₂ calcined under air condition, (B) 1 wt % Ag-TiO₂ (prepared by the in situ technique) calcined under the air condition, (C) 1 wt % Ag-TiO₂ (prepared by the in situ technique) calcined under an N₂ atmosphere, and (D) 1 wt % Ag-TiO₂ (prepared by the wetness impregnation technique) calcined under an N₂ atmosphere. Numbers 1 and 2 refer to image magnifications of 50k (scale bar = 1 μm) and 100k (scale bar = 500 nm), respectively.

**Figure 1.** SEM images of mechanically broken nanofibers of (A) TiO₂ calcined under air condition, (B) 1 wt % Ag-TiO₂ (prepared by the in situ technique) calcined under the air condition, (C) 1 wt % Ag-TiO₂ (prepared by the in situ technique) calcined under an N₂ atmosphere, and (D) 1 wt % Ag-TiO₂ (prepared by the wetness impregnation technique) calcined under an N₂ atmosphere.
solution contains the TiO$_2$ sol with methanol in polymer solution before spinning, and the TiO$_2$ sol is rapidly converted to the TiO$_2$ gel. Therefore, liquid–liquid phase separation results in TiO$_2$-rich and PVP-rich phases. These separated phases cause formation of nanofibers. For different calcination conditions (i.e., under air and N$_2$ atmospheres), as shown in Figure 1B,C, it was found that Ag-TiO$_2$ nanofibers calcined under air showed similar morphology with pristine TiO$_2$ nanofibers (average diameter, ~220 nm), while Ag-TiO$_2$ nanofibers prepared by in situ technique and calcined under an N$_2$ atmosphere have a rough surface (average diameter, ~150 nm). Comparing methods of Ag doping (i.e., in situ and wetness impregnation), it was found that in situ electrospinning changed greatly the morphology of the obtained fibers, while wetness impregnation did not (average diameter, ~250 nm) (see Figure 1C,D). This is because the nature of wetness impregnation in which a metal solution is dropped on the solution before spinning, and the TiO$_2$ sol is rapidly converted to the TiO$_2$ gel. Therefore, liquid–liquid phase separation results in TiO$_2$-rich and PVP-rich phases. These separated phases cause formation of nanofibers.

Among all catalysts, the average diameters of all 1 wt % Ag-TiO$_2$ nanofibers were smaller than those of the pristine one due to Ag causing the phase transition of TiO$_2$ and reducing the size of crystals, as shown in Table 1. The metal content on TiO$_2$ nanofibers was determined by energy-dispersive X-ray (EDX) spectrometry. It was found that the metal content in 1 wt % Ag-TiO$_2$ nanofibers fabricated by the in situ technique was significantly higher than those fabricated by wetness impregnation (see Table 1). This is because wetness impregnation is the method wherein the support makes contact with the solution of the metal precursor, so the maximum load depends on the ability of the support to have ion exchange with the metal. In this sense, Ag in the fibers from the in situ method were lost less during the synthesis process.

XRD patterns of TiO$_2$ nanofibers and 1 wt % Ag-TiO$_2$ nanofibers (Ag was loaded by the in situ or wetness impregnation technique) under different atmospheres are shown in Figure 2. All catalysts show diffraction peaks of anatase at 25.4°, 38.5°, 48.0°, 54.9°, 70.2°, and 75.0°. Meanwhile, the peaks located at 27.5°, 36.1°, 41.3°, and 56.6° determine the (110), (101), (111), and (220) planes, respectively, of the rutile phase. Even though Ag was detected by EDX, there is no diffraction peak of Ag observed in the XRD patterns due to its existence as small crystals whose sizes are below the resolution limit of the technique. By comparing the in situ preparation technique with the wetness impregnation method, the results of 1 wt % Ag-TiO$_2$ prepared by wetness impregnation showed a high anatase phase. In addition, the crystallite size of catalysts prepared by wetness impregnation (17.06 nm) was found to be larger than those of pristine TiO$_2$ nanofibers (14.03 nm) and the fibers prepared by the in situ method (9.54 nm). This is because heat supplied during the Ag loading process in wetness impregnation promoted higher densities of defects on the anatase grains resulting in larger anatase grains. By comparing the TiO$_2$ nanofibers with 1 wt % Ag-TiO$_2$ nanofibers prepared by the in situ method and calcined under different atmospheres, it was found that 1 wt % Ag-TiO$_2$ nanofibers calcined under an N$_2$ condition showed mixed phases of anatase and rutile with a small crystallite size of 9.5 nm. This is caused by defects that act as nucleation centers during the crystallization process. Therefore, N$_2$ could promote the crystallization and phase transition. Besides, 1 wt % Ag-TiO$_2$ prepared by the in situ method exhibited the highest surface area of 58.28 m$^2$g$^{-1}$ due to Ag becoming the crystal growth center, leading to an increase in pore volume and small size (see Table 1). Generally, the surface area of catalysts is an important factor in catalytic processes.

