materials

MDPI

Supporting Information

Visible-Light Activated Titania and its Application to Photoelectrocatalytic Hydrogen Peroxide Production

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Determination of aqueous hydrogen peroxide

The quantity of the photoelectrocatalytically produced hydrogen peroxide can be monitored by the following procedure. First, it is necessary to make a standard solution of about 200 mg/L of aqueous H_2O_2. This concentration fits the spectroscopy data as it will be explained below. For this purpose, we used commercial 30% aqueous H_2O_2. This product was diluted 2000 times and the quantity of H_2O_2 in the diluted sample was determined by potassium permanganate titration. More specifically, the commercial product was first diluted 100 times. Then in a conic flask containing water acidified with H_2SO_4 (about 5 ml of sulfuric acid added to 150 ml of water), we added 7.5 ml of the diluted sample. This approximately makes a 2000 times dilution of the original sample. Then a solution of 20 mM potassium permanganate was added dropwise under stirring until a persistent pink color was obtained. The concentration of hydrogen peroxide in the conic flask was determined by the following formula

$$C_{H_2O_2} = 2.5 C_{per} \frac{v}{V + v}$$

where C_{per} is the concentration of the added permanganate solution (20 mM in the present case), v its volume and V is the volume of the solution before permanganate addition. The multiplication factor 2.5 comes from the well-known reaction scheme

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

which relates 2 permanganate molecules with 5 hydrogen peroxide molecules. The above titration allowed us to determine the exact concentration of hydrogen peroxide in the diluted solution and thus allowed us to make a standard aqueous H_2O_2 solution of 200 mg/L. In other words, permanganate titration was used in order to determine H_2O_2 concentration in the original commercial sample and thus safely prepare a 200 mg/L standard aqueous H_2O_2 solution.

The next step was to make a calibration curve with the help of potassium titanium oxalate (PTO). For this purpose and by following literature suggestions, a second standard aqueous solution was prepared, containing 25 mM PTO and 1M H_2SO_4. In 1 cm cuvette, we mixed 1 ml of the standard PTO solution with 0.2, 0.4, 0.6, 0.8 or 1.0 ml of the standard H_2O_2 solution. The mixture was completed by adding water so as the total volume of the water mixture to be always 2 ml. The mixture became yellow after mixing the components and gave a UV-Vis absorbance, which peaked at 400 nm. The absorbance was related with the nominal H_2O_2 concentration and produced the diagram of **Figure S1**. It is seen that with a solution of 200 mg/L H_2O_2, the corresponding absorbance remained in the range of accurate measurement by a UV-Vis spectrophotometer and this is the reason that this concentration was chosen as a standard. For the same reason, 25 mM of PTO was also chosen as a standard.

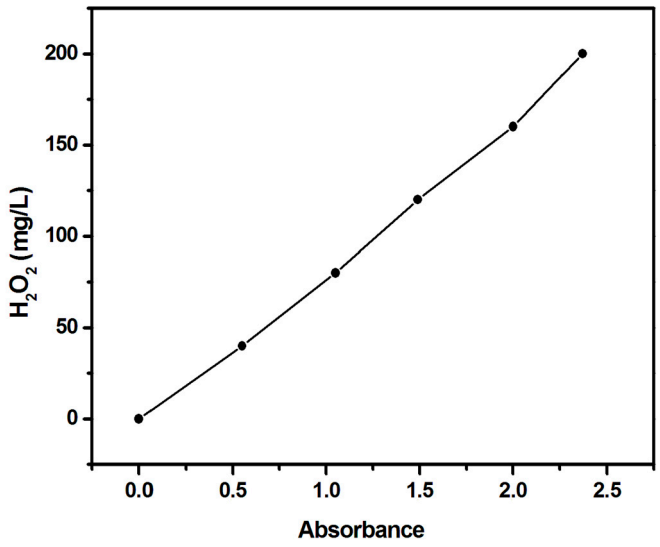

Figure S1. Nominal H_2O_2 concentration as a function of light absorbance at 400 nm. Each sample was made by mixing the same PTO solution with H_2O_2 solutions of various concentrations.

Once the calibration curve is made, we are ready to determine H_2O_2 concentration in any given sample. 1 ml of the sample is mixed with 1 ml of PTO standard solution and the corresponding hydrogen peroxide concentration is obtained by relating the obtained absorbance with the above diagram. The approximate H_2O_2 concentration can be monitored by using hydrogen peroxide detection strips (Quantifix). If the strip indicates a H_2O_2 concentration larger than 200 mg/L, the sample can be accordingly diluted. Always the quantity of the diluted sample should be 1 ml and it should be mixed with 1 ml of the standard PTO solution.