Supporting information

One-pot synthesis of porous Ag@Pt core-shell cocatalysts on g-C_3N_4 for enhanced photocatalytic H_2 production from lignocellulose reforming

Wenchang Li[a], Weiwu Chen[b], Jianzhong Guo[a]*, Chunzheng Wu[a]*

[a] *College of Chemistry and Materials Engineering, Zhejiang A&F University, Hangzhou 311300, P. R. China.*

[b] *Yangtze Delta Region Institute (Huzhou), University of Electronic Science and Technology of China, Huzhou, 313001, PR China.*

* Corresponding authors: guojianzhong@zafu.edu.cn (J. Guo) and wucz@zafu.edu.cn (C. Wu)

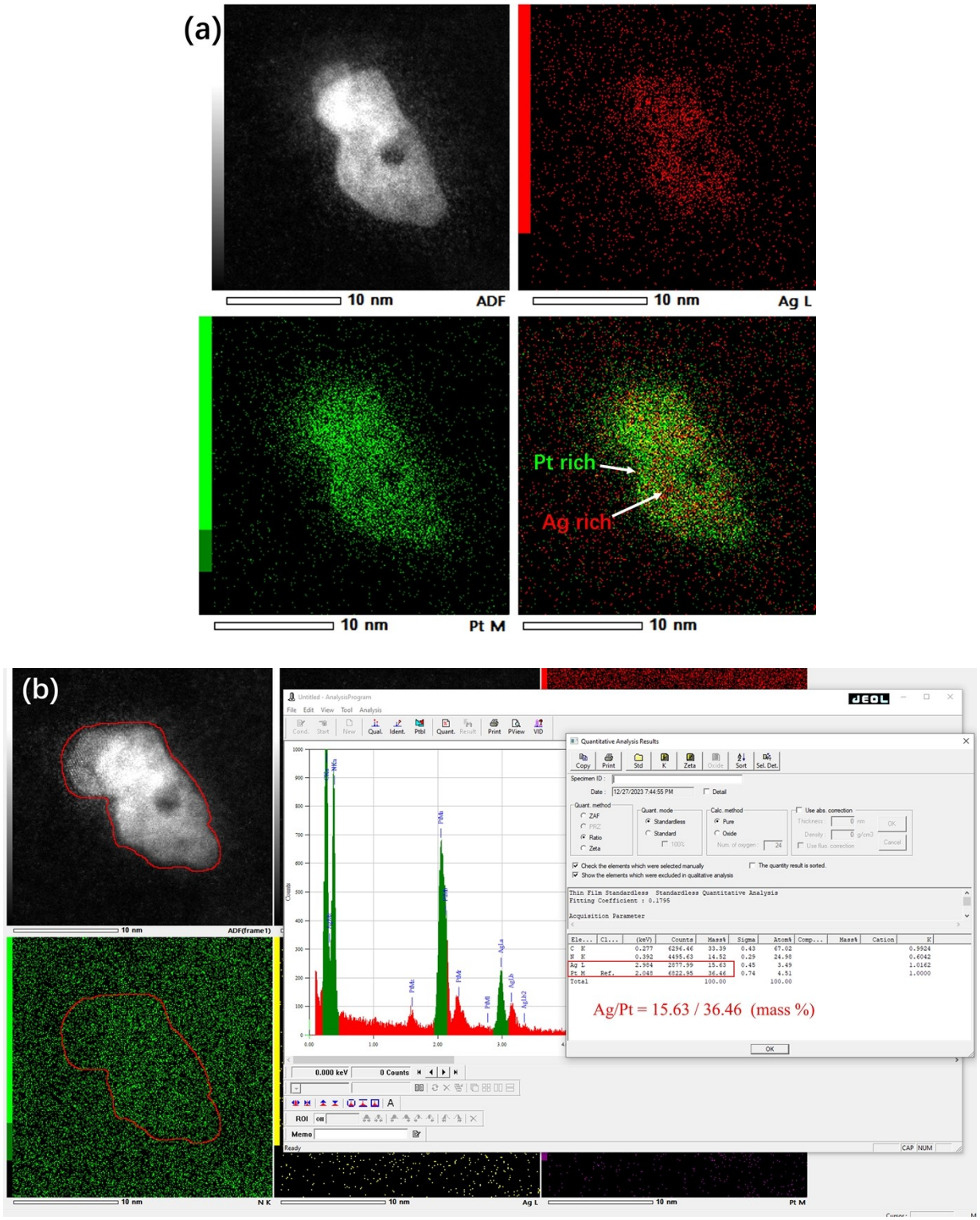

Figure S1. (a) EDS mapping of Ag_1Pt_3/CN, and (b) the corresponding metal ratio analysis.

