



Visible light selective photocatalytic conversion of glucose by TiO₂



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ABSTRACT

The visible-light mediated selective photo-oxidation of glucose using unmodified TiO₂ as a catalyst is reported for the first time. The effect of the catalyst to substrate ratio, lamp power and TiO₂ crystalline phases on the conversion and product distribution under both visible and UVA light is explored. Higher conversions were obtained under UVA light but as a result of substantial mineralization through an unselective pathway. Optimization of the reaction conditions resulted in 42% glucose conversion under visible light with 7% selectivity to gluconic acid and 93% selectivity to other partial oxidation products with the total suppression of a mineralization pathway to CO₂. It is also shown that selective glucose conversion can occur under natural sunlight light after 7 h exposure. In this systematic study, we prove that it is indeed possible to use TiO₂ as a photocatalyst to upgrade biomass derivatives selectively by tailoring the reaction conditions. Most importantly, we find the ligand-to-metal charge-transfer effect as a result of glucose adsorption to the surface of TiO₂ determinant in the photo-activity observed under visible light irradiation. Knowledge of this effect along with the careful control of reaction conditions means that the selective photo-catalytic conversion of other biomass derived carbohydrates under visible light is a viable route to higher value chemicals.

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1. Introduction

The conventional selective oxidation of glucose to gluconic, glucaric or even glycolic acid has been studied extensively using enzymes and heterogeneous catalysts comprising supported metal nanoparticles [1–8]. The application of photocatalysis in the upgrading of biomass, particularly glucose, is receiving increasing attention. There are a number of studies on the photocatalytic reforming of glucose for hydrogen production, in these cases, glucose is used as a sacrificial electron donor and is degraded in the process [9–11]. It has been shown that “biohydrogen” can be successfully generated using TiO₂ supported Pt and Pd photocatalysts allowing simultaneous water purification and energy production [12]. In only a few cases have the products of glucose oxidation been identified or highlighted as valuable side products of water splitting [13]. Recently, glucose oxidation products were identified as by-products when glucose was used as a sacrificial agent for the *in situ* reduction of organic compounds using the hydrogen produced from water splitting [14,15]. The recent excellent work by Colmenares [16,17] Palmisano [13,18] and Chong [19] deserves to be mentioned

in particular. They reported that the partly selective photocatalytic oxidation of glucose to aldoses such as arabinose, erythrose and glyceraldehyde can be carried out under UV light for a number of photocatalytic systems [17–21] in agreement with observations in our group. However, the ultimate goal for photocatalysis is the development of a catalytic system that can ultimately work within the solar biorefinery concept using sunlight as the energy source. For this, it is fundamental that we develop photocatalytic systems that are active under visible light. This is why most attention is now directed at the modification of TiO₂ by adding a second component to confer visible light activity. However, it would be ideal to perform these transformations using just TiO₂ and visible light. Many photocatalytic processes are associated with unselective or total mineralization reactions aimed at the purification of water and gas streams through the abatement of organic pollutants and contaminants [22–24]. In these applications, TiO₂-based materials show great potential as they are generally chemically stable, non-toxic and have high reactivity. However, TiO₂ is not photoactive under visible light and hence is understandably disregarded for visible-light-driven selective photocatalysis. When considering photocatalyst candidates, we are typically concerned with the mobility and the production rate of the active radical species, but the interaction between the substrate and the catalyst surface is also of fundamental importance and offers new unforeseen opportunities. In fact, the

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formation of a complex between TiO₂-glucose was recently identified as being responsible for the activity under visible light of TiO₂ powders for the reduction of Cr (VI) to Cr (III) in solution. The presence of a ligand-to-metal-charge-transfer complex (LMCT) allowed electrons to be injected directly on the conduction band of TiO₂ thus making them available to react [25]. Given these results, we decided to exploit this recent observation to drive the photo-activity of TiO₂ in the photo-conversion of glucose itself, with glucose acting as the reactant and co-catalyst via the formation of the LMCT system. In this work, we report for the first time the activity of TiO₂ for the conversion of glucose under visible light and study the effect of varying the light source, TiO₂ phase, and reaction conditions. The beneficial effect of using visible light on the product distribution, as compared to UVA light, is particularly noteworthy.

2. Experimental

2.1. Materials

The following reagents were used: Titanium (IV) oxide Aeroxide P25 (Acros Organics), titanium (IV) oxide anatase 99.8% (Sigma-Aldrich), titanium (IV) oxide rutile 99.99% (Sigma-Aldrich), acetonitrile (MeCN) HPLC grade 99.9% (Fisher Chemical). HPLC calibration standards: D-(+)-glucose $\geq 99.5\%$ (GC), D-gluconic acid sodium salt $>99\%$, D-(–)-arabinose $\geq 98\%$, D-(+)-glyceraldehyde $\geq 98\%$, D-(–)-erythrose $\geq 75\%$, formic acid $\geq 95\%$ were all purchased from Sigma-Aldrich and used without further purification.

2.2. Catalyst preparation

The different TiO₂ phases were dried under vacuum at 100 °C prior to reaction, and the Degussa P25 was heat treated under static air at 500 and 600 °C to increase the rutile to anatase ratio. After heat treatment, the catalysts were ground and stored in a desiccator until further use.

