Direct Deposition of Trivalent Rhodium Hydroxide Nanoparticles onto a Semiconducting Layered Calcium Niobate for Photocatalytic Hydrogen Evolution

Hideo Hata,†§ Yoji Kobayashi,† Vince Bojan,‡ W. Justin Youngblood,† and Thomas E. Mallouk*†

Department of Chemistry and Materials Research Institute, The Pennsylvania State University, University, Park, Pennsylvania, 16802

Received October 5, 2007; Revised Manuscript Received January 20, 2008

ABSTRACT

Well-dispersed Rh(OH)₃ nanoparticles were deposited in the interlayer galleries of a Dion−Jacobson type layered perovskite (ACA₂Nb₃O₁₀: A = H or K). X-ray photoelectron spectra and ζ potential measurements suggest covalent bonding (Rh−O−Nb) between the nanoparticles and the niobate sheets. After calcination of Rh(OH)₃/KCa₂Nb₃O₁₀ at 350 °C in air, interlayer Rh(OH)₃ nanoparticles were transformed to Rh₂O₃ and showed higher photocatalytic activity for hydrogen evolution using methanol as a sacrificial electron donor.

The direct photochemical cleavage of water to generate hydrogen and oxygen has been studied since the early 1970s and still attracts considerable interest today because of its potential for low-cost solar energy conversion. A number of metal and metal oxide catalysts (e.g., NiO, RuO₂, Rh₂−ₓCrₓO₃, Rh₂Cr₂O₇, Pt) deposited on wide band gap semiconducting materials have been investigated in this context. Layered oxides (e.g., Na₂Ti₃O₇, K₂Ti₄O₉, K₄La₂−Ti₃O₁₀, K₄Nb₆O₁₇, and KCa₂Nb₃O₁₀) are interesting wide band gap semiconductors for photocatalytic reactions because they readily intercalate water and because ion-exchange reactions can be used to deposit noble metal cocatalysts at specific interlayer sites. In most of these materials, however, intercalation reactions are limited to cationic guest species. Ebina et al. reported that Pt or cationic Ru clusters could be loaded onto sheets of the layer perovskite KCa₂Nb₃O₁₀ by precipitation with strong base and the restacked high surface area composites showed high activity for water splitting. However, it is still very challenging to control the dispersion of such catalytic nanoparticles on the host semiconductor sheets. Although we recently succeeded in intercalating noble metal nanoparticles into layered oxides by first intercalating coordinating polyamines, in that case, there was no direct bonding between the nanoparticles and the host layers, which is important for redox catalysis.

In this paper, we report the direct deposition of Rh(OH)₃ nanoparticles, which can be converted to catalytic Rh₂O₃ nanoparticles by calcination, into the interlayer of HCa₂-Nb₃O₁₀ or KCa₂Nb₃O₁₀. Surprisingly, the reaction appears to involve covalent bonding of the clusters to the sheets, and this results in uniform dispersion of nanoparticles even at high loading.

