Highly Dispersed Noble-Metal/Chromia (Core/Shell) Nanoparticles as Efficient Hydrogen Evolution Promoters for Photocatalytic Overall Water Splitting under Visible Light

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Experimental

The GaN:ZnO solid solution as the base photocatalyst was prepared according to the method described in previous papers.[9] Briefly, a mixture of Ga_2O_3 and ZnO powders (1.08 g Ga_2O_3 and 0.94 g ZnO) was heated at 1123 K under NH_3 flow (250 mL·min^{-1}). After 15 h of nitridation, the sample was cooled to room temperature, maintaining the NH_3 flow throughout. The production of GaN:ZnO with Zn/Ga molar ratio ≈ 0.13 was confirmed by powder X-ray diffraction (XRD) and energy-dispersive X-ray (EDX) analysis. The band gap energy of the as-obtained GaN:ZnO is 2.68 eV, as estimated from the onset of the diffuse reflectance spectrum.

The preparation of Rh/Cr_2O_3 (core/shell) nanoparticles was carried out in a Pyrex inner irradiation-type reaction vessel connected to a glass closed gas circulation system. The Rh-loaded sample (0.25 g) was then dispersed in aqueous K_2CrO_4 solution (400 mL, 0.18 mM). After evacuation, the solution was exposed to visible irradiation ($\lambda > 400$ nm) for 8 h to reduce K_2CrO_4 to Cr_2O_3. Irradiation was conducted using a 450 W high-pressure Hg lamp (UM-452, Ushio) and a Pyrex tube filled with sodium nitrite aqueous solution as a filter to block ultraviolet light.[9] The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the preparation procedure. The final product was washed well with distilled water and dried overnight at 343 K.

Photocatalytic reactions were carried out using the same experimental setup as used for the preparation of Rh/Cr_2O_3 (core/shell) nanoparticles. The reactant solution consisting of 0.15 g of the catalyst and 400 mL of pure water was evacuated several times prior to the reaction to ensure that no air remained in the reaction vessel. The evolved gases were analyzed by a gas chromatograph connected directly to the closed gas circulation system.

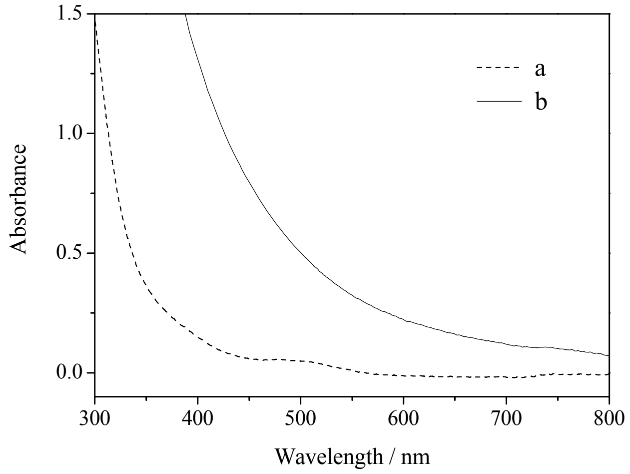

Figure S1. Ultraviolet-visible spectra for the aqueous preparation solution (a) before and (b) after reduction by sodium borohydride

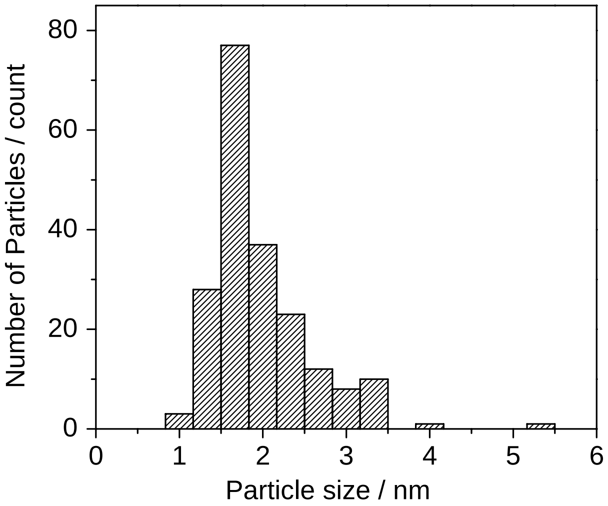

Figure S2. Particle size distribution histograms for Rh nanoparticles on GaN:ZnO.

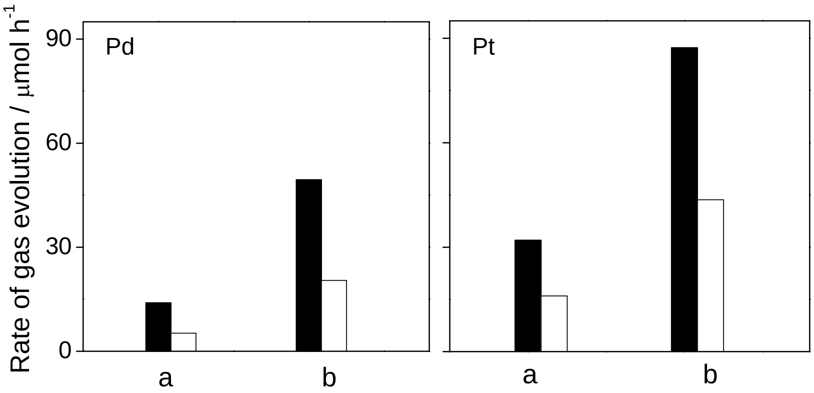

Figure S3. Photocatalytic activity of Cr_2O_3/M/GaN:ZnO (M = Pd, Pt) for overall water splitting under visible irradiation (λ > 400 nm). (a) Previous photodeposition method, (b) present preparation method. Reaction conditions: catalyst, 0.15 g; distilled water, 400 mL; light source, high-pressure mercury lamp (450 W) via aqueous $NaNO_2$ solution filter to cut ultraviolet light; reaction vessel, Pyrex inner-irradiation type.