Supporting Information

Visible light mediated upgrading of biomass to biofuel

Sanny Verma[a†], R. B. Nasir Baig[a†], Mallikarjuna N. Nadagouda[b] and Rajender S. Varma[a*]

[a]Sustainable Technology Division, National Risk Management Research Laboratory, U. S. Environmental Protection Agency, MS 443, Cincinnati, Ohio 45268, USA. Fax: 513- 569-7677; Tel: 513-487-2701.E-mail:varma.rajender@epa.gov

[b]WQMB,WSWRD, National Risk Management Research Laboratory, U. S. Environmental Protection Agency, MS 443, Cincinnati, Ohio 45268, USA

1. Synthesis of materials

a) **Synthesis of g-C_3N_4**

b) **Synthesis of AgPd@g-C_3N_4 catalyst**

c) **Screening of AgPd@g-C_3N_4 for biofuel upgrading**

2. XPS Spectra of AgPd@g-C_3N_4 (S2)

3. Recycling of AgPd@g-C_3N_4 catalyst (S3)

4. XPS spectra of AgPd@g-C_3N_4 after 10^{th} recycle: a) Ag 3d XPS spectra; b) Pd 3d XPS spectra

5: ^1H and ^{13}C NMR of the product

1. Synthesis of materials

a) Synthesis of g-C_3N_4:

The graphitic carbon nitride g-C_3N_4 was synthesized by calcination of urea (10 g, 2 hours) at 500 ^oC.

b) Synthesis of AgPd@g-C_3N_4 catalyst:

1.0 g g-C_3N_4 was dispersed in 200 ml water using sonication. The aqueous solution of $AgNO_3$ was added in the dispersed solution of g-C_3N_4. After 10 min the solution of $Pd(NO_3)_2$ was added. The reaction mixture was stirred for 12 h. After 12 hours, the reaction temperature was raised to 50 ^oC and 2.0 g of sodium borohydride was added in portion with constant stirring. The reaction mixture becomes black after $NaBH_4$ addition (Figure S1). The reaction was further stirred for 12 hours and cool down to room temperature. The catalyst was filtered off, washed with methanol and dried under vacuum at 50 ^oC. The AgPd@g-C_3N_4 catalyst was isolated as off black powder and characterized using SEM. XRD, XPS, BET and ICP-AES analysis (Figure S1).

