Contribution ID: **44** Type: **Poster**

Metallic binary alloyed superconductors as a new class of photocatalytic materials for photogeneration of hydrogen through water splitting

Saturday, 13 November 2021 13:00 (4 minutes)

We present a direct experimental evidence for photogeneration of the electric current from dissociated water molecules using a new class of catalytic materials - binary layered metals (BLM) with layered graphite-like structures [1-3]. BLM consists of alternative layers of metals (Al, Mg, Cr, etc.) and metalloids (B) where the ionic (covalent) exchange between layers results in alternating charges (electrons and holes) sitting on alternating layers. We have shown, for the first time, a series of metallic binary alloyed superconductors (MgB2, AlB2, NbB2, and NbSe2) that can be used as photoanodes and cathodes in a photocatalyst composite for both hydrogen production and water oxidation reactions. Interestingly, it was found that the highly active ion binary metal-based photocatalyst can be used as a low-cost alternative to Pt for water photolysis. For example, a MgB2 layer was formed with the help of inexpensive spraying technique from a suspension produced by liquid-phase exfoliation of MgB2 powder (Sigma Aldrich) in ethanol solution by sonication with a homogenizer. The resulting MgB2 flakes were mostly single polycrystals with lateral dimensions of 1-2 □m, as characterized by optical microscopy. The exfoliated suspension of MgB2 was sprayed onto a clean glass substrates covered by either Au(50nm), or Ag (50nm), or Cu standard foil (100□m) at 120oC using a spray gun. The produced H2 bubbles (clearly seen by eyes) gathered on the cathode surface of MgB2 (or Pt) electrode, while O2 bubbles were gathered on the MgB2 photoanode. The conversion efficiency has been calculated using bubble microscopy (and following gas chromatography). These measurements confirmed 0.95% Faraday efficiency (every 2 electrons generated ~0.95 molecules H2). The hydrogen production was directly related to the photocurrent through the reaction 2H++2e-=H2. The BLMs exhibit high activity toward both the oxygen and hydrogen evolution reactions in pure distilled and seawater. The combination of the two such photoanodes and cathodes yields water splitting photocurrent density of around 1 mA/cm2, corresponding to a solar-to-photocurrent efficiency of 34% [1,2]. A strong correlation between the values of superconductive temperature and photocatalytic water splitting efficiency for investigated diborides has also been revealed.
The photogeneration of current in MgB2-based solar cell is unexpectedly efficient, suggesting that a new model may be needed to describe water splitting mechanism in such systems. We suggest that unusual surface states of electrons in ionic binary metals are responsible for creation of electron-hole pairs that creates ions of H+ and OH- in this simple single particle picture. In reality, the situation is more complicated. Indeed, metals interact with light through collective oscillations of electron plasma which yield quantized collective plasmon states. In BLM, plasmons are characterized by plasmon bands which can strongly interact with surface states and affect creation of surface electron-hole pairs [4]. The relation between BLM plasmons and surface states is an open question that requires further investigation. It is well known that the electron plasma provides negative values of metal permittivity in visible range and hence the light absorption in metals happens in thin (skin) layer where the catalytic reaction takes place. This makes metal catalysts to be more effective than semiconductor ones as the light absorbed in the bulk of a semiconductor catalyst is effectively lost for the reaction.

Topics

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Session Classification: Poster Session