Experimental

**General.** Commercial chemicals were used as received for catalyst preparation and hydrazine decomposition experiments. Hydrazine monohydrate ($\text{H}_2\text{NNH}_2\cdot\text{H}_2\text{O}$, 99%), sodium borohydride (NaBH₄, 99%), hexadecyltrimethyl ammonium bromide (CTAB, 95%), hexadecyltrimethyl ammonium chloride (CTAC, 95%) and FeCl₂·4H₂O (95%) were obtained from Aldrich. H₂IrCl₆, CoCl₂·6H₂O (99.5%), NiCl₂·6H₂O (99.9%), and CuCl₂ (95%) were purchased from Wako.

**Instrumentation.** Mass analysis of the generated gases was performed using a Balzers Prisma QMS 200 mass spectrometer. Powder X-ray diffraction (XRD) studies were performed on a Rigaku RINT-2000 X-ray diffractometer (Cu Kα). UV-visible spectral analyses were performed on Shimadzu UV-2550 spectrophotometer. Scanning electron microscope (SEM, Hitachi S-5000) and transmission electron microscope (TEM, FEI
TECNAI G²) equipped with selected area electron diffraction (SAED) and energy dispersed X-ray detector (EDX) were applied for the detailed microstructure information. The SEM and TEM samples were prepared by depositing few droplets of the nanoparticle suspension onto the amorphous carbon coated copper grids, which were dried under argon atmosphere. The surface area measurements were performed by N₂ adsorption at liquid N₂ temperature using automatic volumetric adsorption equipment (Belsorp II). ¹⁵N NMR spectra were recorded on a JEOL JNM-AL400 spectrometer at an operating frequency of 40.40 MHz. Liquid samples were contained in 5.0-mm-o.d. sample tubes, in which coaxial inserts containing CD₃CN (¹⁵N, δ -134.00 ppm) as an external reference and a lock were placed. XPS analysis was carried out on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg Kα source (10 kV, 10 mA). The Ar sputtering experiments were carried out under the conditions of background vacuum 3.2 × 10⁻⁶ Pa, sputtering acceleration voltage 1 kV.

**Preparation of Ni₀.₉₅Ir₀.₀₅-B, Ni₀.₉₀Ir₀.₁₀-B, Ni₀.₇₅Ir₀.₂₅-B, Ni₀.₆₀Ir₀.₄₀-B, Ni₀.₅₀Ir₀.₅₀-B and Ni₀.₂₅Ir₀.₇₅-B nanocatalysts.** To a 2.0 mL aqueous suspension of NiCl₂·6H₂O (0.045 g) and CTAB (0.100 g), 500 µL of H₂IrCl₆ (0.02 M) were added and the light-yellow suspension was subsequently sonication and stirring for 5 min. The resulting homogenous suspension was heated at 50 °C in a water bath, leading to the appearance of a bright orange suspension. The suspension was cooled to room temperature, to which a 1.5 mL aq. NaBH₄ (0.35 M) solution was added dropwise. The content of the flask is vigorously shaked for 5 min, resulting in the generation of Ni₀.₉₅Ir₀.₀₅-B nanocatalyst as a black suspension, which was used for the catalytic reaction. Ni₀.₉₀Ir₀.₁₀-B, Ni₀.₇₅Ir₀.₂₅-B, Ni₀.₆₀Ir₀.₄₀-B, Ni₀.₅₀Ir₀.₅₀-B and Ni₀.₂₅Ir₀.₇₅-B nanocatalysts were prepared by using 0.008
and 0.043 g, 0.020 and 0.036 g, 0.032 and 0.028 g, 0.041 and 0.024 g, and 0.061 and 0.012 g of H$_2$IrCl$_6$ and NiCl$_2$·6H$_2$O, respectively, by following the above procedure for Ni$_{0.95}$Ir$_{0.05}$-B nanocatalyst.