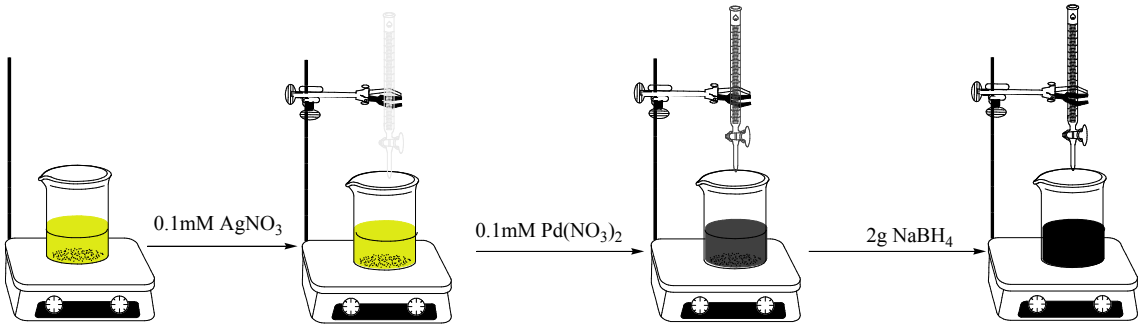


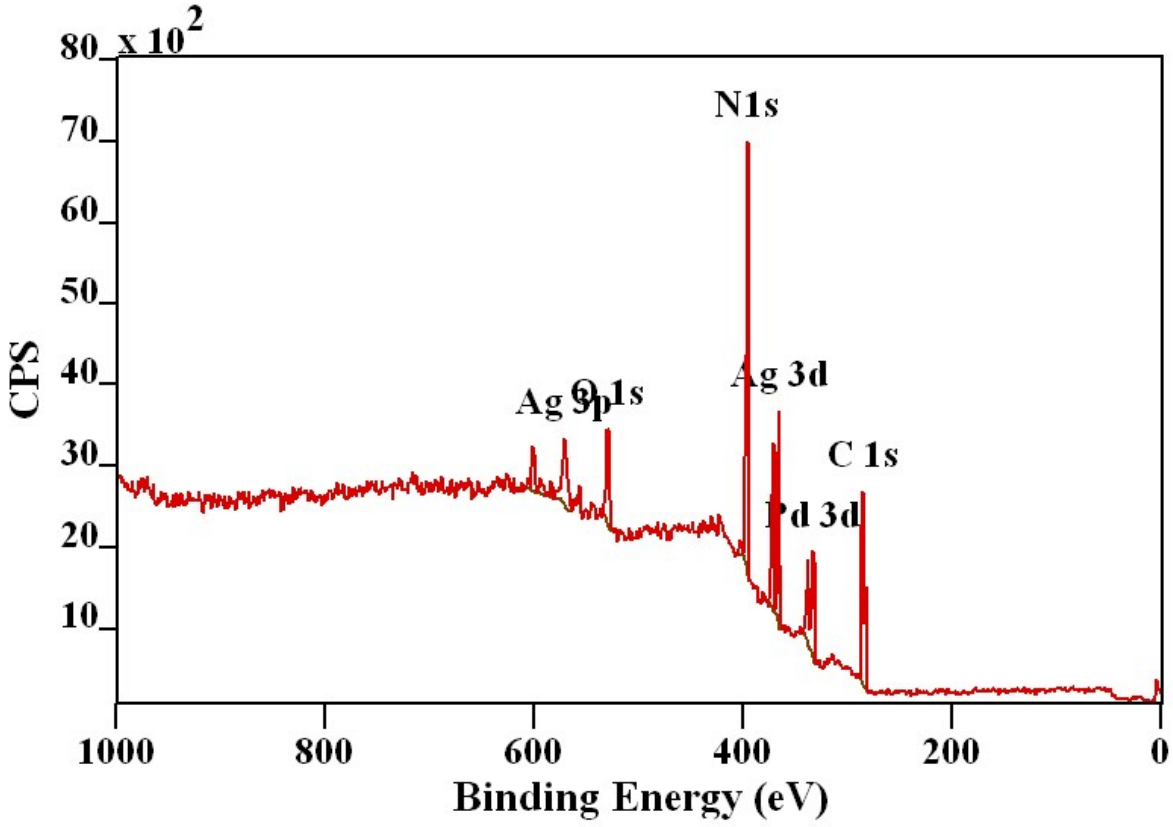
Figure S1: Pictorial presentation of the synthesis of AgPd@g-C_3N_4

c) Screening of AgPd@g-C_3N_4 for biofuel upgrading:

Vanillin (1.0 mmol), catalyst (25 mg), H_2O (1.0 mL), and formic acid (1.5 equivalent) were taken in a reaction tube (10 mL) and sealed with rubber septa. The reaction mixture was exposed to visible light using 40 Watt domestic bulb at ambient temperature and the reaction was monitored

using thin layer chromatography (TLC). After completion of the reaction, the catalyst was separated using a centrifuge. The reaction product was extracted using ethyl acetate and concentrated under reduced pressure. The isolated product was analyzed using GC-MS and NMR.

