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Photocatalytic Reduction of Nitrobenzene to Aniline over CdS Nanorods: the Impacts of Reaction Conditions and the Hydrogenation Mechanism

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Fig. S1. a) Picture of the reaction cell for PHNB. b) Emission spectrum of the light source used for the PHNB test

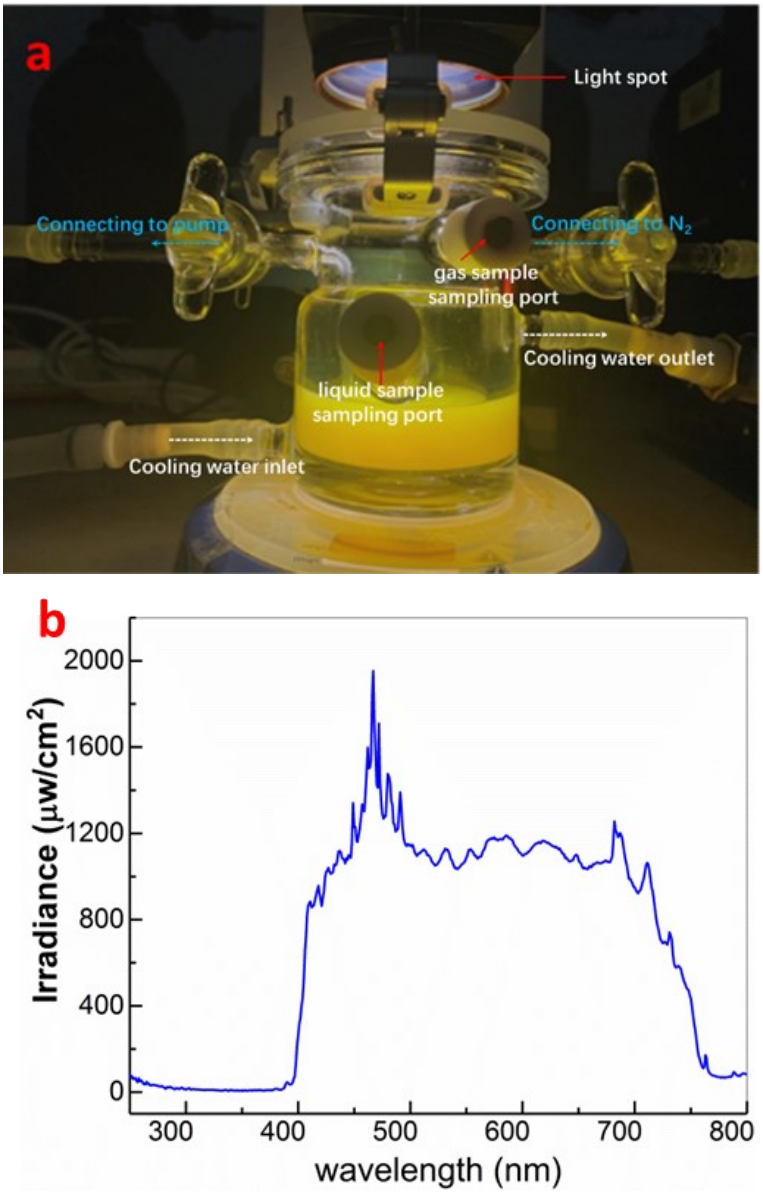


Fig. S2. The high resolution XPS of Pt 4f, Au 4f and Ru 3d on the corresponding CdS samples