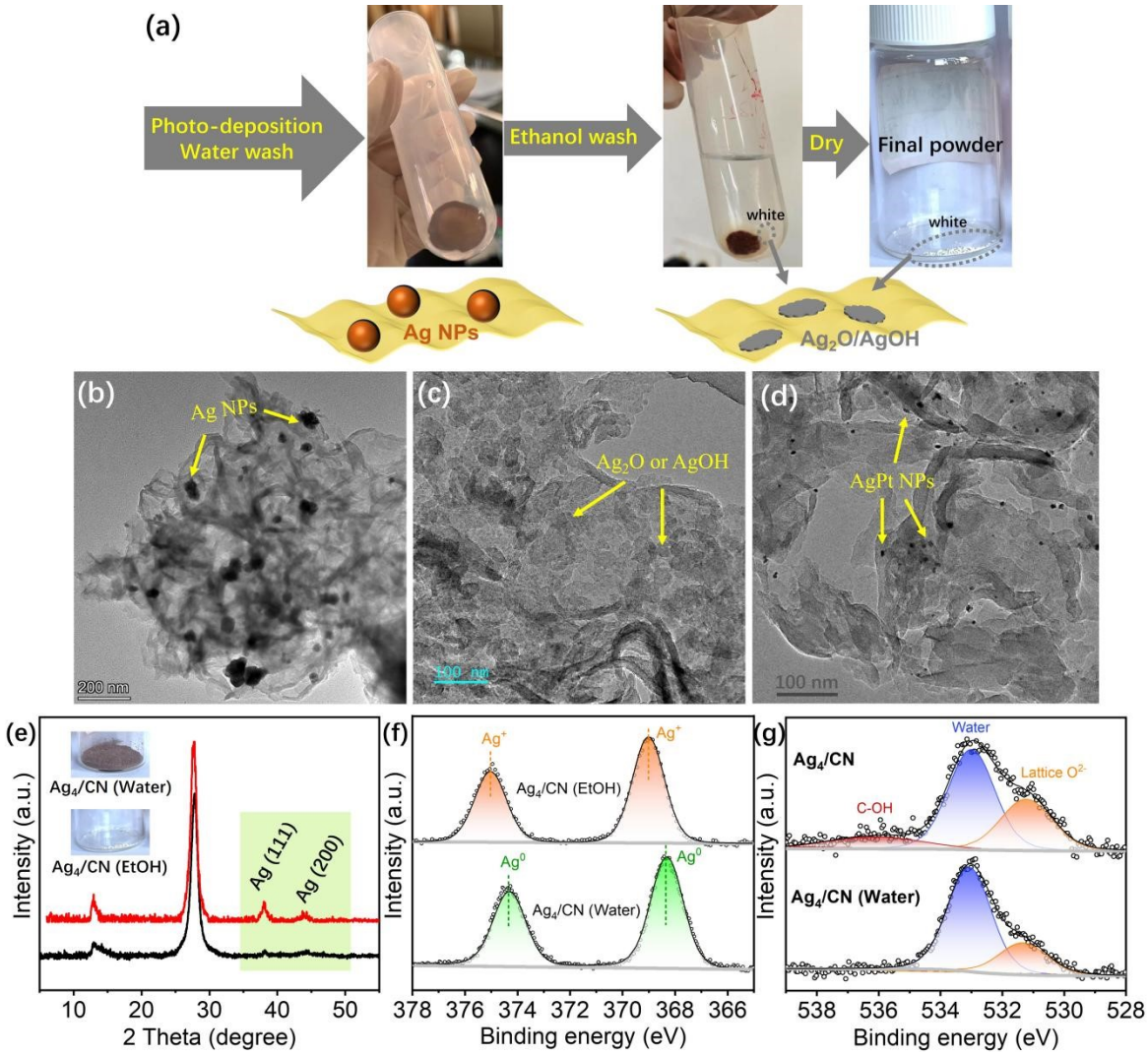

Figure S2. (a) Scheme illustrates the transformation of Ag NPs when washed with ethanol. TEM images of (b) water-washed Ag_4/CN, (c) ethanol-washed Ag_4/CN, and (d) ethanol-wahsed Ag_1Pt_3/CN. (e) The XRD patterns of water-washed Ag_4/CN and ethanol-washed Ag_4/CN. (f) XPS Ag3d and (g) XPS O1s spectra of water-washed Ag_4/CN and ethanol-washed Ag_4/CN.

