Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

In-situ synthesis of Cu nanocatalysts on ZnO whiskers embedded in a microstructured paper composite for autothermal hydrogen production

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Experimental details

Preparation of ZnO whisker-containing paper by a papermaking technique

Paper composite preparation details have been described in our previous reports.[1,2] The outline of a papermaking procedure is summarized as follows. A ceramic fibers (IBIWOOL, IBIDEN, Ltd.) and ZnO whiskers (Panatetra, Matsushita Amtec Co., Ltd.)/water suspension (1.6%, w/v) was mixed with cationic polydiallyldimethylammonium chloride (0.5 wt% per solids, molecular weight: ca. 3×10^5; charge density: 5.5 meq g^{-1}; Aldrich, Ltd.), an alumina sol binder (Snowtex 520, Nissan Chemicals, Ltd.), and anionic polyacrylamide (0.5 wt% per total solids, HH-351; molecular weight: ca. 4×10^6; charge density: 0.64 meq g^{-1}; Kurita, Ltd.) in that order. The mixture was added to the suspension of commercial bleached hardwood kraft pulp fiber (0.125%, w/v), and solidified by dewatering using a 200-mesh wire. The handsheets were dried in an oven at 105°C for 1 h, following pressing at 350 kPa for 3 min. The obtained paper composite (2×10^4 mm^2) consisted of ZnO whiskers (3.1 g), ceramic fibers (5.0 g), alumina sol (0.50 g) and pulp fibers (0.25 g). The ZnO whisker-containing paper obtained was calcined at 350°C for 12 h to remove pulp fibers and to improve the physical strength by binder sintering.

Preparation of Cu/ZnO powder, CuNPs@ZnO whisker and CuNPs@ZnO paper

The preparation procedure of CuNPs@ZnO whiskers is illustrated in **Fig. S1**. $Cu(NO_3)_2{\cdot}3H_2O$ (99.9% purity, Wako Pure Chemical Industries, Ltd.) was dissolved in deionized water. ZnO whiskers (3.72 g) were mixed with the aqueous solution of $Cu(NO_3)_2$ (9.4×10^{-2} M, 100 mL), followed by stirring for 20 min, filtration and washing with deionized water. Subsequently, the obtained products were dried at 105°C for 12 h and reduced in a stainless steel cylindrical reactor with a hydrogen flow (30 mL/min) at 250°C for 1.5 h. In the case of CuNPs@ZnO paper, ZnO whisker-containing paper was cut into disc-shaped pieces (8×10^2 mm^2) and immersed in the aqueous solution of $Cu(NO_3)_2$ (9.4×10^{-2} M, 100 mL) for 20 min. The discs were then removed from the aqueous solution using a pair of tweezers, washing with deionized water, drying at 105°C for 12 h and reduced in hydrogen at 250°C for 1.5 h. Cu/ZnO powders were obtained according to the conventional co-precipitation method [3] and reduced in hydrogen at 250°C for 1.5 h before catalytic performance testing.

Analyses

The Cu and Zn contents of the samples were determined by atomic absorption analysis using a Shimadzu AA-6600F apparatus.[1,2] The concentrations of Cu^{2+} or Zn^{2+} eluted from the Cu/ZnO component with 35% nitric acid were quantified through flame atomic absorbance. Transmission electron microscopy (TEM) was carried out with a JEM1010 instrument (JEOL, Ltd.) at an accelerating voltage of 80 kV. The chemical states of the component elements were analyzed by an X-ray photoelectron spectroscopy (XPS, AXIS-HSi spectrometer, Shimadzu/Kratos, Ltd.). The X-ray diffractometry (XRD) studies were conducted using an XD-D1 X-ray diffractometer (Shimadzu, Ltd.) with Ni-filtered Cu$K\alpha$ radiation (λ = 1.5418 Å) with a scanning angle (2θ) of 30°-60° at a voltage of 30 kV and a current of 40 mA; the Scherrer formula was used to calculate the Cu crystallite size on the basis of the full width at half maximum of Cu(111) reflection.[4] Surface observation of CuNPs@ZnO paper was performed using a scanning electron microscope (SEM, JSM-5600, JEOL, Ltd.).

