**Influence of Operational Parameters and Kinetics Analysis** **on Photocatalytic hydrolysis of Ammonia Borane for H2 Production Used Heterojunction FeTiO3/TiO2-decorated Carbon Nanofibers**

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**2. Experimental**

***2.1. Materials***

Titanium isopropoxide (TIPP, 97%, sigma Aldrich, USA)***,*** poly(vinylpyrrolidone) (PVP, sigma Aldrich, USA)***,*** iron acetate (FeAc, 98%, sigma Aldrich, USA), ammonia–borane complex (AB, 97.0%) were obtained from Sigma-Aldrich. Ethanol and acetic acid were obtained from Scharlau, Spain.

***2.2. Synthesized of FeTiO3/TiO2-decorated CNFs***

The sol-gel approach is used to produce the pristine TiO2-decorated CNFs. First, a drowsy 1.5 mL of TIPP was added to the 10 wt.% PVP solution. The procedure for making the PVP solution is described in (Yousef et al., 2016). The solution is agitated until a translucent yellow sol-gel forms. During the electrospinning process, the produced sol-gel was exposed to A copper pin immersed in sol-gel serves as the anode while a steel drum covered with aluminum foil serves as the cathode. High voltage (20kV) is applied between the electrodes while keeping a 15-cm spacing throughout the electrospinning process. After removing the produced NF mats from the aluminum foil, they remain overnight drying in a vacuum dryer set to 50 °C before being calcined in an argon atmosphere at 800 °C for 5 hours. The preceding solution was mixed with 0.6 g FeAc and stirred in order to produce FeTiO3/TiO2-decorated CNFs. After the sol-gel has been made transparent by electrospinning and calcination, it is used in the same ways as described above.

***2.3. Characterization***

The characterization of the prepared NFs membrane was identical to our recent reports (Yousef et al., 2012, Yousef et al., 2013, Yousef et al., 2015).

***2.5. Photohydrolysis of AB***

**Following our earlier work (Yousef et al., 2015), we tested the photocatalytic activity of TiO2@CNFs and FeTiO3/TiO2@CNFs for AB hydrolysis under visible light irradiation. Light was provided by a visible lamp (ʎ= 420-700 nm, I = 23-40 Wm-2). As a summary, a flask with a Teflon-coated stir bar was placed on a magnetic stirrer. The volume of H2 gas released from the photocatalytic reaction was measured using a graduated cylinder filled with water that was connected to the apparatus through rubber tubing. The reaction flask was then exposed to visible light after 1mmol of AB and a specified amount of catalyst had been added and the solution was stirred at 800 rpm mixing rate. Ammonia was removed by passing the produced H2 through a standard HCl solution of 0.001M. Several variables (the amount of AB, the amount of catalyst, the reaction temperature, and the intensity of light) have been investigated. Displacement on the water level was used to determine the volume of the released H2 gas.**

 (S2)

kapp: Reaction rate constant (min-1)

k': Equation constant (mg L-1)

KR: Rate equilibrium constant (L mg-1)

Ea: Activation energy (J mol-1)

R: Universal gas constant (J K-1 mol-1).

Ci: Initial AB concentration (mg L-1)

T: Reaction temperature (K)

m: Coefficient for light intensity (m2 W-1 min-1)

I: Light intensity (W m-2)

KNFs: Rate constant for catalyst dose (L mg-1)

CNFs: Catalyst dose (mg L-1)

 (S3)

 (S4)

 (S5)

 (S6)

 (S7)

y = ax + b

x = Ci

a =1/kLH

kLH = 1/a = 1/52.825 = 1.89\*10-2

b =1/(kLH \*KR)

KR = 1/(kLH \* b) = 1/(1.89\*10-2\* (-1.7893)) = -29.52

The best-fit line estimated slope was 0.13, indicating that the H2 production rate follows pseudo-zero order kinetics with respect to AB.

 (S8)

 (S9)

y = ax + b

x = 1/T

a=Ea/R

Ea = a\*R = 3627.8\*8.314 = 3.0162\*104

 (S10)

y = ax + b

x=I

a=m

m=55\*10-4

 (S11)

 (S12)

y = ax + b

x=1/CNFs

b=1/Ko

Ko=1/0.2823 = 3.54

a=1/(KoKNFs)

KNFs=1/(0.8133\*3.54)=0.34

**Table S1:** Rate constants of reactions of AB photohydrolysis at different AB concentration, reaction temperature, light intensity, **FeTiO3/TiO2@CNFs** dose.

|  |  |
| --- | --- |
| AB concentration (M) | Rate constant, K1 (min-1) |
| 0.1 | 0.2318 |
| 0.2 | 0.1308 |
| 0.3 | 0.072 |
| 0.4 | 0.0504 |
| Reaction temperature (°C) | Rate constant, K2 (min-1) |
| 25 | 0.2318 |
| 30 | 0.3186 |
| 35 | 0.377 |
| 40 | 0.4148 |
| Light intensity (Wm-2) | Rate constant, K3 (min-1) |
| 25 | 0.2318 |
| 30 | 0.2431 |
| 35 | 0.2762 |
| 40 | 0.3131 |
| Catalyst dose (gmL-1) | Rate constant, K4 (min-1) |
| 0.2 | 0.2318 |
| 0.3 | 0.3293 |
| 0.4 | 0.4152 |
| 0.5 | 0.5533 |

**Table S2**: Constants Values obtained using multiple regression analysis for model equation.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| k’ | KR (L mg-1) | Ea (J mol-1) | R (J K-1 mol-1) | m (m2 W-1 min-1) | Kcat (L mg-1) | Parameter |
| 3.39\*105 | -29,52 | 3.0162\*104 | 8.314 | 55\*10-4 | 0.34 | Value |

**References**

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