Intercalation of Nanoparticles. The Rh₂O₃-loaded photocatalyst was prepared by exfoliation and intercalation of proton-exchanged KCa₂Nb₃O₁₀ (see Supporting Information for details). HCa₂Nb₃O₁₀ (0.13 g) was exfoliated by shaking in 50 mL of aqueous tetra(n-butyl)ammonium hydroxide (TBAOH) (25.0 mM) for 1 month. To obtain 1.5 wt % loading of Rh(OH)₃, which corresponds to 1 wt % loading of Rh, 20 mM aqueous RhCl₃ (0.632 mL) was added to 50 mL of the exfoliated TBAOH/Ca₂Nb₃O₁₀ suspension (pH ∼ 12.0) together with methanol (10 vol %), followed by photoirradiation with a 300 W Xe lamp for 18 h. The loading was adjusted by changing the amount of RhCl₃ solution. Immediately after adding the red RhCl₃ solution to the TBAOH/Ca₂Nb₃O₁₀ suspension, the color of the sheets in the suspension became lemon yellow, which is typical of Rh(OH)₃ under basic conditions. After the intercalation reaction, the yellow suspension was dispersed in 2 M KOH solution to precipitate the restacked Rh(OH)₃/Ca₂Nb₃O₁₀
sheets while exchanging the interlayer cations from TBA\(^+\) and H\(^+\) to K\(^+\). If excess RhCl\(_3\) solution was used (beyond a Rh loading of 24.7 wt %), the supernatant solution remained yellow, and peaks attributed to Rh(OH)\(_3\) were observed in XRD pattern in addition to peaks from Rh(OH)\(_3\)/Ca\(_2\)Nb\(_3\)O\(_{10}\) (see Supporting Information, Figure S1). The solid obtained is designated Rh(OH)\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\)(n), where n denotes the Rh loading in wt %. To transform the interlayer Rh(OH)\(_3\) nanoparticles to Rh\(_2\)O\(_3\), Rh(OH)\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\) was heated at 623 K for 1 h in air. The calcined samples are abbreviated Rh\(_2\)O\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\)(n) as well as Rh(OH)\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\) were tested as photocatalysts for hydrogen evolution in aqueous methanol solutions.

Figure 1 compares XRD patterns of HCa\(_2\)Nb\(_3\)O\(_{10}\), TBAOH/ Ca\(_2\)Nb\(_3\)O\(_{10}\), and Rh(OH)\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\) composites at different loadings (0.1, 1.0, and 10.0 wt %). In the intercalated samples, only 00\(_l\) and hh\(_0\) reflections were present, indicating turbostratic restacking of the sheets. The interlayer spacings of HCa\(_2\)Nb\(_3\)O\(_{10}\) and TBAOH/HCa\(_2\)Nb\(_3\)O\(_{10}\) prior to the deposition were 1.45 and 2.57 nm, respectively, and the estimated \(d\)-spacings of Rh(OH)\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\) (0.1, 1.0, and 10.0 wt %) were 1.60, 1.66, and 1.99 nm, respectively. This layer expansion relative to HCa\(_2\)Nb\(_3\)O\(_{10}\) implies intercalation of Rh(OH)\(_3\) nanoparticles in the interlayer gallery. Subtracting the thickness of the calcium niobate layer (1.16 nm), the gallery heights were 0.44, 0.50, and 0.83 nm for Rh(OH)\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\) (0.1, 1.0, and 10 wt %), implying that the intercalated nanoparticles are less than 1 nm in diameter. We did not observe any diffraction peaks that could be attributed to Rh\(_2\)O\(_3\), which is evidence that crystalline aggregates of Rh(OH)\(_3\) do not form in the galleries. In addition, the decrease in gallery height relative to TBAOH/ Ca\(_2\)Nb\(_3\)O\(_{10}\) indicates that TBA\(^+\) and residual H\(^+\) cations were substituted by K\(^+\) ions after washing with KOH solution. The loss of TBA\(^+\) was confirmed by FT-IR spectra in which the C–H stretching vibration (2800–3000 cm\(^{-1}\)), clearly visible in the TBA\(^+\) intercalated material, was not observed in Rh(OH)\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\) (see Supporting Information, Figure S3). Analytical data for samples restacked with KOH showed no significant difference (K/Ca/Nb mole ratio 0.8/2.3/3.0 in both cases) between 0 and 10 wt % Rh loaded samples. This indicates that Rh(OH)\(_3\) that is bound to the niobate sheets is ionizable in base and that the overall ion exchange capacity is the same after loading with Rh(OH)\(_3\).

Typical TEM images of Rh(OH)\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\) (1.0 and 10.0 wt %) are shown in Figure 2. Even at high loading, the Rh(OH)\(_3\) nanoparticles were well dispersed within the galleries. From the TEM images, the estimated average particle diameters in Rh(OH)\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\) (at 1.0 and 10.0 wt %) were 0.7 ± 0.2 and 1.1 ± 0.3 nm, respectively. The increase of the average particle size with the loading is consistent with the expansion of \(d\)-spacing observed in XRD measurements (Figure 1). EDX spectra showed Rh in all areas sampled in TEM imaging, consistent with the apparent uniform dispersion of Rh(OH)\(_3\) nanoparticles.

