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Rapid Screening of Effective Dopants for Fe$_2$O$_3$ Photocatalysts with Scanning Electrochemical Microscopy and Investigation of Their Photoelectrochemical Properties

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Scanning electrochemical microscopy in the photoelectrochemical (PEC) mode was used to search for more efficient doped iron oxide photocatalysts under visible light irradiation ($\lambda \geq 420$ nm). Iron oxide doped with one or two different metal cations was investigated to improve its PEC performance. Among various dopants, Sn or Ti as single dopants and Be or Al as codopants showed an improved photocurrent response of Fe$_2$O$_3$ under visible light irradiation ($\lambda \geq 420$ nm). Fe$_2$O$_3$ doped with 4% Sn(IV) and 6% Be(II) showed the highest photocurrent as well as a good photosensitivity and stability in alkali solution (0.2 M NaOH) under UV and visible light irradiation.

Introduction

Visible light-driven photocatalysts that can produce hydrogen from water splitting under solar light irradiation have been actively sought.\textsuperscript{1-3} A photoelectrochemical (PEC) system is a potentially effective method of producing hydrogen from sunlight and water. While a great deal of progress has been made in our understanding of PEC systems, practical, inexpensive, efficient, and stable devices have not yet been realized. The search for efficient photocatalysts for water splitting under visible light irradiation has been approached from several directions: (i) to find new single phase materials,\textsuperscript{4,5} (ii) to tailor the band gap by modifying cations or anions of UV or visible photocatalysts with substitutional doping,\textsuperscript{6-8} (iii) to fabricate multicomponent photocatalysts by forming composites,\textsuperscript{9-11} (iv) to decorate UV-active photocatalysts with a photosensitizer absorbing visible light,\textsuperscript{12,13} and (v) to improve PEC properties of photocatalysts by loading or doping with a metal or noble metal.\textsuperscript{14-16} Among various candidate materials, iron oxide very early on was considered a good candidate for a PEC system because of its small band gap (approximately 2.2 eV), good stability, convenient processing, and low cost.\textsuperscript{17} The theoretical maximum efficiency of Fe$_2$O$_3$ is 12.9%.\textsuperscript{18} Although iron oxide possesses many advantages, it has severe limitations, such as a small optical absorption coefficient in the visible region, short carrier diffusion lengths, and rapid electron–hole recombination rates.\textsuperscript{19,20} Many studies have sought to improve the PEC properties of iron oxide by doping with various metals.\textsuperscript{21-27} Most dopants have been shown to increase carrier concentrations, but some have decreased the photocurrent by introducing electron or hole traps. Sartoretti et al. reported that Fe$_2$O$_3$ doped with metal cations such as Al$^{3+}$/Ti$^{4+}$ and Zn$^{2+}$/Ti$^{4+}$ affected the hole diffusion length, leading to a negative shift of the photocurrent onset potential.\textsuperscript{23} As a result of this doping, the photocurrent of a doped Fe$_2$O$_3$ thin film could be improved. Hu et al. prepared Pt-doped Fe$_2$O$_3$ thin films by an electrochemical route and reported improvement of the photocurrent of the pure Fe$_2$O$_3$. Most research with doped Fe$_2$O$_3$ has focused on single dopants to improve its photoresponse.\textsuperscript{26} By use of scanning electrochemical microscopy (SECM) in the PEC mode, arrays of doped materials may be rapidly screened; this can be used to quickly search and develop new photocatalysts sensitive to UV or visible light irradiation.

Recently our group reported a SECM method, modified by replacing the usual ultramicroelectrode (UME) tip with an optical fiber for rapid screening of photocatalysts,\textsuperscript{28} analogous to the use of SECM for electrocatalyst discovery.\textsuperscript{29} The optical fiber connected to a light source illuminates $\sim300$ µm diameter photocatalyst spots in an array, one at a time, and signals the photocactivity of each from the substrate current that is recorded at that spot. In the present work, we report the effects of various single and double dopants on the PEC effect of iron oxide using the SECM and measure the photocurrent of undoped and doped iron oxides in alkaline solution under UV and visible ($\lambda \geq 420$ nm) light irradiation.