Table 1. Summary of Diameters and Physical Properties of TiO$_2$ Nanofibers and 1 wt % Ag-TiO$_2$ Nanofibers (Prepared by In Situ and Wetness Impregnation Techniques)

| photocatalyst | diameter of nanofibers (nm) | percentage of anatase phase | crystallite size (nm)$^a$ | BET surface area (m$^2$g$^{-1}$) | pore volume (cm$^3$g$^{-1}$) | composition of Ag in catalyst (wt %) |
|---------------|-----------------------------|-----------------------------|---------------------------|-----------------------------|-----------------------------|-----------------------------------|
| TiO$_2$ (air) | 278 ± 10                    | 97                          | A (14.33)                 | 35.97                       | 0.08                        | 1 ± 0.05                          |
| 1 wt % Ag-TiO$_2$ (in situ, air) | 220 ± 10                    | 100                         | A (14.02)                 | 31.07                       | 0.11                        | 0.34 ± 0.01                       |
| 1 wt % Ag-TiO$_2$ (in situ, N$_2$) | 150 ± 10                    | 8                           | A (9.54)                  | 58.28                       | 0.21                        | 0.77 ± 0.02                       |
| 1 wt % Ag-TiO$_2$ (wetness, N$_2$) | 250 ± 13                    | 97                          | A (14.06)                 | 38.88                       | 0.17                        | 0.17 ± 0.02                       |

$^a$A = anatase, $^b$analyzed by SEM–EDX

Figure 2. XRD patterns of TiO$_2$ nanofibers and 1 wt % Ag-TiO$_2$ nanofibers (Ag was doped by the in situ or wetness impregnation technique). All samples were calcined at 500 °C for 3 h under an air condition or N$_2$ atmosphere. Standard peaks of anatase TiO$_2$, rutile TiO$_2$, and Ag are included.
that affects the photocatalytic activity by promoting the dispersion and more reaction sites.36

Optical properties and band gap energy ($E_g$) of photocatalysts have significant effects on photocatalytic reactions, so the nanofibers were investigated using a UV–vis spectrophotometer. Figure 3 shows the comparison of UV–vis absorption spectra of pristine TiO$_2$ and 1 wt % Ag-TiO$_2$ nanofibers (prepared by different techniques and calcination conditions). The pristine TiO$_2$ nanofibers present an absorption edge at 398 nm corresponding to a band gap energy of 3.11 eV. Ag-doped TiO$_2$ nanofibers exhibited red shifts of the absorption edges and significant enhancements of light absorptions in the visible light region compared with the pristine TiO$_2$ nanofibers. For Ag-doped TiO$_2$ nanofibers prepared by different atmospheres, it was found that Ag-doped TiO$_2$ prepared by the in situ technique and calcined under an N$_2$ atmosphere increases absorption in the visible light region with an absorption edge of about 425 nm, corresponding to the lowest value of $E_g$ (2.92 eV) due to the fact that the crystal structure contained a high content of the rutile phase37 (see Figure 2).