ATR performance test

ATR performance testing was conducted according to our previous reports.[2] Ten disc-shaped CuNPs@ZnO paper composites were vertically stacked (8×10^3 mm^3) and placed inside a stainless steel cylindrical reactor. In a similar way, Cu/ZnO catalyst powders or CuNPs@ZnO whiskers were loaded inside the reactor, whereas ceramic powders were mixed to adjust the occupied volume to 8×10^3 mm^3. The reactor setup details are referred to in the previous papers.[2] In each case, the amount of Cu and the weight ratio of ZnO to Cu was set at 0.2 g and 5.2, respectively. A mixed gas with methanol/water/oxygen (molar ratio: 1.00/1.50/0.125) vaporized at 200 °C was fed into the reactor at 250°C or 310°C at a constant gas space velocity of 1130 h^{-1}. The gas generated in the ATR reaction was passed through a cold trap in an ice bath; then the unreacted methanol and water residues were separated from the gaseous components. After 2 h of the ATR operation, the flow rate of the generated gas was monitored every second for 3 h using a mass flow meter (3810S, KOFLOC, Ltd.). The methanol conversion was calculated by averaging the gas flow rate as compared to the theoretical flow rate at maximum by taking the unreacted methanol and water in the cold trap into consideration. The major gaseous products, hydrogen (ca. 73%) and carbon dioxide (ca. 27%), were analyzed online using a gas chromatograph (GC)-thermoconductivity detector equipped with a Porapak-Q column (3 mm × 2 m, Shinwa Chemical Industries, Ltd.). Carbon monoxide as a minor by-product (less than 1%) was measured using a GC-flame ionization detector equipped with a Porapak-Q column after the complete conversion of carbon monoxide to methane by an online methanizer (MTN-1, Shimadzu, Ltd.).

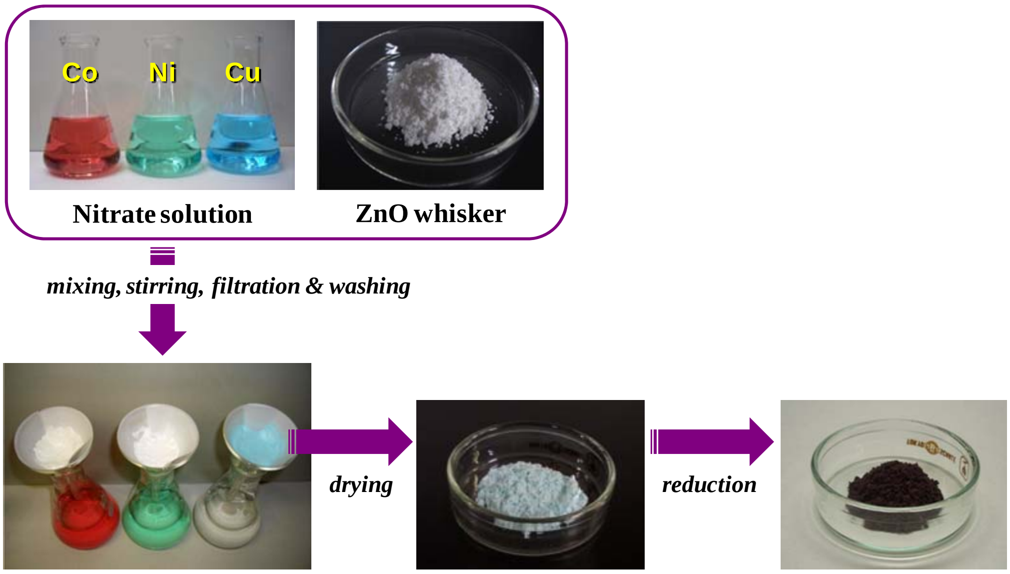

Fig. S1 The adsorption of Cu species from Cu nitrate solution on ZnO whiskers.

