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Open-Framework Gallium Borate with Boric and Metaboric Acid Molecules inside Structural Channels Showing Photocatalysis to Water Splitting

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Supporting Information

ABSTRACT: An open-framework gallium borate with intrinsic photocatalytic activities to water splitting has been discovered. Small inorganic molecules, H_3BO_3 and $H_3B_3O_6$, are confined inside structural channels by multiple hydrogen bonds. It is the first example to experimentally show the structural template effect of boric acid in flux synthesis.

Water splitting is considered to be one of the most promising techniques to convert solar energy to chemical energy in the form of H_2. Since the pioneering work on semiconducting TiO_2,[1] increasing efforts have been made to discover novel photoactive materials, for example, graphene-based composites, core–shell nanostructured materials, and also microporous photocatalysts.[2] However, most microporous photocatalysts are inorganic–organic hybrid polymers thus far; there is no purely inorganic open-framework photocatalyst, which will have an advantage in thermal stability. Metal borates have a significant variety in structural chemistry. Usually they were considered to be important optical materials, like nonlinear optical crystals and luminescent materials;[3] however, people have not paid enough attention to their photocatalytic activities in the past, with only a few exceptions; for instance, $InBO_3$ can photocatalyze the degradation of 4-chlorophenol;[4] CuB_2O_4 and $Cu_3B_2O_6$ (by loading platinum as a cocatalyst) can catalyze water splitting under visible-light excitation.[5]

It is known that 3-fold-coordinated boron shares its sp^2-hybridized orbitals with surrounding ions and leaves a 2p orbital unoccupied. So, we speculate that this type of boron can server as an acceptor to photoinduced electrons and, furthermore, behave as a photocatalytic site. In addition, a recent report shows that gallium oxide possesses an outstanding photocatalytic activity of overall water splitting, especially when made as an $\alpha-\beta$ phase junction.[6] Therefore, we are interested in a gallium–oxygen open framework decorated with triangular borate units. In the literature, there are only two condensed gallium borates, $Ga_4B_2O_9$ and $GaBO_3$, with accurate structural details reported.[7,8] $Ga_9B_{18}O_{33}(OH)_{15}\cdot H_3B_3O_6\cdot H_3BO_3$ (denoted as Ga-PKU-1) was first mentioned in 2003 as an analogue to $HAl_3B_6O_{12}(OH)_4\cdot nH_2O$ (Al-PKU-1), evidenced by similar powder X-ray diffraction (XRD) patterns.[9] It was difficult to even determine the formula at that time.

By solving the difficulty in synthesis (see the Supporting Information, SI), we obtained single-crystal samples and determined its exact structure, which is, in fact, noncentrosymmetric (in space group *R*3). The main framework of Ga-PKU-1 is topologically the same as that of Al-PKU-1. Specifically, 18-octahedra-membered channels go along the *c* axis. Here in Ga-PKU-1, two kinds of neutral molecule species, i.e., H_3BO_3 and $H_3B_3O_6$, are observed to be confined in the channels by hydrogen bonds. More importantly, Ga-PKU-1 is an intrinsic photosensitive semiconductor that can catalyze H_2 production from water under UV-light irradiation, and its efficiency is larger than that of commercialized TiO_2 (P25).

A qualified single crystal of Ga-PKU-1 was selected for XRD analysis, and its structure was determined unambiguously, as shown in Figure 1. Detailed structure and refinement parameters can be found in the SI (Table S1). Compared to Al-PKU-1, it has a lower symmetry; therefore, there are in total 30 crystallo-