Photocatalytic glucose conversions on pristine TiO$_2$ nanofibers, 1 wt % Ag-TiO$_2$ nanofibers prepared by the in situ method at different atmospheres (air and N$_2$), and 1 wt % Ag-TiO$_2$ nanofibers prepared by the wetness impregnation method were carried out for 120 min, as shown in Figure 4. The smallest anatase crystallite size (14.02 nm), the highest $S_{BET}$ (58 m$^2$/g), and relatively small band gap (3.02 eV) in 1 wt % Ag-TiO$_2$ nanofibers prepared by the in situ method calcined under N$_2$ are the reasons for the highest photocatalytic activity. The conversions of glucose (85.49 and 68.61% on 1 wt % Ag-TiO$_2$ nanofibers prepared by in situ and wetness methods, respectively) are reasonably higher than the results previously reported by other researchers. For example, Chong et al.38 used hydrothermal-synthesized TiO$_2$ with a cocatalyst (i.e., Rh) as the photocatalyst to achieve the glucose conversion of 61.3%. In addition, they reported that the selective products from photocatalytic oxidations of glucose were arabinose and erythrose. In contrast, the experimental results in this work indicated that four organic compounds, i.e., gluconic acid, arabinose, xylitol, and formic acid, were produced after the 120 min reaction. At the highest glucose conversion of 85.49% (from 1 wt % Ag-TiO$_2$ nanofibers prepared by the in situ method calcined under N$_2$), the yields of gluconic acid, arabinose, xylitol, and formic acid were 8.55, 44.41, 21.97, and 24.48%, respectively (Figure 4). Bellardita et al.39 reported the steps of oxidation of glucose to value-added chemicals. Glucose is first oxidized at the anomeric center (C1) to form gluconic acid, and then an oxidant attack at the C2 carbon gives rise to a formation of formic acid and arabinose. From these steps, it can be implied that gluconic acid can also transform to arabinose and formic acid. Hence, the highest yield of gluconic acid in this work (16.17%) was found at 60 min of the reaction on 1 wt % Ag-TiO$_2$ prepared by the in situ method (calcined under an N$_2$ atmosphere). After that, the yield slightly decreased because gluconic acid was converted to arabinose, formic acid, and other organic chemicals in the solution. From the product analysis, we found that the main product obtained was arabinose, wherein the possible reaction pathway of glucose conversion followed the previous report.38 First, glucose can be converted to gluconic acid, and the gluconic acid can be then converted to arabinose and formic acid by...
photocatalytic decarboxylation. Finally, xylitol was produced from photocatalytic decomposition of glucose or gluconic acid.

**Effect of Ag Content on Properties of TiO₂ Nano-fibers.** In the previous section, we found that the in situ method with calcination under N₂ is the suitable condition for the synthesis of Ag-TiO₂ nanofibers. The effect of Ag content (varied as 1, 2, and 4 wt %) on the properties of nanofibers was then investigated. All catalysts presented a rough surface, but Ag was not clearly observed on the surface of nanofibers (see Figure 5A−C). It was found that, at a low Ag content, the average diameters of all Ag-doped TiO₂ were smaller than those of the undoped TiO₂ nanofibers. With increasing Ag content, the average diameter of nanofibers was found to increase (Table S1). This result is in line with the report of Nalbandian et al.⁴⁹ They found that AgNO₃ not only increased the metal content in the electrospinning solution but also increased the viscosity of the solution, which can affect the nanofiber diameter size. From the data of EDX, Ag on TiO₂ nanofibers could be obviously observed. The amount of the detected Ag was not equal to the desired loading because EDX analysis represents only the surface concentration, so many other effects such as layer thickness, Ag cluster size, and surface coverage can strongly influence in EDX analysis.⁴⁰ However, the detected Ag amount was found to increase with increasing loading percentage, as theoretically expected. In addition, the appearance of Ag in TiO₂ nanofibers can be confirmed by X-ray photoelectron spectroscopy. Ag₂O (≈367.7 eV) and Ag⁰ (≈368.2 eV) peaks could be observed from the samples (the result not shown here).