Experimental Section

Preparation of Photocatalyst Spot Arrays. F-doped tin oxide (FTO) coated glass was obtained from Pilkington (Toledo, OH). Squares (15 mm $\times$ 15 mm) were cleaned by sonickating successively in ethanol and isopropanol and rinsed with deionized water. Fe(NO$_3$)$_3$$\cdot$9H$_2$O (Aldrich) and ethylene glycol (Fisher) were used as received. All metal precursor solutions were made with ethylene glycol (EG) with a metal nitrate or chloride salt of concentration 0.2 and 0.04 M.

A CH Instruments model 1550 Dispenser (Austin, TX) was used to fabricate the photocatalyst arrays. The model 1550 consists of a stepper motor operating an XYZ stage with a piezodispenser (MicroJet AB-01-60, MicroFab, Plano, TX) attached to the head. The system is connected and controlled with a personal computer. The substrate (FTO) was placed under the piezodispenser tip. The XYZ stage moved the dispenser head in a preprogrammed pattern, while voltage pulses were applied to the piezodispenser to eject different numbers of $\sim100$ pL drops of the metal precursor solutions onto the substrate. The first component (metal precursor solution) was loaded and dispensed in a preprogrammed pattern onto the FTO substrate. After the piezodispenser was washed and flushed, the second metal precursor solution was loaded into the dispenser and dispensed into an overlaying pattern. These steps were repeated...
when a third component was added. The patterned arrays were calcined at 500 °C for 3 h.

**Screening the Spot Array.** A schematic of the SECM setup in the PEC mode (abbreviated as SPECM) was depicted in a previous communication. An optical fiber (FT-400-URT, 3M, St. Paul, MN) connected to a 150 W xenon lamp was attached to the tip holder of a CHI model 900B SECM. The array was placed in a SECM cell made of Teflon with the FTO/photocatalyst working electrode exposed at the bottom through an O-ring. A Pt wire counter electrode and an Ag/AgCl reference electrode were used to complete the three-electrode configuration. The electrolyte was 0.2 M NaOH. Light from the xenon lamp was passed through the optical fiber, which was positioned perpendicular to the working electrode surface, and illuminated the working electrode. A 420 nm long-pass filter was used for visible light illumination experiments. The optical fiber tip was held and scanned 50 μm above the working electrode surface, while a potential bias was applied to the working electrode array via the FTO substrate. The photocurrent produced during the scan was measured and displayed as a two-dimensional image. Generally the applied potential was 0.2 V vs Ag/AgCl or about 0.4 V vs NHE, where the photoreaction is oxidation of hydroxide ion to oxygen, as demonstrated in earlier work.

**Preparation and Measurement of Photoelectrochemical Properties of Bulk Spot Array Electrode.** A mixed solution containing metal precursor with specific compositions was prepared in ethylene glycol. Bulk spot array was fabricated on FTO-coated glass with a CH Instruments model 1550 Dispenser. The patterned bulk spot arrays were calcined at 500 °C for 3 h. The electrochemical cell was comprised of a thin film electrode (0.18 cm²), Ag/AgCl, and Pt gauze as photoanode, reference electrode, and counter electrode, respectively. The photoanode was illuminated with a Xe lamp (150 W) equipped with a UV cutoff filter (λ ≥ 420 nm). The photocurrent vs potential (i–V) was measured in a 0.2 M NaOH solution (pH = 13.3) under UV or visible light irradiation (λ ≥ 420 nm). Chronoamperometry curves were obtained at 0.4 V vs Ag/AgCl for photosensitivity measurements of the electrode under dark or illuminated conditions.

**Physicochemical Characterization.** X-ray diffraction (XRD) measurements were carried out using a Bruker-Norius D8 advanced diffractometer. The CuK radiation source was operated at 40 kV and 40 mA. All measurements were carried out in the (θ/2θ) mode. Samples for XRD analysis were prepared using the same metal salt solution used to fabricate the photocatalyst arrays. The solutions were mixed in 25 mL vials according to the ratio determined by SPECM experiments and were then heated at 500 °C for 3 h. The optical properties of undoped and doped iron oxide films were analyzed with a UV-visible diffuse reflectance spectrophotometer (Milton Roy Spectronic 3000 Array).