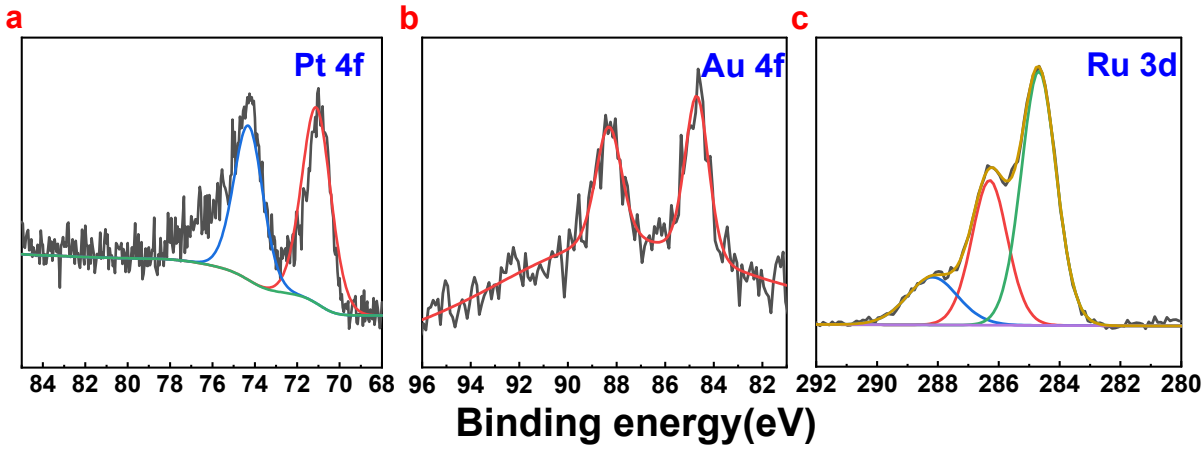


Fig. S3. High resolution mass spectroscopic data of the products except NSB were further recorded on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF (LC/Q-TOF/MS) system, (a) AOB, (b) AB, (c) PHA, and (d) AN.

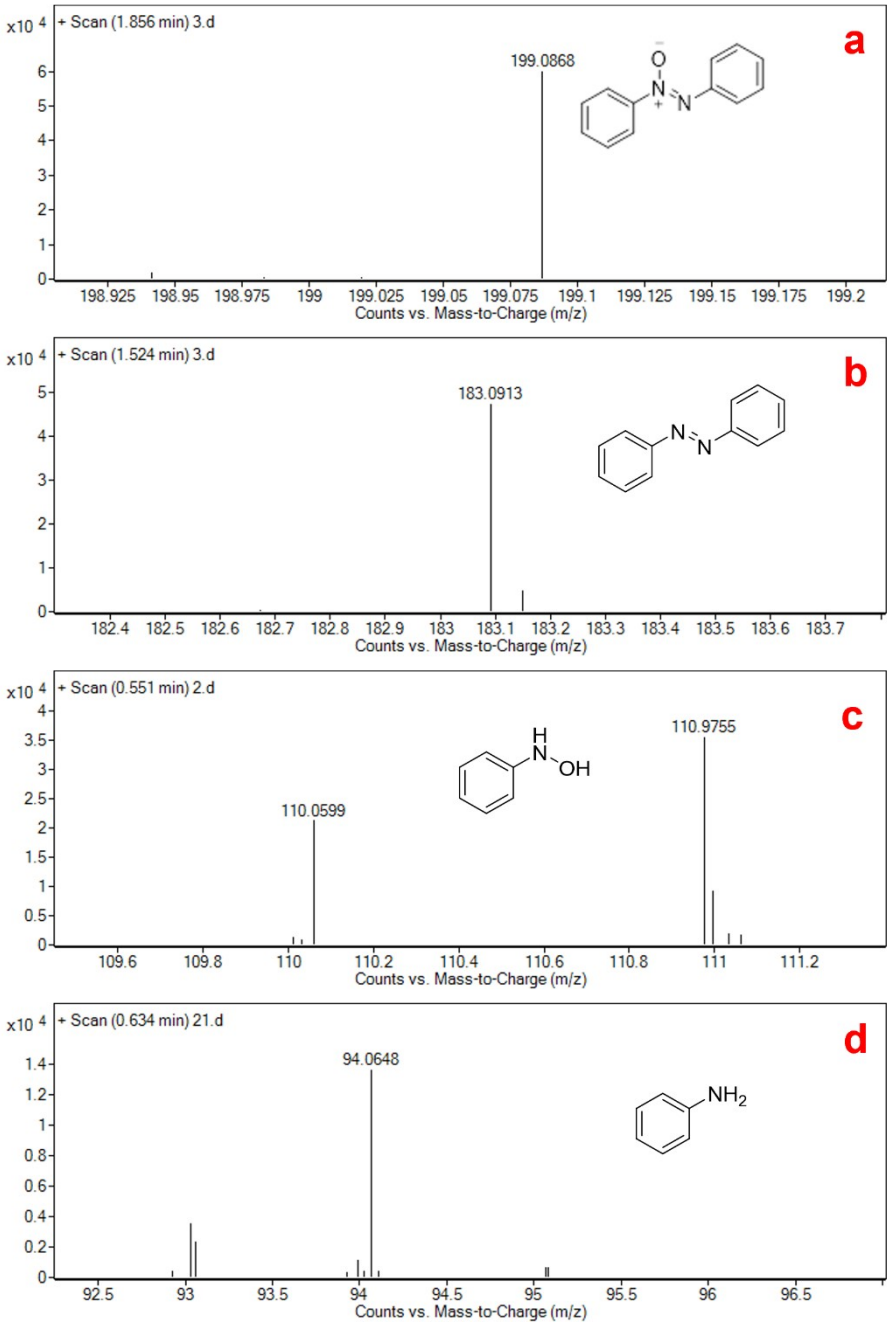
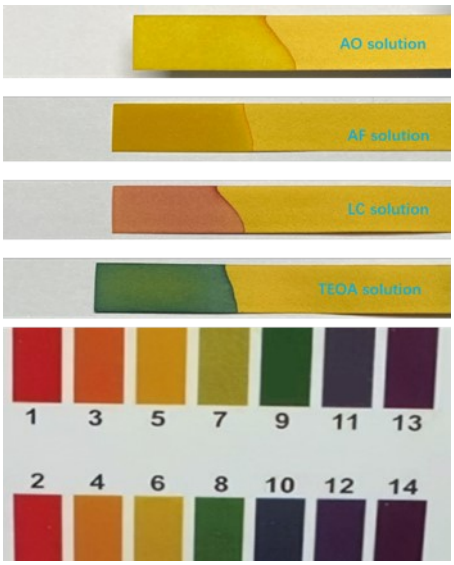


