BRIEF COMMUNICATIONS

Photocatalyst releasing hydrogen from water

Enhancing catalytic performance holds promise for hydrogen production by water splitting in sunlight.

Direct splitting of water using a particulate photocatalyst would be a good way to produce clean and recyclable hydrogen on a large scale[1], and in the past 30 years various photocatalysts have been found that function under visible light[2–4]. Here we describe an advance in the catalysis of the overall splitting of water under visible light: the new catalyst is a solid solution of gallium and zinc nitrogen oxide[5,6], $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$, modified with nanoparticles of a mixed oxide of rhodium and chromium. The mixture functions as a promising and efficient photocatalyst in promoting the evolution of hydrogen gas.

$(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ is a yellow powder with an absorption edge at about 510 nm (sample A, see supplementary information). Used alone, it has little photocatalytic activity. We impregnated $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ with nanoparticles of rhodium–chromium mixed oxide (for methods, see supplementary information). Scanning and transmission electron microscopy revealed that fine particles (10–20 nm) were distributed uniformly on the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ surface and that the loaded nanoparticles were crystalline, as indicated by the lattice fringes in the transmission electron micrograph image (for details, see supplementary information). Energy-dispersive X-ray analysis confirmed that these nanoparticles contained both rhodium and chromium.

This photocatalyst modification markedly enhances the overall splitting of water driven by visible light. Modification with either chromium or rhodium oxide alone did not appreciably increase this photocatalytic activity.

Figure 1a shows the quantum efficiency of overall water splitting by the photocatalyst as a function of the wavelength of the incident light. The quantum efficiency decreases with increasing wavelength, and the longest wavelength suitable for overall water splitting coincides with the absorption edge of the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution; this indicates that the reaction proceeds through light absorption by the solid solution. The quantum efficiency of overall water splitting on this catalyst is about 2.5% at 420–440 nm, which is about an order of magnitude higher than the previously reported activity of photocatalysts used in overall water splitting under visible light[4,6].

A typical time course for overall water splitting on the impregnated $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ photocatalyst under visible light (at wavelengths longer than 400 nm) is shown in Fig. 1b. Stoichiometric evolution of hydrogen and oxygen was evident from the start of the reaction, and there was no noticeable degradation of activity in repeated runs for 35 h. The total evolution of hydrogen and oxygen after 35 h was 16.2 mmol, exceeding the amount of catalyst (3.7 mmol) used in the reaction. Radiation from a high-pressure mercury lamp through Pyrex glass of a suspension of the photocatalyst powder in water induced gas evolution as bubbles at atmospheric pressure (for movie, see supplementary information). The photocatalyst is therefore stable during overall water splitting that is driven by visible light.

If silver nitrate is used as a sacrificial electron acceptor, the quantum efficiency for oxygen evolution rises to 51% at 420–440 nm, which is 20 times higher than that for overall water splitting. The photocatalytic activity of the modified $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution could therefore be increased further by improving the hydrogen-evolution site. Its composition could also be modified to extend the absorption edge to longer wavelengths. For now, our results demonstrate the feasibility of using photocatalysts and solar energy to produce hydrogen from water.

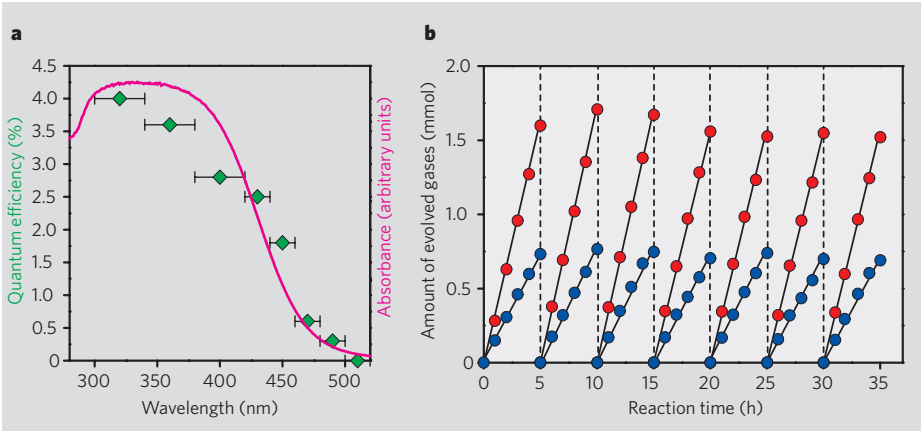

Figure 1 | Photocatalytic performance of the photocatalyst $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ loaded with mixed oxides of rhodium and chromium in overall water splitting. a, Quantum efficiency of the photocatalyst (sample C, see supplementary information) plotted as a function of wavelength of the incident light. Quantum efficiency was estimated by using several cut-off filters; each plot is in the middle of two cut-off wavelengths (for methods, see supplementary information). **b,** Time course of overall water splitting under visible light (of wavelength longer than 400 nm) on the photocatalyst (sample B, see supplementary information). The reaction was continued for 35 h, with evacuation every 5 h (dotted line). Red circles, hydrogen; blue circles, oxygen.

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