Supplementary Information

Bi-functionality of organic acids as acid catalysts and hydrogen source for one-pot production of secondary amines from primary amines and aromatic aldehydes over an Au-C_3N_4 photocatalyst

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Experimental

1. Chemicals

All chemicals (guaranteed reagents) were purchased from FUJIFILM Wako Pure Chemical, Osaka and used without further purification except for alcohols, which were dried before reactions using molecular sieves.

2. Preparation of C_3N_4

Melamine and urea were mixed in an alumina crucible in a 1:9 mass ratio. The crucible was covered with a lid and heated in a muffle furnace at 450°C under a continuous flow of nitrogen gas. The solid product was crushed in a mortar, suspended in a sulfuric acid solution with pH of 4 for 4 h, and washed with distilled water. After suction filtration, the sample was dried in an incubator under vacuum for 4 h and then in an oven at 80°C for 12 h.

3. Preparation of Au-C_3N_4

C_3N_4 powder (99 mg) was suspended in a mixture of methanol (1 cm^3), an aqueous solution of tetrachloroauric(III) acid ($HAuCl_4$, 1 cm^3) and water (8 cm^3) in a test tube. The test tube was sealed with a rubber septum under argon (Ar). Loading of Au nanoparticles on C_3N_4 was achieved through a repetitive cycle of photodeposition (P) and ultrasonic treatment (U). Photodeposition was conducted at 20°C in a water bath, using a 400 W high-pressure mercury arc (KPI, Hyogo, Japan) as the UV light source ($\lambda >$ 300 nm) to facilitate the reduction of Au(III) to Au(0) on the surface of C_3N_4. Ultrasonic treatment was subsequently applied to reduce the size of Au particles loaded on the surface of C_3N_4. The sequence of P and U was repeated as follows: P5-U1-P15-U1-P30-U1-P60-U1-P90 (number indicating time in minutes). Subsequently, the Au-loaded C_3N_4 (Au-C_3N_4) was washed with distilled water, dried for 4 h under vacuum, and

then dried in an oven at 80°C for 12 h. Atomic absorption spectrometry for the liquid phase after the photodeposition revealed that Au was almost quantitatively loaded on C_3N_4.

4. Characterization

Powder X-ray diffraction of C_3N_4 was recorded on a MiniFlex (Rigaku, Tokyo, Japan) in the Joint Research Center (JRC) at Kindai University using Cu$K\alpha$ radiation with a monochromator. Fourier transform infrared (FT-IR) spectra of samples were measured on an FT-IR spectrometer (FT/IR-6600, JASCO, Tokyo, Japan), and a KBr pellet of the sample was previously prepared in vacuo. Diffuse reflectance spectra of the samples were acquired using a UV-visible spectrometer (UV-2400, Shimadzu, Kyoto) together with a diffuse reflectance measurement unit (ISR-2000, Shimadzu). Morphology and particle size of the prepared samples were observed under a scanning electron microscope (SEM, S-4800, Hitachi, Tokyo) after platinum sputtering and under a transmission electron microscope (TEM, JEM-2100F, JEOL, Tokyo) operated at 200 kV in JRC at Kindai University. The specific surface areas of samples were calculated using the BET single point method based on nitrogen uptake measured at -196°C.

5. Formation of imine by condensation of aldehyde and amine in the dark

Fifty mg of C_3N_4 or Au-C_3N_4 was suspended in 5 cm^3 of 2-propanol (guaranteed reagents, FUJIFILM Wako Pure Chemical) in the absence and presence of an organic acid (100 μmol) in a test tube. After sealing the tube with a rubber septum under argon (Ar), an alcohol solution containing BAD (50 μmol) and an alcohol solution containing AN (45 μmol) were quickly injected into the test tube in that order. The suspension was stirred in the dark for 1 h until the condensation of AN and BAD reached an equilibrium. The compounds (BAD, AN and BAN) in the liquid phase were analyzed by an FID-type gas

chromatograph (GC-2025, Shimadzu) with a DB-1 column. Toluene was used as the internal standard sample.

6. Photocatalytic hydrogenation of imine to secondary amine over Au-C_3N_4

The suspension in the test tube after the above condensation process was photoirradiated with a high-pressure mercury arc (KPI) at 20°C. The compounds (BAD, AN, BAN and PBA) in the liquid phase were analyzed by an FID-type gas chromatograph (GC-2025, Shimadzu, Kyoto) with a DB-1 column. Unreacted 2-propanol and acetone that were formed in the liquid phase were analyzed by an FID-type gas chromatograph (GC-2025, Shimadzu) with a DB-WAX column. Toluene was used as the internal standard sample. Hydrogen (H_2) and carbon dioxide (CO_2) in the gas phase were analyzed by a TCD-type gas chromatographs (GC-8A, Shimadzu) with an MS-5A column and a Porapak Q-S column, respectively.