![Figure 1. Summary of doping effects on Fe₂O₃ for a number of metals as found with the SPECM array.](image1)

**Results and Discussion**

**Screening Arrays by SECM.** To develop a doped iron oxide (Fe₂O₃) photocatalyst active for water or hydroxide oxidation under visible light illumination, we screened various candidates as single or double dopants. Different dopants exhibited positive or negative effects on the UV and visible light induced photocurrent response compared to undoped Fe₂O₃ as summarized in Figure 1. Spot arrays of Fe₂O₃ with different concentrations of various dopants (0–10% dopants in 2% or 4% increments) were fabricated and screened. For the screening of single dopants, the array pattern was prepared from solutions containing 0.2 M Fe(NO₃)₃ and 0.04 M dopant solutions as the nitrate salts as shown in Figure 2a. The first and sixth spots in the row were 100% Fe₂O₃ (20 drops of Fe(NO₃)₃) and 20% metal-doped Fe₂O₃, respectively. Figure 2b shows a typical SECM image obtained from a photocatalyst spot array consisting of Fe and Sn under visible light (λ ≥ 420 nm). The sample spot with highest photocurrent had a dark brown color, while that with the smallest was dark green. Note that there is a small cathodic current of unknown origin on the FTO substrate at a potential of 0.2 V. Figure 3 shows the averaged photocurrent results obtained from multiple SPECM measurements. The largest photocurrent value was obtained at the 4% Sn–Fe spot (the values represent the atom percent relative to elemental iron), which was 8 times that of pure Fe₂O₃ (8 nA), and then decreased gradually with further increase in the amount of Sn. This may be caused by the change of cation charge of Fe³⁺ to Fe²⁺ and its amount in the photoactive material (Fe₂O₃). The addition of titanium to iron oxide also showed similar trends as that of tin dopant on Fe₂O₃ in the photocurrent (not shown). The mechanisms for the photocurrent enhancement by Sn⁴⁺, Ti⁴⁺, and
Si\textsuperscript{4+} as dopants on iron oxide have been proposed.\textsuperscript{21–25} Fe in the hematite lattice is substituted by Sn or Ti. In the presence of ethylene glycol (a reducing agent), Sn(IV) and Ti(IV) might be reduced to lower oxidation states (i.e., Sn(II), Ti(III)) at high temperatures, and these could play the roles of electron donors, improving the electrical conductivity of hematite. In our work we also tested two dopants which produce a dramatic improvement in the photocurrent of Fe\textsubscript{2}O\textsubscript{3} under visible light.

To investigate an effect of a second dopant on Fe\textsubscript{2}O\textsubscript{3}, we fixed 4% Sn as the first dopant. The array pattern was prepared from the mixture solution containing Fe and 4% Sn and another second dopant (0.04 M) as shown in Figure 4a. The first and sixth spots in a row are 4% Sn–Fe\textsubscript{2}O\textsubscript{3} and 4% Sn–Fe\textsubscript{2}O\textsubscript{3} with 10% of a second dopant, respectively. Among various second dopants, only Be\textsuperscript{2+} and Al\textsuperscript{3+} showed positive effects while all other dopants tested, such as Cu, Ni, Mg, Zn, In, and Cr, showed negative effects on the photocurrent response of 4% Sn–Fe\textsubscript{2}O\textsubscript{3}.

Figure 4b shows the SECM image obtained from photocatalyst spot arrays consisting of Fe, Sn, and Be under visible light (\(\lambda \geq 420\) nm) illumination. The largest photocurrent (130 nA) was observed at the composition of the 6% Be–4% Sn–Fe spot, which was twice that of the 4% Sn–Fe\textsubscript{2}O\textsubscript{3} spot (65 nA). The photocurrent then decreased gradually with further increase of the amount of Be. It is not clear why second dopants such as Be and Al improve the photocurrent of Fe\textsubscript{2}O\textsubscript{3} photocatalyst doped with Sn, although perhaps Be\textsuperscript{2+} can change the surface of Fe\textsubscript{2}O\textsubscript{3} and Sn-doped Fe\textsubscript{2}O\textsubscript{3} or control the amount of effective cation charge of Fe\textsuperscript{3+} to Fe\textsuperscript{2+} on the surface of photoactive material (Fe\textsubscript{2}O\textsubscript{3}).

Figure 5 shows the photocurrents obtained from SECM images of a Be–Sn–Fe\textsubscript{2}O\textsubscript{3} spot array. The photocurrent generated under visible light irradiation (\(\lambda \geq 420\) nm) increased in the following sequence: 6% Be–4% Sn–Fe\textsubscript{2}O\textsubscript{3} (130 ± 15 nA) > 4% Sn–Fe\textsubscript{2}O\textsubscript{3} (65 ± 10 nA) > 6% Be–Fe\textsubscript{2}O\textsubscript{3} (15 ± 2.5 nA) > Fe\textsubscript{2}O\textsubscript{3} (8 ± 2 nA).