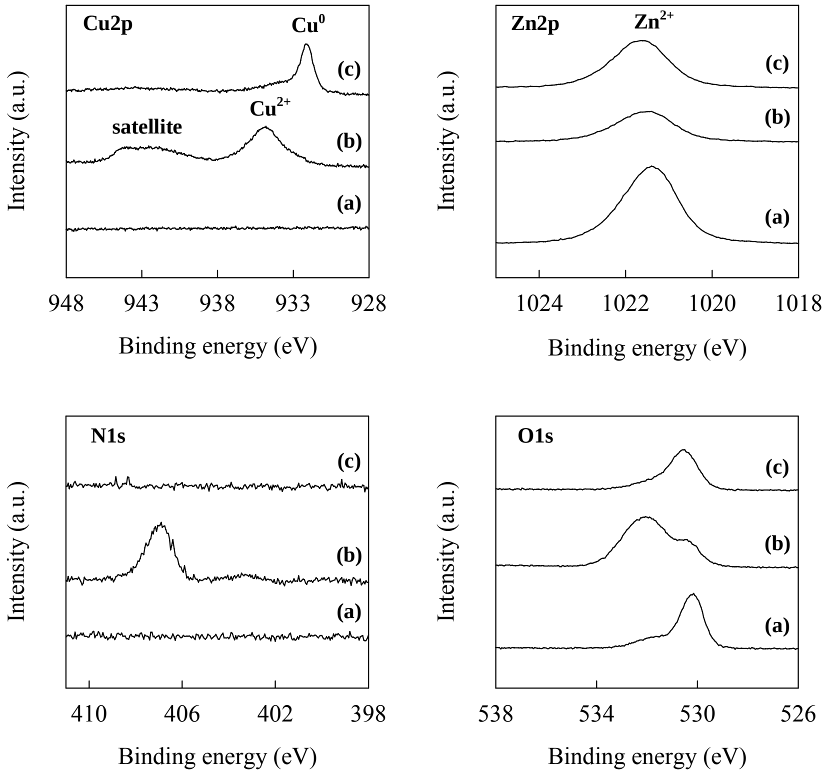

Fig. S2 X-ray photoelectron spectra of original ZnO whiskers (a) and ZnO whiskers treated with Cu nitrate solution; as-dried (b) and reduced (c).

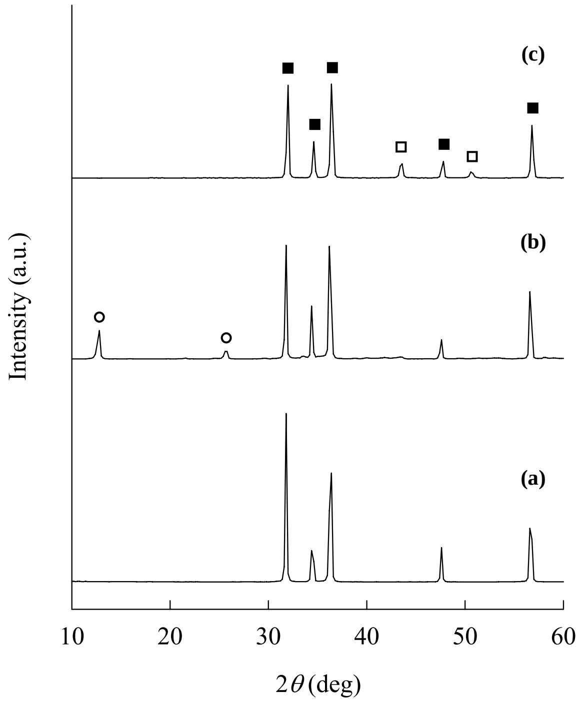

Fig. S3 XRD patterns of original ZnO whiskers (a) and ZnO whiskers treated with Cu nitrate solution; as-dried (b) and reduced (c). ○: $Cu_2(OH)_3(NO_3)$, □: Cu, ■: ZnO.

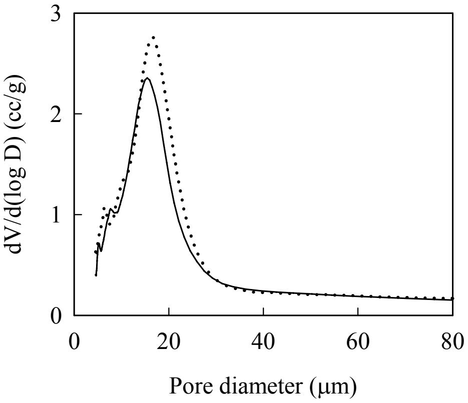

Fig. S4 Pore size distribution; ZnO whisker-containing paper composite (dotted line) and CuNPs@ZnO whisker-containing paper composite (solid line).

References

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