7. Action spectrum measurement

To investigate the efficiency of light energy utilization at specific wavelengths in photocatalytic reactions, we calculated the apparent quantum efficiency (AQE) and measured action spectra. The reaction mixture was irradiated with visible light from an Xe lamp equipped with band-pass filters (Asahi Spectra, Tokyo, Japan). The quantity of PBA was quantified in accordance with the methodology described in the preceding section, after which AQE was determined by Equation 1.

$$\mathrm{AQE} = \frac{2\times\text{amount of PBA}}{\text{number of incident photons}} \times 100. \quad (1)$$

Results

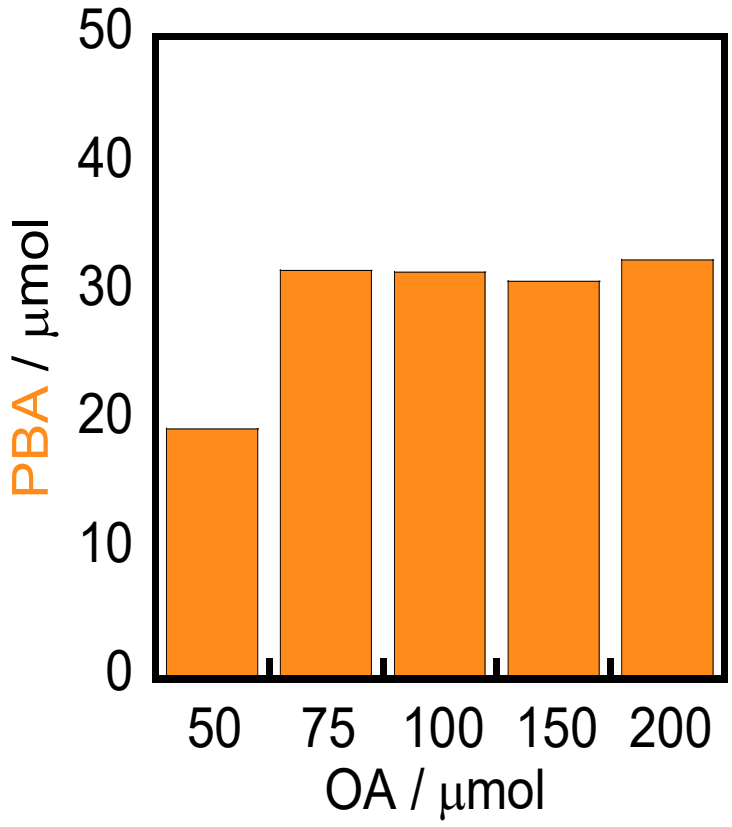

Fig. S1 Effects of different amounts of OA on production of PBA from AN and BAD via BAN in a 2-propanol suspension. The reaction was carried out in the dark for the first 0.5 h and under irradiation of UV light from a mercury lamp for 3 h.

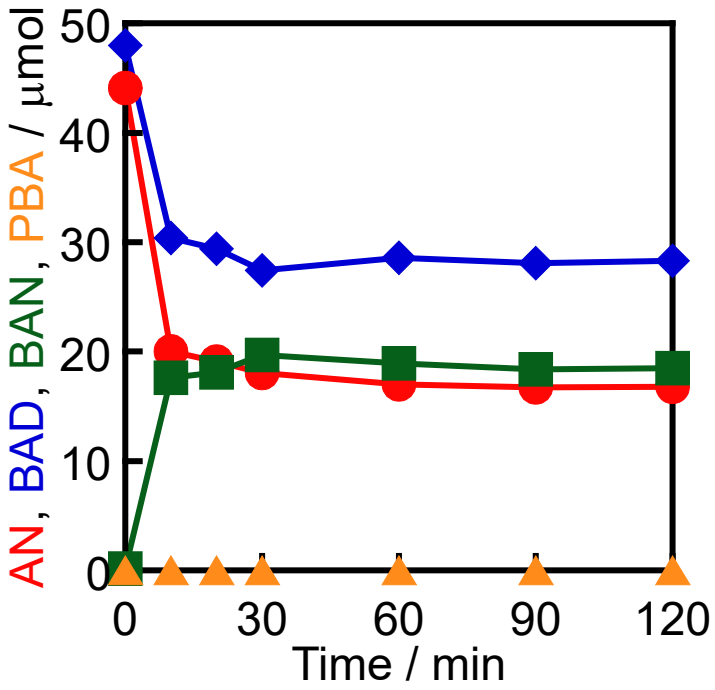

Fig. S2 Time courses of the amounts of BAD (◆), AN (●), BAN (■) and PBA (▲) in a 2-propanol suspension of Au-C_3N_4 in the presence of OA in the dark under 1 atm H_2.

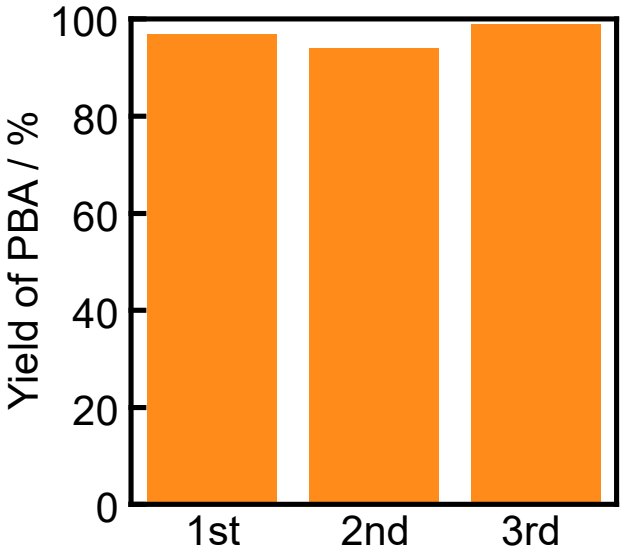

Fig. S3 Durability test of 1wt%Au-C_3N_4 in production of PBA from AN and BAD via BAN in the 2-propanol suspension in the presence of OA as an acid catalyst and a hole scavenger. The reaction was carried out in the dark for 0.5 h and under irradiation of UV light from a mercury lamp for 5 h.