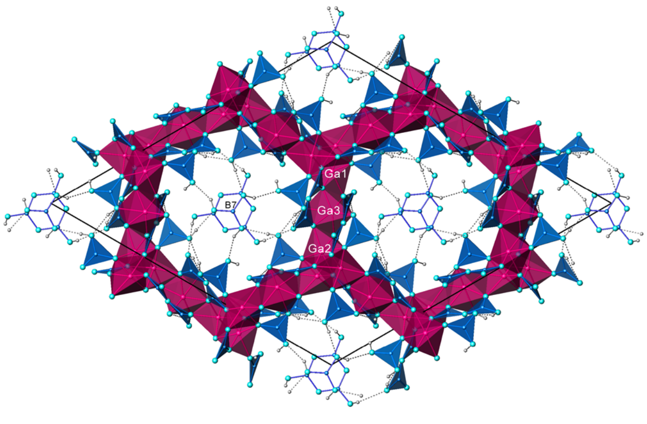

Figure 1. Structure of Ga-PKU-1 viewed along the *c* axis. Color code: purple octahedra, GaO_6; blue triangles, BO_3. Blue, cyan, and gray spheres represent boron, oxygen, and hydrogen, respectively. Hydrogen bonds are shown as dotted gray lines. *R*3, *a* = 22.666(2) Å, *c* = 7.2085(5) Å.

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graphically independent non-hydrogen atoms, including 3 gallium, 8 boron, and 19 oxygen. All atoms locate at general positions, except B7, which is on the 3-fold axis (3a site, shown in Figure 1). Determinations of the hydrogen coordinates are based on XRD analyses and bond-valence-sum calculations.

The framework of Ga-PKU-1 consists of GaO_6 octahedra exclusively edge-sharing, forming 18-GaO_6-membered structural channels along the *c* axis. Borate groups, in the form of $BO_2(OH)$ and $B_2O_4(OH)$ fragments, attach to the GaO_6 framework and neutralize the negative charges by sharing vertex oxygen atoms. As shown by the formula $Ga_9B_{18}O_{33}(OH)_{15}\cdot H_3B_3O_6\cdot H_3BO_3$, boric and metaboric acids are extraframework species. Because the topological connectivity of the Ga-PKU-1 framework is the same as that of Al-PKU-1, their common structural characteristics will not be discussed here.[9] Our discussion will focus on their major differences including the symmetry descendent and newly discovered guest molecules in large channels.

There is a cationic radii expansion from Al- to Ga-PKU-1 (0.535 and 0.62 Å for CN = 6, respectively). In order to maintain efficient connectivity between GaO_6 and borate groups, which are very rigid motifs; at least some of GaO_6 should afford strong static stress, which can be released by the geometrical distortion of octahedra. Indeed, Ga3 is located at a strongly distorted environment with five short (1.87−1.97 Å; see Table S2 in the SI) and one long (2.43 Å) bonds, while $Ga1O_6$ and $Ga2O_6$ both have regular Ga−O bond lengths (1.90−2.03 Å; see Table S2 in the SI). This elongation of the Ga3−O_6 bond, on the other hand, can be viewed as the displacement (∼0.4 Å) of Ga3 from its ideal position (see Figure S1 in the SI), which is the inversion center in the $R\overline{3}$ structure (Al-PKU-1). This deviation of the heavy atom from its hypothetical special position is the major cause of the symmetry descendent of the framework. In addition, the total structure symmetry lowering is also a consequence of structural synergism between neutral guest molecules and the host framework; i.e., the alternate arrangement of $H_6B_3O_6$ and H_3BO_3 species along the *c* direction certainly breaks the supposed inversion center.

The internal diameter of the structural channel in Ga-PKU-1 is measured as 7.26 Å on the basis of the distance between opposite oxygen atoms on borate groups, wherein ordered $H_6B_3O_6$ and H_3BO_3 species were enclosed. The size and spatial matching between H_3BO_3/$H_6B_3O_6$ monomers and borate groups grafted on the inner surface of channels allow the existence of multiple hydrogen bonds, which, in fact, lock the neutral molecules inside the channel (see Figure 1). From the viewpoint of synthesis, it is the first observation of H_3BO_3 and $H_6B_3O_6$ acting as structural templates, although there have been numerous polyborates synthesized by the boric acid flux method during the past decade.[9,10] The nitrogen adsorption isotherm of as-prepared Ga-PKU-1 exhibits a small specific surface area (3.9 $m^2\ g^{-1}$; Figure S2 in the SI) because the inner space was filled by those molecules. However, the inorganic molecules inside the structural channels cannot be removed for now, making no exact multifunction. As shown in Figures S3 and S4 in the SI, the framework of Ga-PKU-1 is maintained until 500 °C. At about 600 °C, $Ga_4B_2O_9$ appears, which further decomposes to $GaBO_3$ at temperatures higher than 700 °C.

