A New Photocatalyst of RuO_2-loaded $PbWO_4$ for Overall Splitting of Water

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Lead tungstate, $PbWO_4$, with a tetragonal structure was found to make a stable photocatalyst for the decomposition of water to produce H_2 and O_2 when combined with RuO_2. This is the first example of tungsten oxide that is photocatalytically active for the reaction. The structural feature of $PbWO_4$ is the presence of tetrahedral WO_4. The DFT calculation showed that Pb^{2+} with $d^{10}s^2$ electronic configuration had significant influences on both valence and conduction band structures.

In view of current interest of solar energy conversion, discovery of new kinds of the photocatalysts for overall water splitting is among important issues. Recently, a group consisting of p-block metal oxides such as MIn_2O_4 (M = Ca, Sr), $ZnGa_2O_4$, Zn_2GeO_4, Sr_2SnO_4 $M_2Sb_2O_7$ (M = Ca, Sr), $CaSb_2O_6$, and $NaSbO_3$ has been found to be photocatalytically active for the reaction when RuO_2 was loaded as a promoter.[1–7] The feature of the group is the involvement of a metal ion having d^{10} electronic configuration. The other is a group of the conventional transition metal oxides. The representative transition metal oxides are $SrTiO_3$, $A_2Ti_6O_{13}$ (A = Na, K, Rb), $BaTi_4O_9$, $A_2La_2Ti_3O_{10}$ (A = K, Rb, Cs), ZrO_2, $A_4Nb_6O_{17}$ (A = K, Rb), $Sr_2Nb_2O_7$, $ATaO_3$ (A = Na, K), MTa_2O_6 (M = Ca, Sr, Ba), and $Sr_2Ta_2O_7$ for which NiO or RuO_2 was used as a promoter.[8] It is to be noted that the transition metal oxides so far developed have been confined to four kinds of the metal ions such as Ti^{4+}, Zr^{4+}, Nb^{5+}, and Ta^{5+} with d^0 electronic configuration. It would be greatly beneficial to find active transition metal oxides involving different kinds of metal ions. Kudo et al. reported that W-based photocatalysts ($Na_2W_4O_{13}$, $Bi_2W_2O_9$, Bi_2WO_6) had ability to decompose water in the presence of sacrificial agents, that is, H_2 from H_2O/CH_3OH and O_2 from $AgNO_3$ solution.[9,10] However, to our best knowledge, no tungsten oxides have been found to be active for the overall splitting of pure water yet. Here we report that $PbWO_4$ is the first example of a tungsten oxide that is able to photocatalytically produce H_2 and O_2 from H_2O when combined with RuO_2.

$PbWO_4$ was synthesized in vacuum-sealed or in nitrogen atmosphere conditions. In the former, a mixture of PbO (Nakarai tesque, GR) and WO_3 (Nakarai tesque, for analytical use) was placed in a quartz tube, sealed in vacuum, and heated at 773 K for 16 h (denoted here as (Q)$PbWO_4$). In the latter, the same mixture was heated in a nitrogen flow at 973 K for 16 h ((N)$PbWO_4$). To see the influences of Pb in the synthesis of $PbWO_4$, the ratio of PbO to WO_3 in the mixture was changed from 1.0 to 1.3((Q)Pb_xWO_4 ($x = 1.0$–1.3)). For loading of RuO_2, $PbWO_4$ was impregnated up to incipient wetness with a ruthenium carbonyl complex, $Ru_3(CO)_{12}$, in THF, dried at 353 K and oxidized in air at 673 K for 4 h to convert the ruthenium species to RuO_2. The photocatalytic reaction of powder photocatalysts was carried out in a gas circulation reaction system using a quartz reaction cell. Ar gas of 13.3 kPa was circulated with a piston pump during the reaction. The powder photocatalysts of 250 mg were dispersed in distilled and ion-exchanged pure water of ca. 30 mL by stirring of Ar gas bubbling and illuminated by an outer Hg–Xe lamp usually operated at 200 W. The evolved gases were analyzed by an on-line gas chromatograph.

Figure 1 shows the X-ray diffraction patterns of (Q) and (N)$PbWO_4$. The diffraction patterns were similar between (Q) and (N) $PbWO_4$. There are two crystal structures in $PbWO_4$: one is tetragonal and the other is monoclinic. All major peaks were consistent with those reported previously for the tetragonal structure.[11] The UV–vis diffuse reflectance spectra showed a threshold light absorption at a wavelength of 330 nm and a maximum at 300 nm.