Al as the second dopant on Ti-doped Fe\textsubscript{2}O\textsubscript{3} was first introduced by Sartoretti et al., who obtained the largest photocurrent from a 5% Ti\textsuperscript{4+} and 1% Al\textsuperscript{3+} doped iron oxide photoanode.\textsuperscript{23} However, no study has been previously reported for Be as a second dopant for Sn-doped Fe\textsubscript{2}O\textsubscript{3} photocatalyst.

For further investigation on the bulk PEC properties of iron oxide with a second dopant, we kept the Be ratio to 6% on 4% Sn–Fe\textsubscript{2}O\textsubscript{3}.

Characterization. After screening studies, it is important to characterize the spot materials, at least in a preliminary way. Figure 6 shows the XRD patterns of the undoped and 4% Sn, 6% Be, and 4% Sn doped Fe\textsubscript{2}O\textsubscript{3} photocatalyst. The phase of undoped or doped iron oxides formed via pyrolysis of iron(III) nitrate solution and the mixed solution containing dopants is primarily \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} (hematite). Sn- and Be-doped Fe\textsubscript{2}O\textsubscript{3} did not show other impurity phases at the dopant levels used.

The optical properties of the undoped and doped thin films were measured by UV–visible absorption spectra and are displayed in Figure 7. Absorption of samples was observed around 590 nm (2.1 eV), a shoulder around 540 nm (2.3 eV), and a peak around 400 nm (3.1 eV). Note that the first two absorptions are much stronger, reflecting the selection rules. When the curves are normalized to the maximum absorbance of Fe\textsubscript{2}O\textsubscript{3}, one does not see any dramatic spectral change, with an “effective” band gap estimated from the absorption spectra of about 1.69 eV. This suggests that the observed effects cannot be attributed to improved absorption of incident radiation, but rather arise from kinetic effects on the photogenerated carriers.
Bulk Film Measurements. Once one finds apparently optimized materials in an array, it is useful to confirm the SECM results with those of bulk films of the same composition prepared in different ways on a larger electrode. As a first test we prepared a patterned bulk spot array of either undoped or doped Fe₂O₃ photocatalysts on FTO glass as shown in Figure 8. The PEC measurements were performed in a glass cell to facilitate the transmittance of light to the photoelectrode surface, and all spots were illuminated simultaneously with the xenon lamp (150 mW/cm²). The working electrode had an active surface area of 0.18 cm², while a platinum gauze and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. The electrolyte solution used for all measurements was 0.2 M NaOH. The doped iron oxide bulk spot array electrode showed higher photocurrents than that of the undoped pure Fe₂O₃ over a potential range of (−0.15)−(0.60) V, as shown in Figure 9. The Sn- or Sn-Be-doped Fe₂O₃ spot array electrode showed an onset photopotential of ∼−0.15 V vs Ag/AgCl, which is ∼0.35 V negative of the thermodynamic potential for water oxidation at pH 13.3. The undoped Fe₂O₃ spot array electrode showed a negligible photocurrent under visible light irradiation (λ ≥ 420 nm), while the 6% Be−4% Sn−Fe₂O₃ spot array electrode exhibited the highest photocurrent of ca. 33 μA/cm² at 0.2 V vs Ag/AgCl in 0.2 M NaOH solution under visible light (λ ≥ 420 nm).

Figure 10 shows the current–time transient responses of Fe₂O₃, 4% Sn−Fe₂O₃, and 6% Be−4% Sn−Fe₂O₃ multispot electrodes under chopped visible (λ ≥ 420 nm) and UV illumination conditions. Both 4% Sn and 6% Be−4% Sn doped Fe₂O₃ spot arrays showed good photosensitivity and stability under UV and visible light, i.e., a higher photocurrent under illumination relative to the dark current and photostability in alkaline solution. The undoped Fe₂O₃ showed a low photocurrent under UV light and negligibly small photocurrent under visible light (λ ≥ 420 nm) as compared to doped Fe₂O₃ photocatalysts.

