Enhanced photoelectrochemical hydrogen production with swift heavy ion irradiation

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Metal oxide semiconductor properties have been modified to achieve split water.

Conventional solar cells directly convert light to electricity. Alternatively, hydrogen production through splitting water in a photoelectrochemical cell has emerged as an advanced alternative to the conventional photovoltaic cell. The key limiting challenge in the process is to design a stable semiconductor electrode that, on exposure to sunlight, creates charge carriers that in turn produce hydrogen and oxygen.

The primary requirements for suitable semiconductor photoelectrodes are sufficient solar-energy absorption, high chemical stability, and favorable band edge positions with respect to water oxidation potential. Various strategies are used to tailor semiconductor properties to suit these requirements, such as doping, dye sensitization, fabricating heterostructures of different metal oxides, developing composite nanomaterials, and nanoarchitecture design. Photoelectrochemical (PEC) performance nevertheless remains less than ideal.

In addition to working on all of these subjects, we have used swift heavy ion (SHI) irradiation on metal oxides towards improving the material performance in PEC cells for hydrogen generation, and have achieved significantly improved PEC responses with irradiated oxides. SHI irradiation is a technique with the capacity to introduce structural and morphological changes in the target material, leading to property alterations such as band gap, resistance, and additional states.

A variety of metal oxides exhibited an enhanced photoelectrochemical response when irradiated with different types of energetic ion beams. The enhancement is a function of the material, ion beam, and irradiation fluence. Iron oxide thin films irradiated with 170MeV Au^{13+} (gold) ion offered improved photoresponse upon irradiation at fluence (10^{12}ions/cm^{2}), due to tubular structure formation (see Figure 1). Furthermore, irradiation of hematite with 120MeV Ag^{9+} (silver) ions at fluence (1 \times 10^{13}ions/cm^{2}) led to a photocurrent density approximately five times larger than an unirradiated sample. This enhancement was attributed primarily to the partial transformation of hematite to magnetite phase of iron oxide (see Figure 2). Irradiation of iron oxide with 100MeV Si^{7+} (silicon) ion at fluence (2 \times 10^{13}ions/cm^{2}) also resulted in improved photocurrent density.

Figure 1. Atomic force microscopy images for the unirradiated and irradiated films: (a) before irradiation; (b) 10^{12}ions/cm^{2}, and (c) 10^{13}ions/cm^{2}. Continued on next page.
Sol-gel-deposited TiO$_2$ (titanium dioxide) thin films, upon irradiation with 120MeV.Ag$^{9+}$ – ion at fluence $5 \times 10^{11}$ to $1 \times 10^{13}$ions/cm$^2$, exhibited a remarkable increase in photocurrent (0.76mA/cm$^2$ at zero bias) relative to an unirradiated sample (see Figure 3). Average grain diameter decreased from 23 to 11nm, and bandgap energy decreased from 3.33 to 3.08eV, upon increasing fluence. This decrease in band gap energy is due to the creation of defect levels near the conduction band, i.e. shallow energy levels, by the ion beam irradiation. These give rise to a transition from valence band to defect levels instead of a band-to-band transition.

The effect of 120MeV Ag$^{9+}$ irradiation on ZnO (zinc oxide), BaSrTiO$_3$ (barium strontium titanate), and SrTiO$_3$ was also studied. ZnO films sintered at 500 and 600°C, irradiated with 120MeV Ag$^{9+}$ ions at different fluences, featured a significant increase in photocurrent density. It was at a maximum (1.9mA/cm$^2$) at fluence $3 \times 10^{12}$ions/cm$^2$. The irradiated BaSrTiO$_3$ thin films at the lowest fluence featured an approximately two-fold increase, whereas strontium titanate thin films irradiated at $3 \times 10^{12}$ions/cm$^2$ featured a four-fold increase, in photocurrent density relative to pristine sample. The photoelectrochemical response of Cu$_2$O (copper oxide) thin films irradiated with 100MeV Ni$^{10+}$ ions at fluence $5 \times 10^{11}$ions/cm$^2$ was a photocurrent (7mA/cm$^2$) that was significantly higher than the unirradiated samples.

In summary, we have established the potential of swift heavy ion irradiation to improve photoresponse for a variety of metal semiconductors. This research will be useful for theoretical and computational approaches towards improving material properties for hydrogen production based on solar-energy-induced water splitting.

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**References**