XRD patterns of pristine TiO₂ nanofibers, 1 wt % Ag-TiO₂, 2 wt % Ag-TiO₂, and 4 wt % Ag-TiO₂ nanofibers prepared by the in situ method with calcination under N₂ are shown in Figure 6. The TiO₂ nanofibers have a mixture of anatase and rutile phases, as described above. The diffraction peaks of Ag(111) and Ag(200) at 2θ of 38.1° and 44.7°, respectively, which were not observed in 1 wt % Ag-TiO₂ nanofibers (because of too low content) as discussed above, were found in a high content of Ag loading (4 wt % Ag-TiO₂ nanofibers). In addition, it was observed that the crystallite size of anatase decreased with loading of Ag onto the TiO₂ nanofibers (Figure 7). This indicates the rearrangement of titanium and oxygen ions in the anatase grain boundaries, which would be greatly

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**Figure 5.** SEM images of (A) 1 wt % Ag-TiO₂ nanofibers, (B) 2 wt % Ag-TiO₂ nanofibers, (C) 4 wt % Ag-TiO₂ nanofibers (prepared by the in situ technique) calcined under an N₂ atmosphere. Numbers 1 and 2 refer to image magnifications of 50.0k (scale bar = 1 μm) and 100k (scale bar = 500 nm), respectively. (D) TEM image of 2 wt % Ag-TiO₂ nanofibers.

**Figure 6.** XRD patterns of TiO₂ nanofibers, 1 wt % Ag-TiO₂ nanofibers, 2 wt % Ag-TiO₂ nanofibers, and 4 wt % Ag-TiO₂ nanofibers prepared by the in situ technique after calcination under N₂ at 500 °C for 3 h.
disturbed with the existence of silver ions. The hindered transfer of the material in the anatase grains increased the energy for the movement of the anatase grain boundaries, resulting in slower grain growth.41 Also, at 4 wt % loading, the crystallite size was relatively unchanged compared with the undoped one. It was found that an increase in silver content decreased the phase transition from anatase to rutile due to the surface oxygen vacancy concentration of anatase grains increased, which hindered the rearrangement of ions and reorganization of the structure for the rutile phase (Table S1).

Ag-doped TiO2 displayed a higher surface area than pure TiO2 nanofibers, as shown in Figure 7B. Among them, 1 wt % Ag-TiO2 represented the highest surface area of 58.3 m²/g. It could be explained by the fact that some Ag ions might remain near the boundary of the particles, obstructing their growth that facilitated the increase in the surface area. On the other hand, the surface area was found to decrease with increasing Ag content due to a high amount of Ag that might be agglomerated on the TiO2 surface (Table S2).

Figure 7. Influences of (A) crystallite size and (B) surface area on photocatalytic activity in glucose conversion on Ag-TiO2 nanofibers.

Figure 8 shows the PL spectra (excitation wavelength = 270 nm) of different amounts of Ag doping in TiO2 nanofibers calcined at 500 °C. The PL emission peaks of Ag-doped TiO2 nanofibers appeared at similar positions compared with pristine TiO2 nanofibers, indicating that the loading of Ag had not induced new emission. However, the relative PL intensity of Ag/TiO2 composites is quenched compared with the pristine one, suggesting that the recombination of photogenerated electrons and holes is suppressed effectively. The photogenerated electrons in the Ag-doped samples can transfer from the conduction band of TiO2 to Ag. An increase in loading content of Ag can relatively reduce the recombination chance of electrons and holes, leading to a relative lower emission intensity.43 However, there is an optimal loading amount. When the loading amount of Ag is relatively high, Ag may adversely work as recombination centers for the electrons and holes, which can reduce the suppression ability.

**Photocatalytic Glucose Conversion and Recycling Ability.** The performance of different photocatalysts was tested for glucose conversion under UVA and carried out for 120 min. It was found that Ag-doped TiO2 nanofibers showed a higher glucose conversion than pristine TiO2 nanofibers. With varying content of the Ag loading, the highest glucose conversion (99.65%) was achieved when 2 wt % Ag-TiO2 nanofibers prepared by the *in situ* method calcined under N2 were used. This glucose conversion was significantly higher than that of the work previously reported by Da Via *et al.*44 They found that the highest glucose conversion under UVA irradiation was ∼12% obtained from 1.5% Ag-TiO2 nanoparticles. At the highest glucose conversion in this work, the yields of gluconic acid, arabinose, xylitol, and formic acid of 9.26, 44.64, 25.22, and 25.8% could be achieved (Figure 9). Interestingly, the yield of xylitol found was three times higher than that found in a previous work (xylitol yield = 6.45%).28 It can be concluded that the photocatalyst made of 2 wt % Ag-TiO2 nanofibers prepared by the *in situ* method and calcined under N2 has the smallest anatase crystallite size (8.25 nm) and relatively high S BET (53.69 m²/g). These good characteristics are the possible reasons of the highest photocatalytic activity.