We previously reported that HCa\(_2\)Nb\(_3\)O\(_{10}\) can be topochemically dehydrated by heating to 463–573 K. To avoid this irreversible transformation, interlayer TBA\(^+\) and H\(^+\) ions were replaced by K\(^+\) by reaction with aqueous KOH. The presence of K\(^+\) was confirmed by EDX in the TEM imaging. Figure 3 shows XRD patterns of Rh\(_2\)O\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\) (0.1, 1.0, 10.0 wt %) obtained by calcining Rh(OH)\(_3\)/KCa\(_2\)Nb\(_3\)O\(_{10}\). After calcination, the basal spacing of Rh\(_2\)O\(_3\)/ KCa\(_2\)Nb\(_3\)O\(_{10}\) (0.1, 1.0, 10.0 wt %) decreased to 1.54, 1.54, and 1.66 nm, respectively (Figure 1), which is still somewhat larger than that of KCa\(_2\)Nb\(_3\)O\(_{10}\) (1.42 nm). The extra gallery height can again be attributed to intercalated nanoparticles, in this case Rh\(_2\)O\(_3\). Again, no diffraction features that could be attributed to Rh\(_2\)O\(_3\) were evident in the XRD patterns.
meaning that regardless of the loading of Rh(OH)$_3$, aggregation of the intercalated nanoparticles does not occur during calcination.

**Covalent Interactions Between Rh-Oxide Nanoparticles and Niobate Sheets.** Because oxide-supported noble metal and metal oxide nanoparticles tend to coalesce and crystallize upon calcination, the persistent dispersion of subnanometer Rh$_2$O$_3$ particles in the niobate galleries is unusual. Another unusual observation was the insensitivity of these nanoparticles to cation exchange in 2 M KOH. It had previously been reported that cationic CrO$_x$ nanoparticles could be intercalated into the layered titanate Ti$_{1.83}$O$_4$, which was first exfoliated by reaction with TBAOH.$^{14}$ On this basis, we expected Rh(OH)$_3$ nanoparticles to intercalate under conditions of pH where their net charge was positive. When Rh(OH)$_3$ was intercalated at saturation coverage (initial Rh loading of 24.7 wt %), IR spectra showed that most of the TBA$^+$ ions were displaced from the galleries without subsequent treatment with 2 M KOH (see Supporting Information, Figure S3). Therefore, our initial impression was that the interaction between Rh(OH)$_3$ and the Ca$_2$Nb$_3$O$_{10}$ sheets was primarily electrostatic.

Zeta potential measurements of Rh(OH)$_3$ nanoparticles$^{15}$ at pH 5.0 to 13.0 (see Supporting Information, Figure S4) showed that their isoelectric point was about pH 7.0. Thus, the nanoparticles have a negative surface charge at pH 12.0, which is the pH of the intercalation reaction. Because the Ca$_2$Nb$_3$O$_{10}$ sheets are also negatively charged at high pH, the Rh(OH)$_3$ nanoparticles cannot be anchored in the galleries by electrostatic forces. Even at high loading, Rh(OH)$_3$ nanoparticles are not displaced by reaction with aqueous KOH, but under these conditions, TBA$^+$ cations are completely removed. As a control experiment, we attempted to intercalate Rh(OH)$_3$ nanoparticles into an exfoliated fluoromica,$^{16}$ which also has negative layer charge at high pH but which has no Nb atoms or surface OH groups. In this case, XRD patterns showed no evidence of Rh(OH)$_3$ intercalation. Although some Rh(OH)$_3$ nanoparticles adhered to the external surface of the clay after washing with water, they were completely desorbed by 2 M KOH. Taken together, these observations imply a different kind of interaction between the guest and host for Rh(OH)$_3$/Ca$_2$Nb$_3$O$_{10}$.