**Preparation of Ni$_{0.95}$Ir$_{0.05}$-C and Ni$_{0.90}$Ir$_{0.10}$-C nanocatalysts.** An analogous synthetic procedure was followed as above to prepare Ni$_{0.95}$Ir$_{0.05}$-C and Ni$_{0.90}$Ir$_{0.10}$-C by using CTAC in place of CTAB.

**Preparation of the physical mixture of Ni and Ir nanocatalysts.** Separately prepared Ni and Ir nanocatalysts were mixed together in the ratio of 95 mol% Ni and 5 mol% Ir.

**Preparation of CTAB stabilized M$_{0.95}$Ir$_{0.05}$ (M = Fe, Co and Cu) nanocatalysts.** The M$_{0.95}$Ir$_{0.05}$-B (M = Fe, Co, Cu) nanocatalysts were synthesized using the similar method as for the Ni$_{0.95}$Ir$_{0.05}$-B nanocatalyst using FeCl$_2$·4H$_2$O (0.038 g), CoCl$_2$·6H$_2$O (0.045 g) and CuCl$_2$ (0.026 g), respectively, in place of NiCl$_2$·6H$_2$O.

**Catalytic hydrous hydrazine decomposition experiments.** Catalytic reactions were carried out at room temperature using a two-necked round bottom flask with one of the flask openings connected to a gas burette and another for the introduction of hydrazine monohydrate. Catalytic decomposition reaction of hydrazine for the release of hydrogen (along with nitrogen) was initiated by stirring the mixture of hydrazine monohydrate (0.1 mL, 1.97 mmol), which was introduced by using a syringe to the reaction flask containing the 4.0 mL aqueous suspension of the nanocatalysts (catalyst/hydrazine molar ratio 1/10). The gases released during the reaction was passed through a trap containing
1.0 M hydrochloric acid to ensure the absorption of ammonia, if produced, of which the volume was monitored using the gas burette.

**Characterization of nanocatalysts.** NiIr nanocatalysts were collected by centrifugation (15000 rpm, 10 min, 298 K) and were washed twice with 5.0 mL of water and 5.0 mL of ethanol. The nanoparticles were washed by acetone and dried under vacuum at room temperature for 8 h before characterisation by SEM, TEM, XPS and powder XRD.