2. XPS Spectra of AgPd@g-C_3N_4

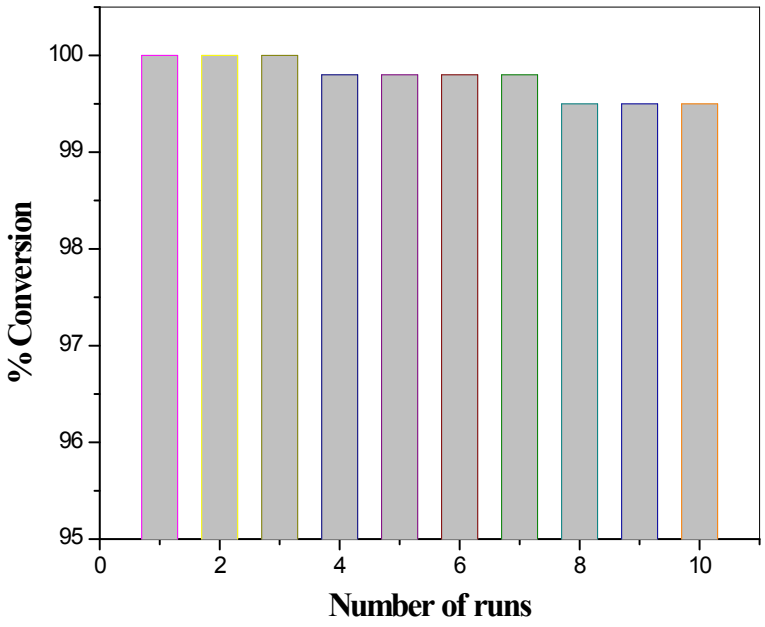


S2: XPS Spectra of AgPd@g-C_3N_4

3. Recycling of catalyst:

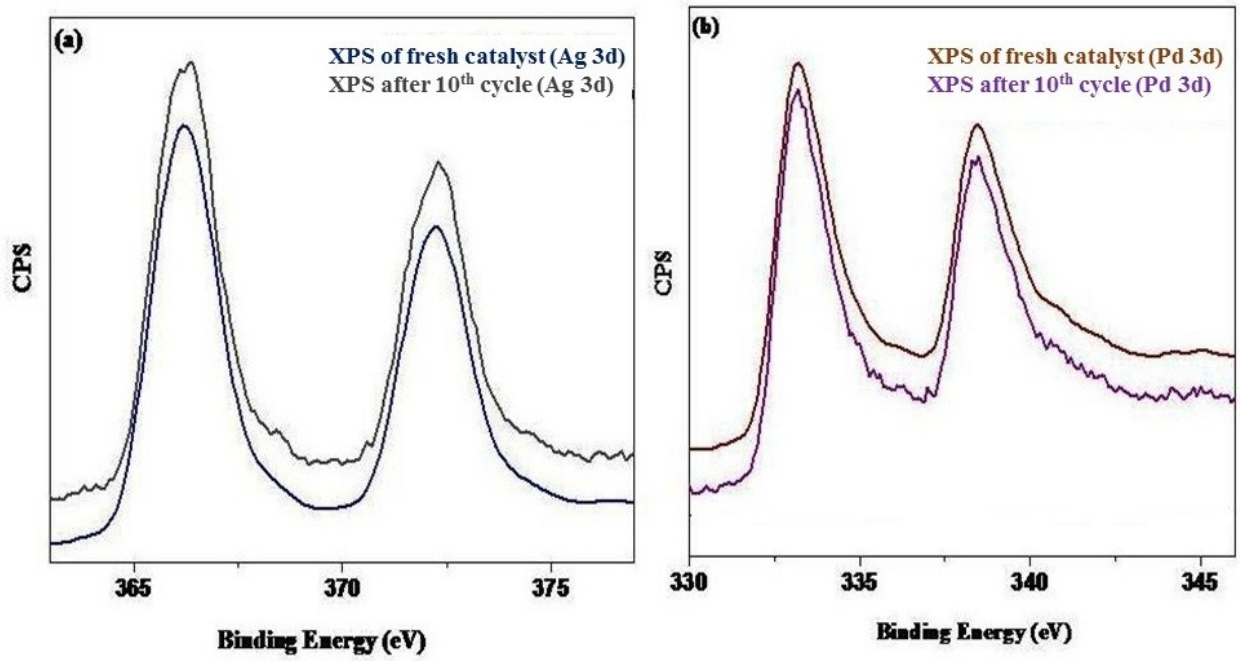
After each reaction, the catalyst AgPd@g-C_3N_4 was recovered by centrifugation, washed with water followed by acetone: methanol (1:1) mixture and dried under vacuum at 50 ^oC. The

recovered catalyst was then used for a new reaction using fresh substrate. It was observed that the catalyst remains active after the reaction can be recycled and reused over ten times without losing activity (S3).