The photocatalytic performance of 2 wt % Ag-TiO2 nanofibers was higher than a commercial TiO2 (P25) in terms of glucose conversion and product selectivity (for arabinose and xylitol) (Figure 10). Interestingly, photocatalytic performance and product selectivity of pristine TiO2 nanofibers that were lower than Ag-doped TiO2 nanofibers were higher than sol–gel synthesized nanoparticles (Figure 11). Moreover, Ag-doped nanofibers still present higher photocatalytic activity than Ag-doped nanoparticles. This confirms
In addition, in this work, it was found that arabinose of 62.1% was achieved after operation under solar light for 360 min. As the photocatalysts, wherein the highest glucose conversion reported by Bellardita et al.45 was comparable with the conversion by nanoparticles operated under solar light irradiation (for 120 min) that achieved a higher glucose conversion (48%) than P25 (16%).

The recycling ability of Ag-doped TiO2 nanofibers was investigated by glucose conversion for four-cycle use. The Ag-doped TiO2 nanofibers were recovered by filtering and washing by deionized water several times with 70 °C overnight drying before reuse. From Figure 13, the photocatalytic efficiency of glucose conversion could be maintained at high photocatalytic activity (~99%) after four-time reuse. Thus, it can be concluded that Ag-doped TiO2 nanofibers were relatively stable and effective in glucose conversion for production of value-added chemicals.

CONCLUSIONS

From different doping methods, the results indicated that 1 wt % Ag-TiO2 nanofibers prepared by the in situ method with calcination under N2 achieved the highest glucose conversion (85.49%). From several Ag loading contents (i.e., 0, 1, 2, and 4 wt %) in Ag-doped TiO2 nanofibers, the nanofibers exhibited different glucose conversions [in order of 2 wt % (99.65%) > 1 wt % (85.49%) > 4 wt % (77.72%) > 0 wt % (29.64%)]. Four high-value chemicals, i.e., arabinose, xylitol, gluconic acid, and formic acid, were found with the photocatalytic reaction of TiO2 and Ag-doped TiO2 nanofibers under UVA irradiation. Product yields of each converted chemicals from different photocatalysts from different Ag loading contents showed relatively same trends with the glucose conversion. From all results, it can be concluded that the good characteristics of 2 wt % Ag-TiO2 nanofibers such as the smallest anatase crystallite size (8.25 nm) and the highest specific surface area (S_BET = 53.69 m²/g) promoted the highest photocatalytic activity. TiO2 and Ag-doped TiO2 nanofibers exhibited higher photocatalytic performance for glucose conversion than commercial P25 and synthesized TiO2 nanoparticles. Finally, Ag-doped TiO2 nanofibers showed recycling ability with high photocatalytic glucose conversion after four-time use.

EXPERIMENTAL SECTION

Fabrication of TiO2 Nanofibers. TiO2 nanofibers were fabricated by combination of sol–gel and electrospinning. Polyvinylpyrrolidone (PVP; Aldrich; Mn of 1,300,000; 0.8 g) was dissolved in 10 mL of methanol (ACL labscan, AR grade). Titanium(IV) butoxide (TiBu, Aldrich; 4 g) and acetylacetone (ACA, Aldrich; 1.175 g) were added to the solution, and the solution was then stirred overnight. The precursor solution was loaded into a plastic syringe (spinneret = 22 gauge needle, w of 1,300,000; 0.8 g) and electrospinning. Titanium(IV) butoxide (TiBu, Aldrich; 4 g) and acetylacetone (ACA, Aldrich; 1.175 g) were added to the solution, and the solution was then stirred overnight. The precursor solution was loaded into a plastic syringe (spinneret = 22 gauge needle, distance from spinneret to collector = 15 cm, and applied electrical potential = 15 kV).20 The feed rate of solution was set at 2 mL/h. The fibers were left at room temperature for 5 h to allow complete hydrolysis followed by calcination at 500 °C for 2 h.