Density functional theory (DFT) calculation on Ga-PKU-1 indicates that it has an indirect band gap of 4.57 eV. The top of the valence band (VB) and the bottom of the conducting band (CB) are contributed by O 2p, Ga 4s, and B 2p orbitals, respectively (see the inset of Figure 2). It consolidates our anticipation that Ga^{3+} and B^{3+} are both important for its photocatalytic activity. The band gap was experimentally estimated to be 4.8 eV by the UV−vis absorption spectrum, according to the onset of a short-wavelength absorption edge (258 nm), which is in deep UV and slightly larger than the calculated value. There is also a notable absorption band ranging from 260 to 330 nm, probably from its extrinsic midgap states.

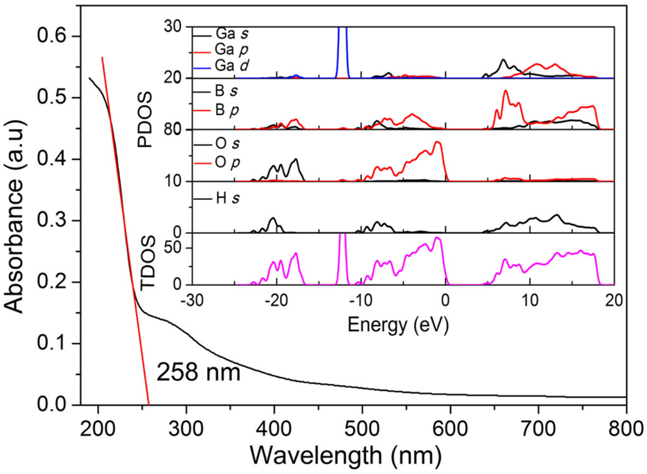

Figure 2. UV−vis absorption spectrum for Ga-PKU-1. Inset: calculated density of states and partial density of states projected on the constituent atoms.

For a water-splitting photocatalyst, it is necessary for its CB and VB potentials to be more negative and positive than H^+/H_2 and O_2/H_2O, respectively. Because the crystal structure of Ga-PKU-1 is very complex, it is not easy to calculate its exact potential edges by DFT calculations. Anyway, in the literature, people estimate the VB and CB positions using Mulliken electronegativity (see the SI for more details).[11] Accordingly, the estimated E_{CB} for Ga-PKU-1 is 0.68 eV higher than H^+/H_2 and E_{VB} is 2.19 eV lower than O_2/H_2O.

Experimentally, the photocatalytic activity of Ga-PKU-1 was first evaluated using catalytic decolorization of a methylene blue (MB) solution. After 1 h of UV irradiation, the concentration of MB decreased from 30 to 4.8 ppm, which shows the apparent photoactivity by comparison to the blank reaction, from 30 to 18.6 ppm (see Figure S5 in the SI). More importantly, Ga-PKU-1 can also photocatalyze the H_2 evolution from pure methanol and its aqueous solutions, using commercial TiO_2 (P25) as a reference. As shown in Figure 3a, without noble-metal loading, the activity of Ga-PKU-1 is 3 times that of P25. After 8 h of irradiation by UV light, the H_2 production rate remains steady, and there is no observable change in the XRD patterns after the catalysis process (see Figure S6 in the SI). The H_2 production rate of Ga-PKU-1 can be further enhanced when using pure methanol. The as-prepared Ga-PKU-1 are single crystals in micrometers (see Figure S7 in the SI). The average distance for photoinduced electrons to move to the sample surface is apparently longer than that in P25 (TiO_2 nanocrystals). Therefore, it is unquestionable that Ga-PKU-1 shows an intrinsic activity superior to that of P25.