It has been reported that Rh$_2$O$_3$ and Nb$_2$O$_5$ react at 700–900 °C to give RhNbO$_4$, a rutile structure oxide containing Rh–O–Nb linkages.$^{17}$ We hypothesized that Rh(OH)$_3$ and Rh$_2$O$_3$ nanoparticles could be anchored to the Ca$_2$Nb$_3$O$_{10}$ by similar covalent bonds. Figure 4 shows XPS spectra in the Rh 3d region for Rh(OH)$_3$/Ca$_2$Nb$_3$O$_{10}$ (10 wt %).
Rh(OH)\textsubscript{3} particles. The Rh 3d\textsubscript{5/2} peak for Rh(OH)\textsubscript{3} appears at 309.6 eV. After intercalation of Rh(OH)\textsubscript{3}, the peak shifts slightly to 309.8 eV. The Rh 3d\textsubscript{5/2} peak for Rh\textsubscript{2}O\textsubscript{3} is typically observed at 308.1–308.4 eV\textsuperscript{5b} These binding energies are easily distinguished from that of Rh metal (306.5 eV\textsuperscript{17b}). Although intercalated Rh(OH)\textsubscript{3} nanoparticles are transformed to Rh\textsubscript{2}O\textsubscript{3} by calcination in air, the Rh 3d\textsubscript{5/2} peak remains at high binding energy (309.4 eV). The Rh 3d\textsubscript{5/2} peak for RhNbO\textsubscript{4} is at 309.1 eV,\textsuperscript{17b} which is close to the binding energy observed in Rh\textsubscript{2}O\textsubscript{3}/KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}. Although they are not definitive, the XPS data are consistent with the picture of trivalent Rh anchored to the surface of the Nb-oxide layer through covalent Rh–O–Nb bonds, as sketched in Scheme 1.

**Photocatalysis.** The activity of Rh(OH)\textsubscript{3} and Rh\textsubscript{2}O\textsubscript{3}/KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} composites as photocatalysts for hydrogen evolution was measured using 10 vol % aqueous methanol solutions under 300 W Xe lamp irradiation. Figure 5 shows the time course of hydrogen evolution on flocculated KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} (fl-KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}), Rh(OH)\textsubscript{3}/KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} at different Rh loadings (0.1, 1.0, 10.0 wt %), and Rh\textsubscript{2}O\textsubscript{3}/KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} (0.1 wt %). With fl-KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} alone, H\textsubscript{2} gas was evolved very slowly (51 μmol/h per 1 g of catalyst). The rate was approximately five times higher (275 μmol/h) using Rh(OH)\textsubscript{3}/KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} (0.1 wt %). Interestingly, the H\textsubscript{2} evolution rate decreased with increasing Rh(OH)\textsubscript{3} loading up to 10 wt %. This may be due in large part to an inner filter effect in which strongly UV-absorbing Rh(OH)\textsubscript{3} prevents light absorption by the semiconducting niobate sheets. However, on the basis of the extinction coefficient of aqueous Rh(OH)\textsubscript{3} at 350 nm (∼1 × 10\textsuperscript{2} M\textsuperscript{-1} cm\textsuperscript{-1}),\textsuperscript{11} the loss in photocatalytic activity is not explained entirely by
Nb₃O₁₀ is not. Thus, Rh₂O₃/HCa₂Nb₃O₁₀ may be a useful mixed oxide (Rh 2 splitting schemes. tions, suggesting that they may be useful in overall water insensitive to cation exchange under acidic or basic condi-

niobate sheets. These covalently bound catalytic clusters are catalyst in aqueous 10% methanol, consistent with the small type layered perovskite (KCa₂Nb₃O₁₀). Calcination trans-

arrangement, Rh₂O₃/KCa₂Nb₃O₁₀ or Rh₂O₃/HCa₂Nb₃O₁₀ Rh₂O₃/KCa₂Nb₃O₁₀ are not active for overall water splitting oxygen.5 Preliminary experiments show that Rh(OH)₃/ and evolution and are remarkably insensitive to the presence of acidic pH.