Calculation of reduction potentials:

(1) Since Ag^+ ions cannot exist in an alkaline solution, we refer to the standard reduction potential for the Ag_2O/Ag pair, which is 0.342 V. The standard reduction potential for the $Pt(OH)_6^{2-}/Pt$ pair is not known, but it can be approximated using the $PtCl_6^{2-}/Pt$ pair, which is calculated to be 0.718 V, based on the $PtCl_6^{2-}/PtCl_4^{2-}$ (0.68 V) and $PtCl_4^{2-}/Pt$ (0.755 V) pairs:

$$\varphi^{\theta}(PtCl_6^{2-}/Pt) \times 4 = \varphi^{\theta}(PtCl_6^{2-}/PtCl_4^{2-}) \times 2 + \varphi^{\theta}(PtCl_4^{2-}/Pt) \times 2$$

$$\varphi^{\theta}(PtCl_6^{2-}/Pt) = \frac{0.68 + 0.755}{2} = 0.718\,V$$

(2) According to the Nernst equation at 298 K, the concentrations of $Pt(OH)_6^{2-}$ and OH^- could influence the reduction potentials (refer to detailed calculations below), resulting in adjusted values of 0.617 V for $Pt(OH)_6^{2-}/Pt$ and 0.314 V for Ag_2O/Ag at the initial state. This suggests that galvanic replacement between $Pt(OH)_6^{2-}$ and Ag is feasible.

For the $Pt(OH)_6^{2-} + 4e^- = Pt + 6OH^-$ reaction, assuming that the standard reduction potential was close to the $PtCl_6^{2-}/Pt$ pair, then the actual reduction potential of the $Pt(OH)_6^{2-}/Pt$ pair at the initial state is calculated to be 0.617 V:

$$\varphi(Pt(OH)_6^{2-}/Pt) = \varphi^{\theta}(Pt(OH)_6^{2-}/Pt) + \frac{0.059}{4} lg \frac{c\left(Pt(OH)_6^{2-}\right)}{c^6(OH^-)} \approx 0.718 + \frac{0.059}{4} lg \frac{1.03 \times 10^{-4}}{3^6} = 0.617\,V$$

For the $Ag_2O + H_2O + 2e^- = 2Ag + 2OH^-$ reaction, the actual reduction potential of the Ag_2O/Ag pair is calculated to be 0.314 V:

$$\varphi(Ag_2O/Ag) = \varphi^{\theta}(Ag_2O/Ag) + \frac{0.059}{2} lg \frac{1}{c^2(OH^-)}$$

$$\approx 0.342 + \frac{0.059}{2} lg \frac{1}{3^2} = 0.314\,V$$

(3) In principle, the galvanic replacement reaction would stop when $\varphi(Pt(OH)_6^{2-}/Pt) = \varphi(Ag_2O/Ag)$. Assuming that the concentration of OH^- did not change (NaOH is excessive), the final concentration of $Pt(OH)_6^{2-}$ was calculated to be 2.97×10^{-15} mol/L, indicating that ~100% of $Pt(OH)_6^{2-}$ would be reacted.

$$\varphi(Pt(OH)_6^{2-}/Pt) = \varphi(Ag_2O/Ag)$$

$$0.718 + \frac{0.059}{4} lg \frac{c\left(Pt(OH)_6^{2-}\right)}{3^6} = 0.314$$

$$c\left(Pt(OH)_6^{2-}\right) = 2.97 \times 10^{-15}\, mol/L$$

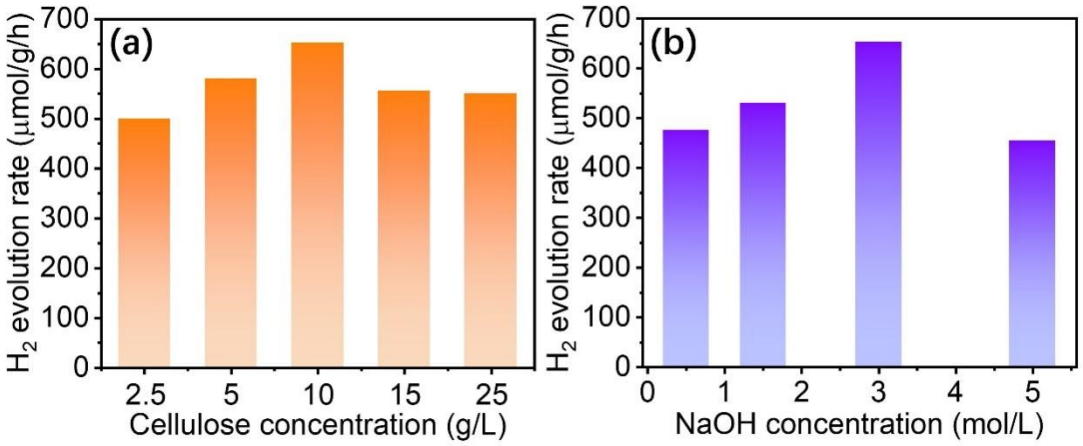

Figure S3. the effects of (a) cellulose concentration and (b) NaOH concentration on H_2 evolution.