The flat-band potentials of the Fe₂O₃, 4% Sn−Fe₂O₃, and 6% Be−4% Sn−Fe₂O₃ spot array electrodes were estimated from the Mott–Schottky (M−S) plots (1/C² vs E), where C is the
space charge capacitance of the material). Figure 11 shows the M–S plots for the undoped and doped Fe\textsubscript{2}O\textsubscript{3} spot array electrodes at pH 13.3 (0.2 M NaOH). Before and after doping with Sn or Sn and Be, the value of $E_{\text{fb}}$ shifted positively from ca. $-0.32$ to $-0.2$ and $-0.12$ V, respectively, at pH 13.3. However, as generally found from such plots, there is often considerable uncertainty in the flat-band potentials estimated in this way.

Figure 12 shows the photocurrent action spectrum of a 6% Be–4% Sn–Fe\textsubscript{2}O\textsubscript{3} bulk spot array electrode. The photocurrent is mainly from direct transitions from the valence band orbitals to the conduction band edge ($2p$ O$^{2-}$ to 3d Fe$^{3+}$, 257–413 nm) and not from indirect transitions (d $\rightarrow$ d type, 564 nm).$^{30}$

To evaluate the incident photon to current conversion efficiency (IPCE) of each undoped and doped Fe\textsubscript{2}O\textsubscript{3} multispot array and from SECM image data, we used monochromatic irradiation with the optical fiber connected to the 150 W Xe lamp, coupled with a 420 nm band-pass filter (bandwidth $\sim$ 10 nm) where the incident radiation was calibrated with a power meter. The photocurrents generated by each spot in undoped and doped Fe\textsubscript{2}O\textsubscript{3} arrays were measured using SECM. Figure 13 shows the monochromatic IPCE at 420 nm. The IPCE was calculated from the SPECM image, neglecting the geometric distribution of light in and outside of the spot and using the maximum photocurrent value. The IPCE of Fe\textsubscript{2}O\textsubscript{3}, 4% Sn–Fe\textsubscript{2}O\textsubscript{3}, and 6% Be–4% Sn–Fe\textsubscript{2}O\textsubscript{3} spot array was about 0.14, 0.7, and 1.2%, respectively, at 0.3 vs Ag/AgCl, and displayed a similar trend as the increase of photocurrent shown in Figure 5. The inset figure shows the SPECM image of the 6% Be–4% Sn–Fe\textsubscript{2}O\textsubscript{3} spot. Although the IPCE of Fe\textsubscript{2}O\textsubscript{3} increased by doping with Sn and Be, the value is still rather small. However, it might be possible to improve the photocurrent further by optimizing the fabrication method for Fe\textsubscript{2}O\textsubscript{3} thin film electrodes.$^{21–23}$

**Effect of Dopants.** Although theoretical modeling of semiconductor materials has not yet allowed prediction of the effects of metal doping, the SPECM screening results, as summarized in Figure 1, show that the addition of many metals caused a decrease (negative effect) in the PEC performance, while relatively few caused a significant increase (positive effect). Dopants such as Sn, Ti, Cr, In, Al, and Be showed a positive effect while Cu, Ni, Mg, Zn, V, and W showed a negative effect on the photocurrent vs undoped Fe\textsubscript{2}O\textsubscript{3}. Among the dopants with a positive effect, Sn and Ti showed the greatest improvement in photocurrent of an iron oxide thin film. This rapid screening (combinatorial) approach may eventually provide guidelines to suggest effective candidates for photosplitting of water.

**Figure 10.** Chopped current–time transient response of (a) Fe\textsubscript{2}O\textsubscript{3}, (b) 4% Sn–Fe\textsubscript{2}O\textsubscript{3}, and (c) 6% Be–4% Sn–Fe\textsubscript{2}O\textsubscript{3} bulk spot array electrodes under visible ($\lambda \geq$ 420 nm) and UV light irradiation. Electrolyte solution, 0.2 M NaOH; light source, 150 W Xe lamp; applied potential, 0.3 V vs Ag/AgCl.

**Figure 11.** Mott–Schottky plots of (a) Fe\textsubscript{2}O\textsubscript{3}, (b) 4% Sn–Fe\textsubscript{2}O\textsubscript{3}, and (c) 6% Be–4% Sn–Fe\textsubscript{2}O\textsubscript{3} bulk spot array electrodes in 0.2 M NaOH solution at 100 Hz under dark conditions.

**Figure 12.** Photocurrent action spectrum of 6% Be–4% Sn–Fe\textsubscript{2}O\textsubscript{3} bulk spot array electrode. Electrolyte solution, 0.2 M NaOH; light source, 150 W Xe lamp; applied potential, 0.3 V vs Ag/AgCl.
References and Notes