In conclusion, well-dispersed Rh(OH)₃ nanoparticles were intercalated into the interlayer galleries of a Dion–Jacobson type layered perovskite (KCa₂Nb₃O₁₀). Calcination transformed intercalated Rh(OH)₃ to well dispersed Rh₂O₃ nanoparticles. Zeta potential, ion-exchange, and XPS experiments point to covalent Rh–O–Nb bonding as the mode of anchoring the nanoparticles to the sheets. The evidence for this bonding is indirect, and further structural studies by NMR and X-ray absorption are currently contemplated. Rh₂O₃/HCa₂Nb₃O₁₀ was found to be a very active photocatalyst in aqueous 10% methanol, consistent with the small size the nanoparticles and their uniform dispersion on the niobate sheets. These covalently bound catalytic clusters are insensitive to cation exchange under acidic or basic conditions, suggesting that they may be useful in overall water splitting schemes.

Recently, Domen and co-workers have found that Rh–Cr mixed oxide (Rh₂₋ₓCrₓO₃) nanoparticles supported on (Gₐₓ₋ₚZnₓ)(N₁₋ₚO) catalyze overall water splitting under visible light. The Rh₂₋ₓCrₓO₃ clusters catalyze hydrogen evolution and are remarkably insensitive to the presence of oxygen.5 Preliminary experiments show that Rh(OH)₃/ and Rh₂O₃/KCa₂Nb₃O₁₀ are not active for overall water splitting with UV irradiation and that they catalyze the recombination of H₂ and O₂ into water. It is possible that by covering the supported Rh₂O₃ nanoparticles with Cr₂O₃ in a core–shell arrangement, Rh₂O₃/KCa₂Nb₃O₁₀ or Rh₂O₃/HCa₂Nb₃O₁₀ might be converted to a water splitting catalyst by inhibiting the recombination reaction. Synthetic experiments along these lines are currently in progress.

Acknowledgment. This research was supported by the Department of Energy under grant DE-FG02-07ER15911. We thank Henry Gong for carrying out the spectroscopic (UV-Vis, FT-IR) analysis. H.H. thanks Shiseido Co. Ltd. for giving him the opportunity to study at the Pennsylvania State University and for financial support. W.J.Y. thanks the donors of the ACS Petroleum Research Fund for support in the form of a postdoctoral fellowship.

Supporting Information Available: Experimental details, analytical results, XRD patterns of Rh(OH)₃, Rh(OH)₃/KCa₂ Nb₃O₁₀ at saturation loading, and Rh(OH)₃/KCa₂Nb₃O₁₀ without photoirradiation, FT-IR spectra of TBAOH/KCa₂Nb₃O₁₀, Rh(OH)₃/Ca₂Nb₃O₁₀ at saturated loading washed with water, and Rh(OH)₃/KCa₂Nb₃O₁₀ (10 wt %). pH dependence of the ζ potential of Rh(OH)₃ particles, and XRD patterns of Rh(OH)₃/F-Mica before and after intercalation. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(15) Rh(OH)₃ nanoparticles were synthesized as followed. To 6.32 mL of RhCl₃ aqueous solution (20 mM) was added 50 mL of 25 mM of TBAOH aqueous solution, and the mixture was stirred for 1 h. The precipitated yellow powder was collected by centrifugation and washed with water. Finally, the sample was dried at 333 K.
(16) Sodium fluotetrasilicic mica with the chemical formula Na₉₆₋₅Mg₂₋₃(Si₁₆₋₅Al₁₂₋₅)O₃₀₋₅(F,OH)₁₆ and a cation exchange capacity (CEC) of 120 mequiv/100 g (ME-100, CO-OP Chemicals) was used.


NL072571W