Fig. S4. The suspension of AO in ethanol solution (25% H_2O).

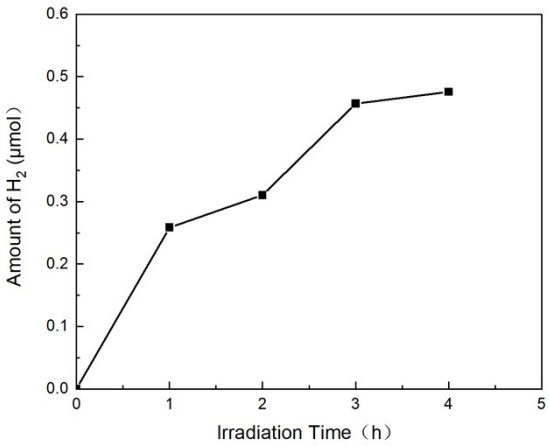
AO can be easily dissolved in H_2O. However, when 75% ethanol was introduced to form the mixture solution, a stratification of AO is occurred. Similar phenomenon was encountered for TEOA.

Fig. S5. the measurements of pH values of the reaction solutions after irradiation for 4 h by universal pH indicator paper.



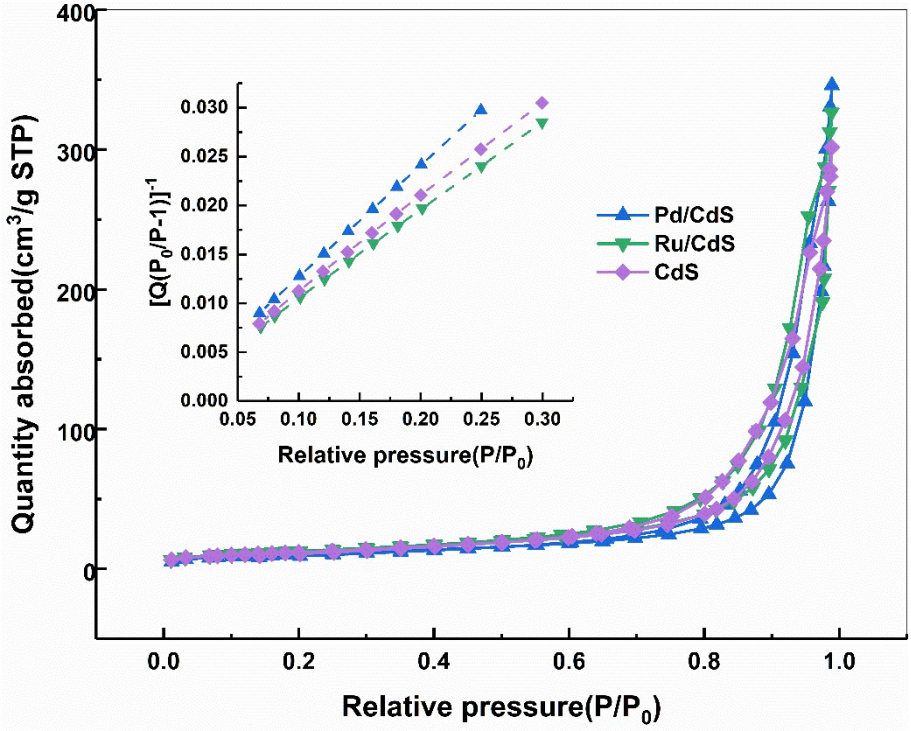
The pH values of the reaction solutions after irradiation for 4 h were measured by universal pH indicator paper. As shown below, the pH of LC solution is ca. 4, while for other solutions, the pH values are in the range of 6-8. It confirms the LC solution is indeed weakly acidic.