Fabrication of Ag-Loaded TiO2 Nanofibers. Ag-loaded TiO2 nanofibers were prepared by in situ and wetness impregnation methods. For the in situ method, PVP (Mn = 1,300,000; 0.8 g) was dissolved in 10 mL of methanol. TiBu (4 g) and ACA (1.175 g) were added to the solution the same as the conventional process. After that, the calculated amount of the silver precursor (AgNO3, VWR chemicals BDH, AR grade)
was added to the solution and stirred overnight. Electrospinning was carried out with the same process as the pristine TiO₂ nanofibers. The nanofibers were left at room temperature for 5 h to allow complete hydrolysis followed by calcination at 500 °C under an air or N₂ atmosphere for 2 h. For the wetness impregnation method, Ag-doped TiO₂ nanofibers were prepared using AgNO₃ aqueous solution as the precursor for Ag loading. Only an Ag composition of 1 wt % in TiO₂ was used for comparison. The solution of AgNO₃ was slowly dropped on as-spun TiO₂ nanofibers at 60 °C. Finally, the Ag-doped TiO₂ nanofibers were sintered at 400 °C under an N₂ atmosphere for 4 h.

**Characterizations of Catalysts.** X-ray diffraction (XRD) (Rigaku, Smartlab) was used to identify the crystalline phase of prepared catalysts using Cu-Kα radiation (λ = 0.15418 nm) at 40 kV and 30 mA. The surface morphology and particle sizes

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**Figure 10.** (a) Photocatalytic conversions of glucose under UVA irradiation for 120 min using P25 and 2 wt % Ag-doped TiO₂ nanofibers prepared by the in situ technique with calcination under an N₂ atmosphere as the photocatalysts. (b) Selectivity of products at 120 min of photocatalysis using those catalysts.
of prepared catalysts were observed using a scanning electron microscope (FESEM, Hitachi SU-6600). Energy-dispersive X-ray spectroscopy (EDX) in FESEM and X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) were used to confirm the appearance of Ag. High-resolution images were obtained using a transmission electron microscope (TEM, JEOL JEM-2100) operated at 200 kV. Surface area, pore size, and pore volume were investigated by N2 adsorption (BEL Japan, BELSORP 18) analyzed by the Brunauer–Emmett–Teller method.

**Photocatalytic Test.** The photocatalytic conversion of glucose was carried out under UV irradiation using a 450 W mercury lamp in a Pyrex cylindrical double-walled reactor at room temperature and ambient pressure. The reaction temperature was maintained using a water cooling system. The initial glucose concentration was 1 g/L in a mixture of distilled water and acetonitrile (10:90 v/v).\(^{20}\) The reaction time for photocatalytic glucose conversion was 120 min. Before photocatalytic reaction, the solution was continuously stirred for 30 min under a dark condition until the homogeneous suspension of the photocatalyst was obtained and surface adsorption was completed. The samples were taken from the photoreactor at specified times and filtrated through a 0.22 mm nylon filter to remove TiO2 nanofibers. The glucose conversion was then monitored, and photocatalytic products were identified and quantitatively analyzed by high-performance liquid chromatography (HPLC Shimadzu, LC-20 AD pump) equipped with a refractive index detector (Shimadzu RID-10A). HPLC separation was performed in an Aminex HPX-87H column (300 × 7.8 mm, Bio-Rad). The mobile phase was sulfuric acid (5 mM) at a flow rate of 0.25 mL/min and an injection volume of 20 μL. Glucose conversion was calculated using eq 1.

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\text{glucose conversion} = \frac{\text{initial concentration of glucose} - \text{concentration of glucose at time} t}{\text{initial concentration of glucose}}
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(1)
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04076.

Summary of diameters and physical properties of TiO2 nanoparticles, 1 wt % Ag-TiO2 nanoparticles, 2 wt % Ag-TiO2 nanoparticles, and 4 wt % Ag-TiO2 nanoparticles prepared by the in situ technique with calcination under N2; summary of surface (from N2 adsorption) and optical (from UV–vis spectroscopy) characteristics of photocatalysts; and product yields of gluconic acid, arabinose, xylose, and formic acid obtained from photocatalytic conversion of glucose with Ag-TiO2 nanoparticles and TiO2 nanoparticles (P25) under solar light for 120 min (PDF)

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Notes

The authors declare no competing financial interest.

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