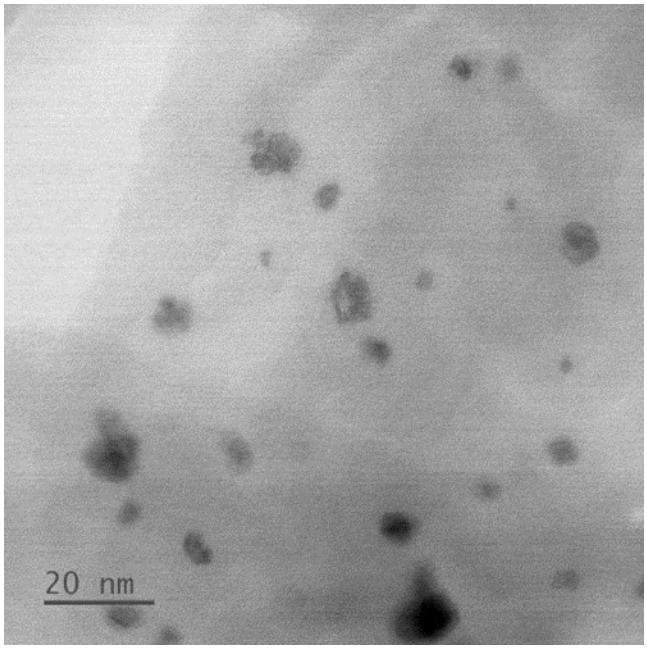

Figure S4. TEM image of Ag_1Pt_3/CN after 12 hours of test.

Table S1. Comparison of our Ag_1Pt_3/CN with the reported g-C_3N_4 and TiO_2 based photocatalysts in H_2 evolution from cellulose reforming.

Photocatalyst	HER rate (μmol/g/h)	Light source	Conditions	Reference
Ag_1Pt_3/CN (10 mg)	652.7	300 W Xe lamp 150 mW/cm^2	5 g/L cellulose 3 M NaOH	This work
0.21 wt.% Pt/C_3N_4 (10 mg)	1110	40 W blue LED (λ = 427 nm)	2 g/L α-cellulose 10 M NaOH	Wang et al.[1]
Pt_1Au_3/CN (10 mg)	1186	300 W Xe lamp 150 mW/cm^2	5 g/L cellulose 3 M NaOH	Ding et al.[2]
4 wt.% Pt/$^{NCN}CN_x$ (5 mg)	~ 10	AM1.5G	33.3 g/L cellulose 10 M KOH	Kasap et al.[3]
0.8 wt.% Pt/HCN-NEA (30 mg)	1007	Xe lamp (λ > 420 nm)	2.5 g/L α-cellulose 5 M NaOH	Liu et al.[4]
1 wt.% Pt/monolayer g-C_3N_4 (50 mg)	72.67	300 W Xe lamp (λ > 420 nm)	5 g/L α-cellulose pH = 10	Rao et al.[5]
2 wt.% Pt/CNNs (50 mg)	94.33	300 W Xe lamp (400 < λ < 780nm)	0.5 g/L cellulose 3 M NaOH	Hong et al.[6]
3 wt.% Pt/K-PHI-450 (200 mg)	190.6	420 < λ < 800nm	50 g/L cellulose 0.8 M NaOH	Nimbalkar et al.[7]
g-C_3N_4-$C_{0.40}$ (20 mg)	104.4	300 W Xe lamp (λ ≥ 630 nm)	20 g/L α-cellulose 10 M NaOH	Xie et al.[8]
0.3 wt.% Pd/TiO_2 (50 mg)	436	3 MH-lamps of 150 W	3.33 g/L cotton linter cellulose	Abdul Razak et al.[9]
1% wt.% Pt/anatase TiO_2 nanosheet (100 mg)	275	300 W Xe lamp	4 g/L cellulose Sonication	Cheng et al.[10]
2 wt.% Pt/P25 (10 mg)	614.7	395 nm LED	5 g/L Napkin 10 M NaOH	Wu et al.[11]
TiO_2/NiO_x@C_g (20 mg)	270	500 W Xe lamp	20 g/L cellulose Sonication	Zhang et al.[12]
1 wt.% Pt/TiO_2 (100 mg)	305.83	300 W Xe lamp	5 mL filtrate of acid treated corn straw	Zhou et al. [13]

Reference

[1] Wang, E.; Mahmood, A.; Chen, S.-G.; Sun, W.; Muhmood, T.; Yang, X.; Chen, Z., Solar-Driven Photocatalytic Reforming of Lignocellulose into H_2 and Value-Added Biochemicals. *ACS Catalysis* **2022,** *12*, 11206-11215.

