Potassium niobate nanoscrolls incorporating rhodium hydroxide nanoparticles for photocatalytic hydrogen evolution

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Well-dispersed rhodium trihydroxide nanoparticles (below 1 nm) were deposited into the interlayer galleries of scrolled K2Nb3O7 nanosheets. The unmodified nanoscrolls are good catalysts for UV light-driven hydrogen evolution from aqueous methanol solutions, and their activity can be significantly improved by anchoring a small amount (0.1 wt% Rh) of Rh(OH)3 or Rh2O3 to the surface. The high hydrogen generation rate achieved in this system, 1480 μmol/h per 1g of catalyst, shows promise towards overall water splitting using these catalytic composites.

Introduction

Layered K2NbO7 is composed of corrugated sheets of edge-sharing NbO6 octahedra. In each layer, the top and bottom faces are different from each other, giving rise to two different interlayer environments for hydration and intercalation.1 The asymmetry is regarded as the driving force leading to spontaneous scrolling when proton-exchanged H+/K2NbO7 (or HxK4+xNb6O17, x = 3) is exposed to aqueous tetra-(n-butyl)ammonium hydroxide (TBA’OH) and exfoliated.2 K2NbO7 loaded with interlayer Ni or Pt clusters has shown high photocatalytic activity for the photolysis of water and alcohols under UV light.3 Porous composites obtained by exfoliation of H/K2NbO7 and subsequent precipitation of MgO fine particles also showed high photocatalytic activity for H2 evolution from various aqueous alcohol solutions.4 The properties of surface-modified, platinized K2NbO7 in the photolysis of HI with visible light have also been investigated.5 However, expansion of K2NbO7 interlayer gallery by silica pillaring was not successful though it could be accomplished for clays and K2Ac3NbO10.6 In our previous report, the uniform dispersion of Rh(OH)3 nanoparticles, which can be converted to Rh2O3 by calcination, in the interlayer galleries of exfoliated–restacked K2Ac3NbO10 and HCA3NbO10 was achieved, which brought about a high rate of H2 evolution under UV light.7 We hypothesized that Rh(OH)3 and Rh2O3 nanoparticles were anchored to the calcium niobate sheets by covalent interactions, i.e., by Rh–O–Nb bonding. This motivated us to investigate another Rh–O–Nb system, specifically based on K2NbO7 nanoscrolls, to look for the possibility of expanding the interlayer space with active Rh(OH)3 nanoparticles and interesting photocatalysis functionalities.

Experimental

Materials preparation and characterization

Synthetic K2NbO7 crystals with a typical size of 1–10 μm were obtained by solid calcination of K2CO3 and Nb2O5.2 1.0 g K2NbO7 was stirred in 300 ml of 1M HCl solution for 4 days to produce HxK4–xNbO7 (x = 3); presumably the remaining K+ ions reside mainly in the slowly exchanging interlayer galleries. The acid solution was renewed 3 times to promote a complete exchange. The proton-exchanged solid HxK4–xNbO7 (0.2 g) was shaken in 50 mL of aqueous TBAOH solution (25 mM, pH ~11) for 24 h to obtain a colloidal suspension of exfoliated (TBA)HxK4–xNbO7. In order to incorporate rhodium hydroxide, the colloidal suspension was combined with different volumes of aqueous RhCl3 (8.2 mM) solution and vigorously stirred for another day. The added amount of RhCl3 corresponded to 0.1, 1.0 and 10.0 wt% Rh loading of HxK4–xNbO7, respectively. The yellowish suspension was then poured into 50 mL of 2 M KOH solution. As TBA+ ions were replaced by K+, the exfoliated (TBA)HxK4–xNbO7 was instantly flocculated into a wool-like sediment. The precipitated product was centrifuged and rinsed with copious amounts of water to remove excess KOH. A portion of the Rh(OH)3/K2NbO7 was calcined at 623 K in air for 1 h to convert deposited Rh(OH)3 into Rh2O3. After calcination, a color change from yellow to grey (0.1, 1.0 wt%) or dark brown (10.0 wt%), indicating the formation of Rh2O3, was observed. Rh2O3/K2NbO7 was further acid-exchanged with 1M HNO3 to obtain Rh2O3/HxK4–xNbO7.