Fig. S6. Tentative measurement of the evolution of H_2 over Pt modified CdS in the reaction system.



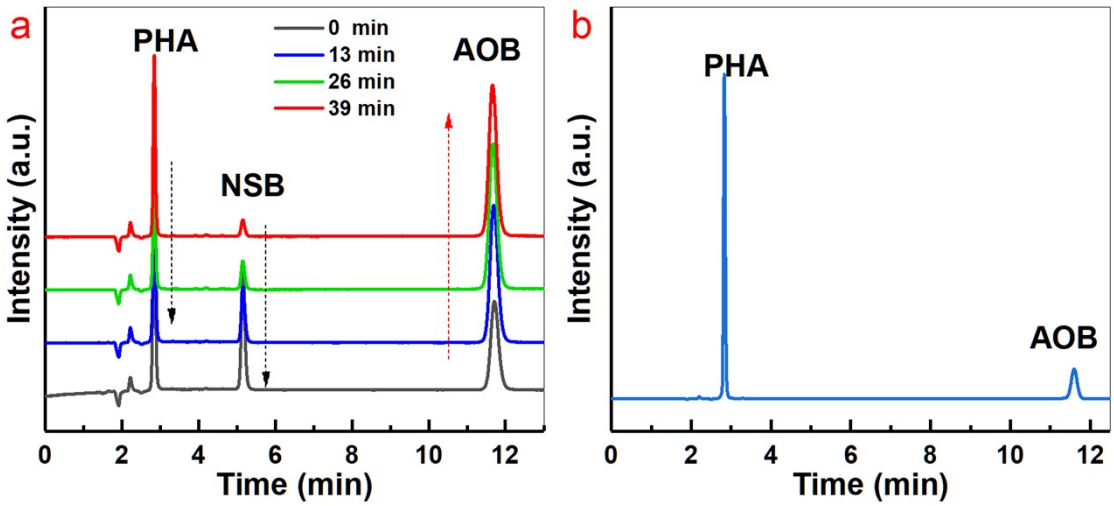
The formation of H_2 over Pt modified CdS in the reaction system has been tentatively measured by offline GC (TCD detector, N_2 as carrier gas). As it shown, a consistent increase of H_2 amount could be observe in the system, suggesting the H_2 evolution is a competing reaction of reduction of NB.

Fig. S7. N_2 adsorption–desorption isotherms of prepared Pd/CdS, Ru/CdS, and CdS samples. Insert shows the corresponding BET transform plots of 1/Q[(P0/P)-1] versus P/P_0.



The BET surface areas of the prepared samples were analyzed by N_2 adsorption at 77 K. The transform plots indicated that the BET surface area of CdS, Pd/CdS, and Ru/CdS are 44, 38, and 47 m^2/g, respectively. There is no significant difference in texture of CdS and the modified CdS samples.

Fig. S8. HPLC chromatogram of (a) the mixture solution of PHA and NSB after stirring for different time, and (b) the PHA solution stored overnight.



To confirm the condensation reaction between NSB and PHA, a qualitative experiment was performed with some PHA and NSB co-dissolved in ethanol. After stirring for deserved time, the HPLC chromatogram of the mixture solution were recorded. The results indicated that some AOB is produced immediately with the mixing of PHA and NSB. With stirring time prolonged, the amount of PHA and NSB gradually decreased, while the amount of AOB gradually increased, indicating a spontaneous condensation between NSB and PHA.

Furthermore, we found that partial of PHA even can undergoes a self-condensation to generate AOB.

Table. S1 Summarize the hydrogenation performance of NB over Pd/CdS for 5 runs. Each round was irradiated for 5 h.

Run	C_{NB}	Y_{AN}	Y_{NSB}	Y_{AOB}	Y_{AB}	Y_{PHA}
1	99.93	77.89	7.50	0.00	2.41	0.27
2	99.83	77.04	8.24	0.00	2.14	0.23
3	99.90	77.29	7.77	0.00	1.07	0.18
4	99.77	76.79	6.96	0.00	0.97	0.15
5	99.98	76.68	7.06	0.00	3.45	0.37