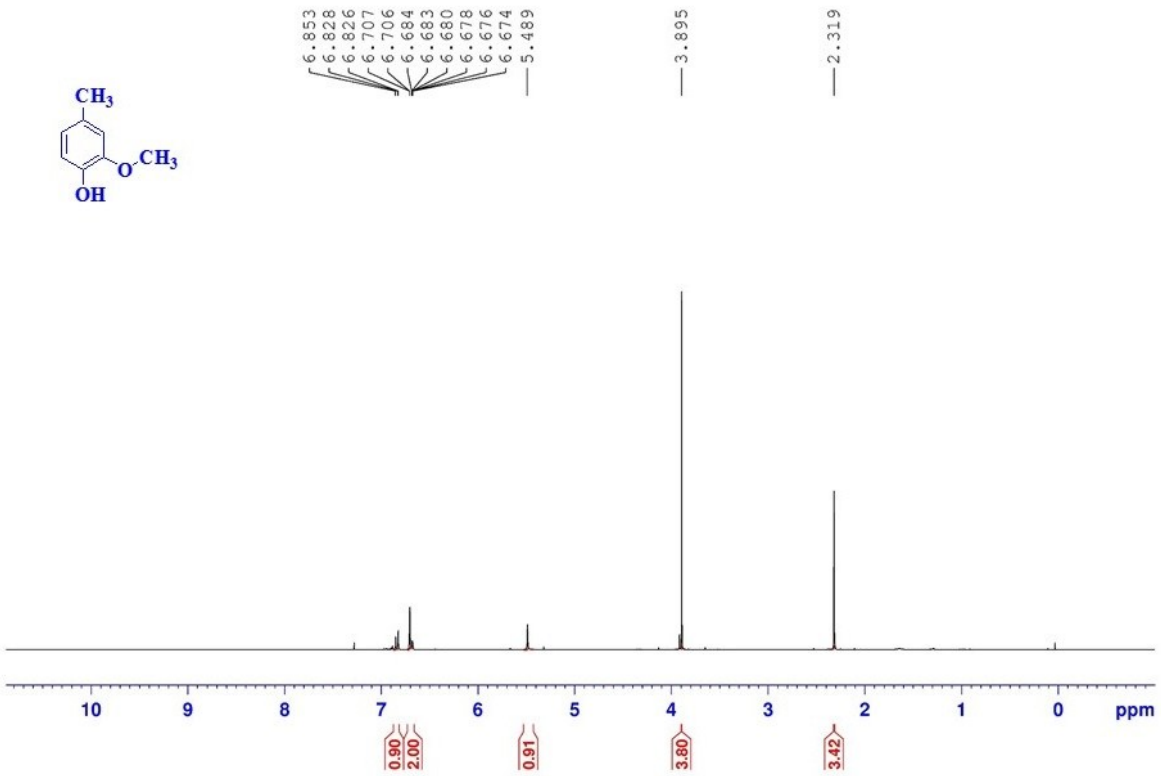
S3. Recycling of AgPd@g-C_3N_4 catalyst.