X-Ray powder diffraction (XRD) patterns were obtained with a Philips X’Pert MPD diffractometer (monochromatized Cu Ka 0.15418 nm). Transmission electron microscope (TEM) images were obtained using a Philips 420 T microscope at an accelerating voltage of 120 kV and a JEOL JM-2010 microscope (operating at 200 kV). Samples for TEM observation were prepared by depositing a drop of ethanol-dispersed sample suspensions onto a carbon-coated copper grid and air-dried.

Photocatalysis

5.0 mg catalyst was suspended in 2.0 mL of aqueous 10 vol% methanol solution in a quartz reaction cell (5.0 mL) sealed with...
a rubber septum. The sample was purged with Ar for 10 min. The reaction cell was then placed in an outer jacket, where an Ar gas flow was introduced to prevent air contamination during the photocatalytic reaction. The suspension, under constant stirring, was irradiated using a UV light source (a 300 W Xe lamp). Throughout the reaction, a headspace gas sample (100 micro-liter) was taken using a syringe at different time intervals. The gas sample was analyzed for hydrogen content by gas chromatography (GC) using a thermal conductivity detector and a 5A molecular sieve column.

Results and discussion

1. Exfoliated–scrolled K₄Nb₆O₁₇ intercalating Rh(OH)₃ nanoparticles

Fig. 1 shows TEM images of the freshly exfoliated (TBA)ₙK₄₋ₙNb₆O₁₇. The sample was imaged by directly dropping the colloidal suspension onto a carbon-coated copper grid. TEM images revealed a mixture of exfoliated nanosheets and scrolled tubular objects, i.e., nanoscrolls. Fig. 1b displays a selected area view of some nanoscrolls. They are approximately 30 nm in diameter and a few hundred nm in length, consistent with previous observations. The top-right inset in Fig. 1b shows an individual nanoscroll with an apparent hollow core and an observed wall thickness of ~5 nm. High resolution observations reveal that the wall thicknesses of the nanoscrolls generally fall between 3 and 8 nm, corresponding to 3–10 radial layers.

Fig. 2 shows TEM images of restacked Rh(OH)₃/K₄Nb₆O₁₇. As can be seen in Fig. 2a, the solid is still a typical mixture of sheets and nanoscrolls, though it appears that the fraction of nanoscrolls is not so predominant as observed in exfoliated (TBA)ₙK₄₋ₙNb₆O₁₇. It is suspected that some particles are unscrolled into nanosheets during the subsequent treatment involving vigorous stirring and restacking with concentrated KOH. It has been noted that there is relatively little free energy difference between the nanoscrolls and nanosheets. Fig. 2b displays restacked nanosheets of Rh(OH)₃/K₄Nb₆O₁₇ with 1 wt% Rh loading. Darker-contrast nanoparticles can be discerned. With a higher loading of 10 wt% (Fig. 2c), a homogeneous distribution of abundant nanoparticles is apparent. The average sizes of the nanoparticle were estimated to be 0.5 ± 0.2 nm and 0.8 ± 0.3 nm for 1 wt% and 10 wt% Rh loading, respectively. Energy dispersive X-ray spectral (EDS) surveys of the samples give an average atomic ratio for K:Nb at 44:56, close to the stoichiometry (K:Nb = 40:60) in K₄Nb₆O₁₇. EDS analysis also identified uniform dispersion of Rh in all sampled areas. For a nominal 10 wt% Rh loading sample, EDS quantification results yield a typical atomic ratio for Rh:Nb at 12:88, ca. 9.6 wt% Rh loading of HₙK₄₋ₙNb₆O₁₇. All the microanalytical data confirm the incorporation of a designated amount of Rh into the exfoliated–scrolled K₄Nb₆O₁₇.