2.3. Catalyst characterization

The solid UV–Vis analysis of the catalysts was performed using a UV-2550 Shimadzu spectrophotometer equipped with an ISR-2200 integrating sphere (Shimadzu Corp, JP) in the range 200–800 nm with a 1 nm sampling interval and a 5 nm slit using BaSO₄ as reference. The reflectance data were used to calculate the Kubelka-Munk function using the absolute reflectance (R_∞) to evaluate the bandgap of the solid samples.

X-ray diffraction (XRD) patterns were recorded using in transmission mode using a PANalytical X'Pert Pro HTS diffractometer with a slit of 0.04° at a scanning rate of 9° min⁻¹ in the range 4–90° 2θ using a Cu-Kα radiation ($\lambda = 1.54 \text{ \AA}$).

The ATR-FTIR spectra were recorded using an HTS-XT Bruker Tensor 27 (Bruker, USA) in the range 6000–400 cm⁻¹ (resolution 4 cm⁻¹) and 32 interferograms were recorded for each sample.

Surface areas were determined by multipoint N₂ adsorption at 77 K using Quantachrome Quadrasorb instrument. Samples were degassed under vacuum at 120 °C for 1 h prior to analysis. The data were treated in accordance with the BET method.

2.4. Catalyst testing

Typically, the catalyst testing was performed in 16 mL glass vials at room temperature. Glucose solutions at different concentration were prepared by solubilizing the substrate in a 50/50 v/v MeCN/H₂O solution. Subsequently, an appropriate amount of catalyst (14 mg) was added to the solution. The reactions were performed at different reaction times, and samples were taken

every 30 min in the first 2 h and at the end of the reaction. Gas sampling studies were conducted on septum sealed vials.

The photocatalytic reactions were performed using three different systems: a Luzchem Photoreactor (Mod. LZC-4, Luzchem Research Inc. ON, CAN) equipped with 14 (8 W each) UVA lamps for a total power of 112 W. The temperature was kept constant at 25 °C for all the reactions. The second system was a 300 W Xenon Oriel Lamp (Mod. 6258, Newport, UK) controlled by a power supply (Mod.69911, Newport, UK). The third lamp used was a 1000 W Xenon Oriel Arc Lamp (Mod.6271, Newport, UK) controlled by a digital power supply (Mod.69920, Newport, UK). Both lamps were equipped with UV filters with a cut-off value of 420 nm (Mod.FSQ-GG420, Newport, UK). Additionally, due to the intense irradiation energy of the lamps, liquid IR filters were installed (Mod.61945 and Mod. 6123NS for the 300 W and 1000 W respectively) to prevent the reaction mixture from overheating. The vials were kept under magnetic stirring and at a constant distance (0.014 m) from the light source for all experiments (Additional Information: Supplementary information Figs. S1–S6).

The glucose conversion and the selectivity towards the partially oxidised products were calculated using the following formulas:

$$\text{Glucose conversion(\%)} = ([\text{Glu}]_{\text{in}} - [\text{Glu}]_{\text{out}}) / [\text{Glu}]_{\text{in}}$$

$$\begin{aligned} \text{Gluconic acid selectivity(\%)} = & ([\text{Gluconic acid}]_{\text{out}} / ([\text{Gluconic acid}]_{\text{out}} \\ & + [\text{Arabinose}]_{\text{out}} + [\text{Erythrose} + \text{Glyceraldehyde}]_{\text{out}} \\ & + [\text{Formic acid}]_{\text{out}})) \end{aligned}$$

Selectivity values are calculated on a molar basis.

2.5. Product analysis

The glucose stock solutions and reaction products were analysed with a 1200 HPLC Agilent (Agilent, USA) system equipped with a photodiode array detector (DAD) and a refractive index detector (RID). The analytical column used was an Aminex HPX-87H (300 mm × 7.8 mm), 9 μm particle size (Bio-Rad CA, USA) kept at 65 °C and using a 0.025 M H₂SO₄ as eluent with a flow rate of 0.65 mL min⁻¹. The products concentration and glucose conversion were determined using calibration curves. The accurate mass of the oxidised products obtained from glucose was analysed with an Agilent 6510 Q-TOF LC/MS system and interpreted using Agilent MassHunter Workstation Software (Version B.06.00). The column used for the mass spectrometry analysis was a Varian MetaCarb 67H (300 mm × 6.5 mm) (Agilent, USA) kept at 65 °C using a 0.1% w/w formic acid aqueous solution at a flow rate of 0.8 mL min⁻¹. The Q-TOF was operated in positive ESI mode. Hydrogen was detected using, and Agilent 7890B fitted with pulse discharge ionization detector and calibrated using a standard gas mix. The pressure rise in the sealed vessel due to gas evolution was considered to be negligible.

3. Results and discussion

3.1. Catalytic activity of TiO₂ under visible and UVA light and substrate concentration effect

Fig. 1 shows the time on line plots of conversions obtained with TiO₂ under both visible and UVA light. We were initially surprised to observe conversion and even glucose photo-oxidation under visible light with unmodified TiO₂. Furthermore, by the end of the reaction time at 240 min, conversion under visible light was surprisingly higher than under UVA when 2.8 mM of glucose was used

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