**Fig. S1** UV-vis absorption spectra after (a) the addition of aqueous solutions of the mixture of Ni\(^{2+}\) and Ir\(^{4+}\) salts, (b) heating the solution (a) for 5 min at 50 °C (inset shows the colours observed for (a) and (b)), (c) reduction of the solution (b) by NaBH\(_4\) for the preparation of surfactant free Ni\(_{0.95}\)Ir\(_{0.05}\) nanocatalysts.
Fig. S2 The XPS profiles of Ni and Ir for the Ni$_{0.95}$Ir$_{0.05}$, Ni$_{0.95}$Ir$_{0.05}$-B and Ni$_{0.95}$Ir$_{0.05}$-C nanocatalysts (a) before and (b) 2, (c) 4, (d) 6, (e) 66 and (f) 186 min after argon sputtering.
**Fig. S3** The XPS profiles of oxygen 2p level for the Ni$_{0.95}$Ir$_{0.05}$-B and Ni$_{0.95}$Ir$_{0.05}$-C nanocatalysts.
**Fig. S4** The XPS profiles of the electron binding energy scanning ranges of B and Cl for the Ni$_{0.95}$Ir$_{0.05}$-B and Ni$_{0.95}$Ir$_{0.05}$-C nanocatalysts.
**Fig. S5** Powder-XRD patterns of (a) $\text{Ni}_{0.95}\text{Ir}_{0.05}$, (b) $\text{Ni}_{0.95}\text{Ir}_{0.05}$-B and (c) $\text{Ni}_{0.95}\text{Ir}_{0.05}$-C nanocatalysts.
Fig. S6 Powder-XRD patterns of (a) Ni$_{0.99}$Ir$_{0.01}$-B, (b) Ni$_{0.95}$Ir$_{0.05}$-B, (c) Ni$_{0.90}$Ir$_{0.10}$-B, (d) Ni$_{0.75}$Ir$_{0.25}$-B, (e) Ni$_{0.60}$Ir$_{0.45}$-B, and (f) Ni$_{0.50}$Ir$_{0.50}$-B nanocatalysts.
**Fig. S7** EDX patterns for (a) $\text{Ni}_{0.95}\text{Ir}_{0.05}$, (b) $\text{Ni}_{0.95}\text{Ir}_{0.05}$-$B$ and (c) $\text{Ni}_{0.95}\text{Ir}_{0.05}$-$C$ nanoparticles.
Fig. S8 $^{15}$N NMR spectra (298 K, referenced to CD$_3$CN, $\delta$ -134.00 ppm) of (a) hydrous hydrazine (0.5 M), (b and c) after the reactions (2 h and 4 h, respectively) of (a) and (d) after the completion of hydrazine decomposition reaction of (a) over the Ni$_{0.95}$Ir$_{0.05}$-B nanocatalyst (catalyst/N$_2$H$_4$ molar ratio = 1:10) at 298 K.
**Fig. S9** Time course plots for decomposition of hydrous hydrazine (0.5 M) catalyzed over nickel-iridium alloy nanocatalysts (a) \( \text{Ni}_{0.90}\text{Ir}_{0.10} - B \) and (b) \( \text{Ni}_{0.90}\text{Ir}_{0.10} - C \) (catalyst/N\(_2\)H\(_4\) molar ratio = 1:10) at 298 K.
**Fig. S10** Selectivity for hydrogen generation by decomposition of hydrous hydrazine (0.5 M) catalyzed by Ni, Ni$_x$Ir$_{1-x}$-B ($x = 0.95, 0.90, 0.75, 0.60, 0.50,$ and 0.25) and Ir nanocatalysts (catalyst/N$_2$H$_4$ molar ratio = 1:10) at 298 K.
Fig. S11 Time course plots for hydrogen generation by decomposition of hydrous hydrazine (0.5 M) catalyzed by Ni$_x$Ir$_{1-x}$-B ($x = 0.95$, 0.90, 0.75, 0.60, 0.50 and 0.25) nanocatalysts (catalyst/N$_2$H$_4$ molar ratio = 1:10) at 298 K.
Fig. S12 Time course plots for decomposition of hydrous hydrazine (0.5 M) catalyzed over (a) Ni NPs, (b) Ir NPs, (c) Ni$_{0.95}$Ir$_{0.05}$, (d) Ni$_{0.95}$Ir$_{0.05}$-B and (e) the physical mixture of Ni and Ir NPs (catalyst/N$_2$H$_4$ molar ratio = 1:10) at 298 K.
Fig. S13  Nitrogen adsorption-desorption isotherms of Ni$_{0.95}$Ir$_{0.05}$, Ni$_{0.95}$Ir$_{0.05}$-$B$ and Ni$_{0.95}$Ir$_{0.05}$-$C$ nanocatalysts at 77 K ($P_0 = 1.0$ atm).
**Fig. S14** Selectivity for hydrogen generation from decomposition of hydrous hydrazine (0.5 M) catalyzed over Fe, Co, Ni, Cu, Ir, Fe$_{0.95}$Ir$_{0.05}$, Co$_{0.95}$Ir$_{0.05}$, Ni$_{0.95}$Ir$_{0.05}$ and Cu$_{0.95}$Ir$_{0.05}$ (catalyst/N$_2$H$_4$ molar ratio = 1:10) nanocatalysts obtained in the presence of CTAB at 298 K.
Fig. S15 SEM images of (a) Ni$_{0.95}$Ir$_{0.05}$, (b) Ni$_{0.95}$Ir$_{0.05}$-B and (c) Ni$_{0.95}$Ir$_{0.05}$-C nanocatalysts.