Fig. 3 compares XRD powder patterns for proton-exchanged HₙK₄₋ₙNb₆O₁₇ prior to exfoliation and the exfoliated–restacked products with different loadings of Rh (0, 0.1, 1, 10 wt%). The layered structure of K₄Nb₆O₁₇ is believed to be preserved during the exfoliation and scrolling, as manifested by the O40 basal reflections. Moreover, hkl reflections generally become extinct whereas the in-plane reflections such as 002 and 400 are retained, indicating an intact host structure of K₄Nb₆O₁₇ during the process. It is noteworthy that no diffraction peaks attributed to Rh(OH)₃ were observed. This is consistent with the very small particle size (Fig. 2) and with the non-crystalline nature of the Rh(OH)₃ nanoparticles. The interlayer spacing (O40) of exfoliated–restacked K₄Nb₆O₁₇ without Rh loading is approximately 8.6 Å, which is increased to 9.1, 9.5 and 10.6 Å for 0.1 wt%, 1 wt% and 10 wt% loadings, respectively. These correspond to an expansion of 0.5, 0.9, and 2 Å, respectively, indicating the size of intercalated Rh(OH)₃ nanoparticles increases accordingly with a higher loading. Unlike KCa₂Nb₃O₁₀, K₄Nb₆O₁₇ nanosheets are corrugated in the sheet.
normal direction. It is difficult to calculate the gallery height, by simply subtracting the atomic thickness of the niobate layer, to gauge \( \text{Rh(OH)}_3 \) size. Instead, the interlayer expansion relative to exfoliated–restacked \( \text{K}_{4}\text{Nb}_5\text{O}_{17} \) without Rh loading was used to estimate the gallery height. As the ionic radius of \( \text{K}^+ \) is 1.38 Å, the expansion in the interlayer spacing can be converted into an intercalation of \( \text{Rh(OH)}_3 \) nanoparticles with sizes of 3.26 (2 × 1.38 + 0.5), 3.66 (2 × 1.33 + 0.9), and 4.76 (2 × 1.33 + 2.0) Å, respectively. The values are close to but somewhat smaller than those estimated from statistical TEM observations. The deviation might imply that the particles are not in a strict spherical shape, possibly in a disc-like shape, namely, slightly thinner in height but somewhat elongated in the in-plane directions.

### 2. Photocatalytic activity

Time courses of \( \text{H}_2 \) generation on different \( \text{K}_{4}\text{Nb}_5\text{O}_{17} \) samples with and without Rh loading are shown in Fig. 4. For synthetic \( \text{K}_{4}\text{Nb}_5\text{O}_{17} \) crystals, the rate of \( \text{H}_2 \) generation is rather low, 0.7 \( \mu \text{mol/h} \) or a converted 140 \( \mu \text{mol/h} \) per 1g of catalyst. After proton-exchange and exfoliation, the rate for the restacked \( \text{K}_{4}\text{Nb}_5\text{O}_{17} \) significantly increases to 5.6 \( \mu \text{mol/h} \), or 1120 \( \mu \text{mol/h} \) per 1g of catalyst. This agrees well with the previous reports asserting that reactants (methanol and water) have better access to the more hydrated galleries.\(^8\)\(^9\) It is also apparent that the nanoscrolls have much higher surface area and open channels than synthetic layered \( \text{K}_{4}\text{Nb}_5\text{O}_{17} \). With the intercalation of 0.1 wt% \( \text{Rh(OH)}_3 \), the rate is increased to 6.7 \( \mu \text{mol/h} \), or 1340 \( \mu \text{mol/h} \) per 1g of catalyst, about a \( \sim 20\% \) increase. This is strikingly higher than the \( \text{H}_2 \) generation rate (275 \( \mu \text{mol/h} \) per 1g of catalyst) under similar conditions for \( \text{Rh(OH)}_3/\text{KCa}_2\text{Nb}_3\text{O}_{10} \) (0.1 wt%).\(^7\)