[2] Ding, F.; Yu, H.; Tu, R.; Li, S.; Chen, L.; Li, B.; Guo, J.; Wu, C., Engineering Au-Pt atomic alloy cocatalysts for enhanced H_2 production from photo-reforming of lignocellulosic biomass wastes. *Chemical Engineering Journal* **2024,** *496*, 154260.

[3] Kasap, H.; Achilleos, D. S.; Huang, A.; Reisner, E., Photoreforming of Lignocellulose into H_2 Using Nanoengineered Carbon Nitride under Benign Conditions. *Journal of the American Chemical Society* **2018,** *140*, 11604-11607.

[4] Liu, Q.; Wang, F.; Jiang, Y.; Chen, W.; Zou, R.; Ma, J.; Zhong, L.; Peng, X., Efficient photoreforming of lignocellulose into H_2 and photocatalytic CO_2 reduction via in-plane surface dyadic heterostructure of porous polymeric carbon nitride. *Carbon* **2020,** *170*, 199-212.

[5] Rao, C.; Xie, M.; Liu, S.; Chen, R.; Su, H.; Zhou, L.; Pang, Y.; Lou, H.; Qiu, X., Visible Light-Driven Reforming of Lignocellulose into H_2 by Intrinsic Monolayer Carbon Nitride. *ACS Applied Materials & Interfaces* **2021,** *13*, 44243-44253.

[6] Hong, Y.; Zhang, X.; Lin, X.; Liu, E.; Wang, L.; Shi, W.; Duan, X., Ultrathin 2D g-C_3N_4 nanosheets for visible-light photocatalytic reforming of cellulose into H_2 under neutral conditions. *Journal of Chemical Technology & Biotechnology* **2022,** *97*, 1717-1725.

[7] Nimbalkar, D. B.; Nguyen, V.-C.; Shih, C.-Y.; Teng, H., Melem-derived poly(heptazine imide) for effective charge transport and photocatalytic reforming of cellulose into H_2 and biochemicals under visible light. *Applied Catalysis B: Environmental* **2022,** *316*, 121601.

[8] Xie, Z.-K.; Jia, Y.-J.; Huang, Y.-Y.; Xu, D.-B.; Wu, X.-J.; Chen, M.; Shi, W.-D., Near-Infrared Light-Driven Photocatalytic Reforming Lignocellulose into H_2 and Chemicals over Heterogeneous Carbon Nitride. *ACS Catalysis* **2023,** *13*, 13768-13776.

[9] Abdul Razak, S.; Mahadi, A. H.; Abdullah, R.; Yasin, H. M.; Ja'afar, F.; Abdul Rahman, N.; Bahruji, H., Biohydrogen production from photodecomposition of various cellulosic biomass wastes using metal-TiO_2 catalysts. *Biomass Conversion and Biorefinery* **2023,** *13*, 8701-8712.

[10] Cheng, Q.; Yuan, Y.-J.; Tang, R.; Liu, Q.-Y.; Bao, L.; Wang, P.; Zhong, J.; Zhao, Z.; Yu, Z.-T.; Zou, Z., Rapid Hydroxyl Radical Generation on (001)-Facet-Exposed Ultrathin Anatase TiO_2 Nanosheets for Enhanced Photocatalytic Lignocellulose-to-H_2 Conversion. *ACS Catalysis* **2022,** *12*, 2118-2125.

[11] Wu, C.; Fang, L.; Ding, F.; Mao, G.; Huang, X.; Lu, S., Photocatalytic hydrogen production from water and wastepaper on Pt/TiO_2 composites. *Chemical Physics Letters* **2023,** *826*, 140650.

[12] Zhang, L.; Wang, W.; Zeng, S.; Su, Y.; Hao, H., Enhanced H_2 evolution from photocatalytic cellulose conversion based on graphitic carbon layers on TiO_2/NiO_x. *Green Chemistry* **2018,** *20*, 3008-3013.

[13] Zhou, Y.; Lin, D.; Ye, X.; Sun, B., Reuse of Acid-treated Waste Corn Straw for Photocatalytic Hydrogen Production. *ChemistrySelect* **2022,** *7*, e202201596.