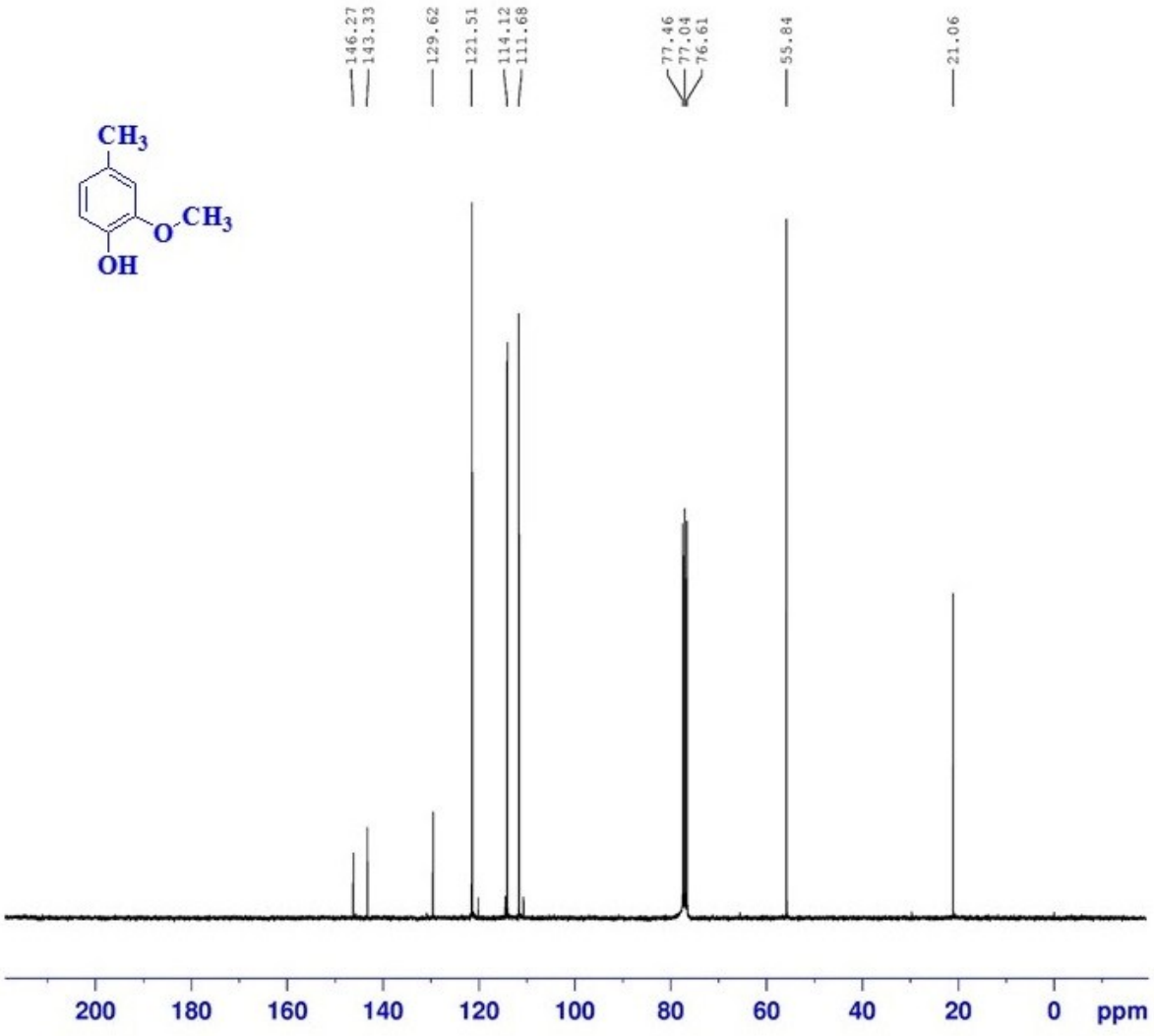
4. XPS spectra of AgPd@g-C_3N_4 after 10^{th} recycle.



S4: XPS spectra of AgPd@g-C_3N_4 after 10^{th} recycle; a) Ag 3d XPS spectra; b) Pd 3d XPS spectra

5. ^{1}H and ^{13}C NMR of the product




146.27
143.33
129.62
121.51
114.12
111.68
77.46
77.04
76.61
55.84
21.06
CH3
O
CH3
OH
200
180
160
140
120
100
80
60
40
20
0
ppm