When the Rh loading was increased to 1 wt%, the rate decreased to 3.2 \( \mu \text{mol/h} \). It further drops to 2.6 \( \mu \text{mol/h} \) for a higher loading (10 wt%) of \( \text{Rh(OH)}_3 \). It appears that 0.1 wt% loading is an optimum combination. This is consistent with results obtained with Rh-loaded \( \text{KCa}_2\text{Nb}_3\text{O}_{10} \) and Ni-loaded \( \text{K}_{4}\text{Nb}_5\text{O}_{17} \),\(^8\) in which the activities also decrease gradually when the loading is above 0.1 wt%. The reduced activity at higher \( \text{Rh(OH)}_3 \) loading, even below that of Rh-free nanoscrolls, is derived from an optical inner filter effect of strongly UV-absorbing \( \text{Rh(OH)}_3 \). A simple calculation based on the extinction coefficient of aqueous \( \text{Rh(OH)}_3 \) (0.1 \( \text{mM}^{-1} \text{cm}^{-1} \) at 350 nm)\(^9\) results in 43% loss of UV absorption by 10 wt% \( \text{Rh(OH)}_3 \) loading (2.42 \( \text{mM} \) \( \text{Rh(OH)}_3 \)) in a 1 cm cell.

\[
\text{Percent transmittance/100} = 10^{-\text{absorbance}} = 10^{-\left(0.1+2.42\times1\right)} = 0.57
\]

This is in semi-quantitative agreement with the reduction of the \( \text{H}_2 \) generation rate from 5.6 \( \mu \text{mol/h} \) (no Rh loading) to 2.6 \( \mu \text{mol/h} \) (10 wt% Rh).

After calcination at 623 K, \( \text{Rh(OH)}_3 \) was transformed into \( \text{Rh}_2\text{O}_3 \), which was evidenced by a color change to brown. Again, no XRD peaks for \( \text{Rh}_2\text{O}_3 \) were detected as the nanoparticles do not form crystalline aggregates. Although \( \text{Rh}_2\text{O}_3 \) is expected to be a better catalyst than \( \text{Rh(OH)}_3 \), the catalytic activity for the sample with 0.1 wt% \( \text{Rh}_2\text{O}_3 \) loading after calcination remained essentially unchanged. This is possibly due to the effect of dehydration in the calcined sample. After another acid-exchange procedure, the hydrogen generation rate for 0.1 wt% \( \text{Rh}_2\text{O}_3 \), increased to \( \sim 7.4 \mu \text{mol/h} \), or 1480 \( \mu \text{mol/h} \) per 1g of catalyst. This suggests that proton-exchange and hydration enable better access of methanol and water to the interlayer galleries of the restacked sheets and nanoscrolls.

### Conclusions

In summary, a uniform deposition of \( \text{Rh(OH)}_3 \) nanoparticles (below 1 nm) into the interlayer galleries of \( \text{K}_{4}\text{Nb}_5\text{O}_{17} \) nanoscrolls has been achieved through an exfoliating–restacking procedure, demonstrating an efficient way to expand the interlayer space with active catalyst nanoparticles and to control the dispersion on semiconductor host sheets. The photocatalysis results indicate that the activity of exfoliated–restacked \( \text{K}_{4}\text{Nb}_5\text{O}_{17} \) can be improved by anchoring a suitable amount (0.1 wt% Rh) of \( \text{Rh(OH)}_3 \) or \( \text{Rh}_2\text{O}_3 \). The high hydrogen generation rate achieved in this system is noteworthy, because it has been shown that hydrogen evolution is the rate-determining process in visible-light overall water splitting using semiconducting oxynitride photocatalysts.\(^9\) In that work, Rh-based nanoparticles were the hydrogen evolving catalysts of choice because, with suitable modification, they do not catalyze the \( \text{O}_2–\text{H}_2 \) recombination reaction. Further work is being directed towards overall water splitting using similar catalytic composites based on dye-sensitized nanoscrolls.\(^10\)

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