Figure 2 shows the decomposition of H_2O on 1 wt % RuO_2-loaded (Q)$PbWO_4$. UV irradiation produced H_2 and O_2 from the initial stage, and their products increased in nearly proportion to irradiation time. The H_2 and O_2 evolution decreased slightly in the second run, but the evolution in the fourth run was nearly the same as that in the third run, which is indicative of the stability of the photocatalyst. The activity of RuO_2-loaded $PbWO_4$ was almost compatible to that of RuO_2-loaded $BaTi_4O_9$ that had the highest activity (approximately 10% quantum yield at 330 nm) in Ti-based metal oxides.[12] Figure 3 shows the photocatalytic activity of 1 wt % RuO_2-loaded (Q)$PbWO_4$ and (N)$PbWO_4$. RuO_2-loaded (Q)$PbWO_4$ showed a slightly larger activity and better H_2/O_2 ratio than those for (N)$PbWO_4$. The photocatalytic activity of RuO_2-loaded (Q) Pb_xWO_4 ($x =$ 1.0–1.3) decreased with increasing x monotonously. This indi-

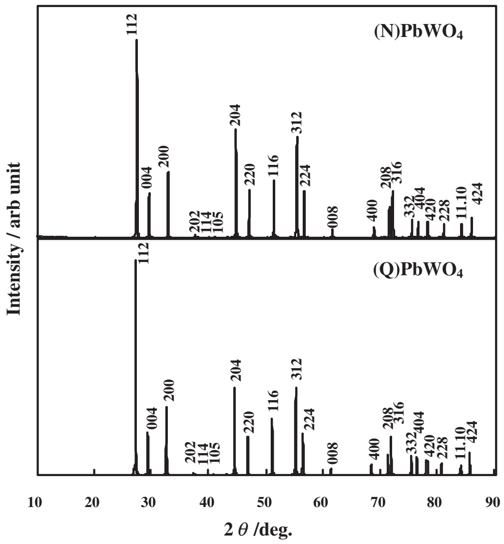

Figure 1. X-ray diffraction patterns of (Q)$PbWO_4$ and (N)$PbWO_4$.

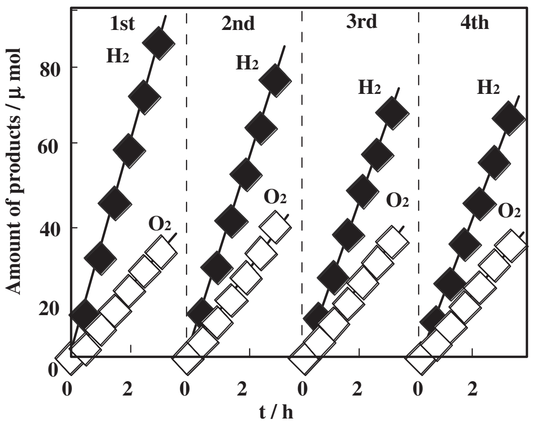

Figure 2. Production of H_2 and O_2 from H_2O on 1 wt %RuO_2-loaded (Q)$PbWO_4$.

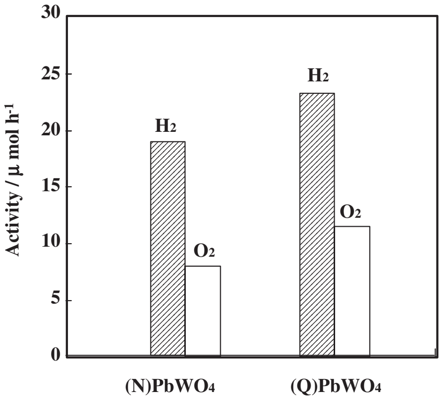

Figure 3. The photocatalytic activity of RuO_2-loaded (Q) and (N)$PbWO_4$.

cates that Pb deficit in the preparation of (Q)$PbWO_4$ occurred to a less extent, and the excess amount of Pb had negative influences on the activity of (Q)Pb_xWO_4.

$PbWO_4$ with a scheelite type tetragonal structure has a lattice parameter of $a = 0.5456(2)$ and $c = 1.2020(2)$ nm.[13] The structural feature of $PbWO_4$ is the presence of tetrahedral WO_4 unit. We have examined the photocatalytic activity for RuO_2-loaded $ZnWO_4$ consisting of an octahedral WO_6 unit, but no significant photocatalytic activity for water decomposition was observed. Since almost all of conventional transition metal oxide photocatalysts are composed of octahedral MO_6 units (M = metal ions), it is interesting to see that the tetrahedral WO_4 unit forms an active site for water decomposition.

The preliminary DFT calculation showed that the valence band was mainly composed of the O2p orbitals, and the Pb 6s orbital was mixed at the higher level of valence bands. The interesting feature is that the valence band has a considerably large dispersion, different from usual flat structure frequently observed for alkaline metal and alkaline earth metal tungstates and $ZnWO_4$. This indicates that the formed holes have large mobility that is associated with high photocatalytic performance. The conduction band consisted of the hybridized W5d + O2p + Pb6p orbitals. The hybridized valence and conduction band structures are likely to be responsible for active photocatalysis, which indicates that the combination of $d^{10}s^2$ configuration of Pb^{2+} ion with d^0 configuration of W^{6+} ion, i.e., $d^{10}s^2$–d^0 electronic configuration, is useful for water decomposition.

Although we need to reveal a correlation of WO_4-based electronic and geometric structures with photocatalytic activity and to extend research to other tungsten oxides, the discovery of W^{6+} ion as a photocatalytically active metal ion is encouraging for the development of new photocatalysts for the overall splitting of water.

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