Because of the unoccupied B 2p orbital, the triangular borate groups might capture photoelectrons, which is beneficial to charge separation and extends the lifetime of the photoelectrons. Possibly, the three-dimensional GaO_6 framework with uninterrupted Ga−O connectivity is responsible for the generation and movement of photoinduced electrons and holes. The exposed borate species might be the active sites for H_2

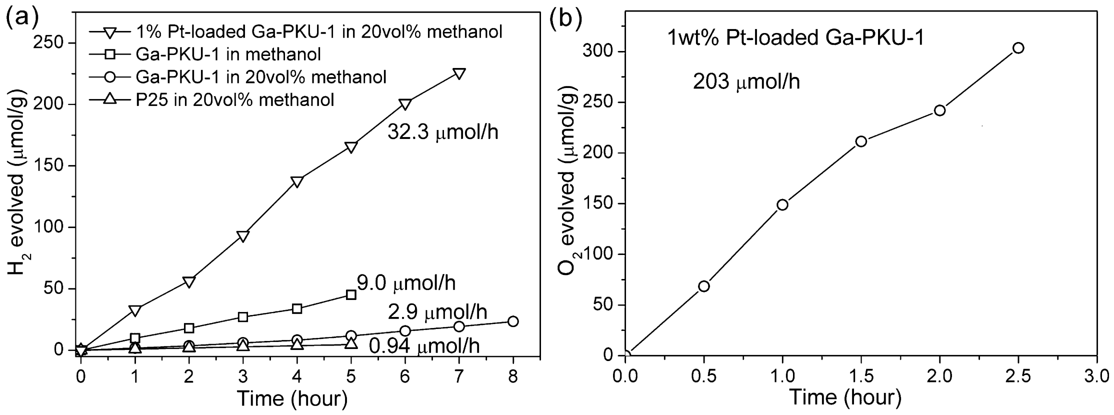

Figure 3. H_2 and O_2 evolution data under UV-light irradiation for as-obtained and post-treated Ga-PKU-1 and P25 samples.

production. The exact physical mechanism needs further investigation. Anyway, numerous gallium-containing or other photosensitive metal borates remain unexplored; our work opens up a new avenue for borates to be photocatalysts, in addition to well-known oxides and sulfides.[12]

For practical applications, the appropriate post-treatment of a catalyst would be even more vital than its intrinsic property, however, is not simple. A preliminary platinum-loading experiment on Ga-PKU-1 shows that the photoactivity increases significantly (see Figure 3). More interestingly, the O_2 production rate using $AgNO_3$ as a sacrificial agent is much higher than H_2 production in a methanol solution. It is consistent with the fact that the VB potential is much more positive than that of O_2/H_2O, while the CB potential is just 0.68 eV higher than that of H^+/H_2. Anyway, our preliminary photocatalytic experiments show that Ga-PKU-1 has the intrinsic ability for water splitting. The loading of platinum would not change the band structure but would be beneficial to the separation of e^- and h^+.

In summary, the observed photocatalysis of Ga-PKU-1 validates our original motivation of searching suitable semiconductors in gallium-containing borates. The notable intrinsic photocatalytic activity of Ga-PKU-1 and its high stability give a good starting point for further investigations, which include the opening of the structural channels, narrowing of the band gap, or creation of midgaps by transition-metal doping, making nanoparticles. Ga-PKU-1 is a pioneering case to show that inorganic open-framework borates may possess photoactivity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystal structure in CIF format, structure view of PKU-1, photograph for single crystals of Ga-PKU-1, scheme of distortion from *R*3 symmetry, and BET, IR, ^{11}B MAS NMR, TG−MS, and XRD after heat treatments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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