A Digital Method for the Identification of Photoelectrolysis Catalysts for Water

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Background

It will become necessary, at some point in the course of this planet's future, for the paradigm of energy production to shift from the burning of fossil fuels to the use of renewable and environmentally benign sources of energy. While the capital required to integrate a purely electrical solar system onto homes and businesses is an unrealistic expectation for the average consumer, the barriers to creating hydrogen, the *ideal* source of energy from the standpoint of emission byproducts, go even beyond the prohibitive issue of cost. All of the potential photoelectrolysis materials which have been identified and studied to this point have suffered from at least one of three problems: the semiconductor electrodes have too large of a band gap for efficient utilization of the solar spectrum, they decompose in aqueous electrolytes, or they do not meet the requirement for thermodynamic effectiveness that the valence band and conduction band edge positions straddle the water redox potentials. Although these facts might discourage a realist from seeking out novel materials, we believe that we have designed and demonstrated a visionary system utilizing a Hewlett-Packard ink jet printer that is capable of producing thousands of novel photocatlysts and a scanning laser-based system for testing their ability to surmount those hurdles.

Materials derived from multiple elements are often needed when a special property needs to be optimized. For example, the highest transition temperature superconductor contains four metals ($HgBa_2CaCu_2O_{6+\delta}$). This is not to imply that one can haphazardly combine elements and expect special results, but it does suggest that each element plays a specific role in the overall functionality of special materials and that specific amounts of the right elements can create a synergy between each of these roles. Perhaps elements suited for each role in the photoelectrolysis of water can be choreographed into a functional device. The traditional parent materials of wide-band gap metal oxide semiconductors (for example, Ti, Sn, W, Ta, and Nb) are needed for structure and stability. It may be necessary to incorporate colored transition metals into those materials to serve the role of visible light absorbers and indeed work done in the past has already shown that the visible response of wide band gap semiconductors can be enhanced by such additions.[1,2] Yet another material may help to suppress electron-hole recombination within the material by acting as charge compensator or as a surface state modifier- a role that has also been shown to increase the efficiency of the same materials mentioned above.[1,3] Finally, it may be necessary to sprinkle the surface of the electrode with catalytic materials such as Pt, Pd, Ir, Ru, or, even better yet, a cheaper element such as Ni.[4-6]

Combinatorial Search Using a Hewlett-Packard Ink Jet Printer

The basic premise behind a combinatorial search is to produce as many combinations, in both the number of materials and their mixed proportions, as possible and screen them for the property of interest. It can be extremely difficult for a scientist, if properly trained to believe in his or her abilities to solve problems largely by deductive reasoning, to believe that such a seemingly chaotic endeavor could ever produce anything useful. Yet many of the greatest inventions, including Edison's discovery of a material for the first electric light bulb, were not synthesized from theory alone but instead were instead the result of painstaking trial-and-error. The quest to find functional materials by empirical methods leads to the combinatorial idea which has already revealed invaluable applications within the pharmaceutical industry but has also been extended to discover new luminescent materials,[7-9] gate dielectrics,[10] and fuel cell catalysts.[11,12] The properties of all of these new materials discovered by combinatorial means appear to be more promising than the previous materials used for the same purpose.

As there is currently no demonstrated way to *a priori* estimate the identity of a suitable water splitting material using sunlight as the energy source, perhaps thousands of mixed metal oxides will have to be produced and tested before a working material is found. The McFarland group has already embarked on the search by generating and screening a small library of binary oxides using an automated array-based electrodeposition and an electrochemical scanning system.[13,14] Through this approach they have identified the optimal tungsten-molybdenum composition. The group has also synthesized electrocatalyst libraries using electron beam evaporation.[15] Unfortunately, the methods used to create their libraries are both relatively time-consuming and expensive and only a few mixtures have thus far been reported.

A much cheaper and faster approach to materials deposition is to use ink jet printers. Ink jet printing of materials for combinatorial searches has also been applied to organic electronic materials[16] and even protein[17] and nucleic acid arrays.[18] Ink jet printing also offers the added advantages that gradients of compositions can easily be created instead of array-based samples and that an unlimited number of materials can be mixed.

We have combined the speed and versatility of ink jet printing with electrochemical screening to search for potentially promising metal oxide photocatalysts. With a software drawing program and a modified HP inkjet printer we have printed metal oxide precursors onto conductive glass substrates. We have printed gradients of one, two, three, or four materials and have screened them for photoactivity using visible wavelength light. From common and inexpensive electrochemical equipment we have already screened thousands of compositions. The system that we have designed and implemented appears to be more versatile, inexpensive, and faster than any others that have been designed for the same purpose. It also appears to be the most realistic as we are testing the materials only as they would practically be used in any real system; we don't introduce any sacrificial reagents into our electrolyte and we use incident radiation that is energetically representative of the actual sun.

Experimental

The experimental details of this process have ultimately proven to be quite simple. Conductive glass substrates (3.0-mm 8-Ω SnO_2:F) obtained from Pilkington Industries are soaked in an isopropanol/KOH base bath for at least thirty minutes. After soaking, the substrates are rinsed with copious amounts of distilled water and ethanol. Metal oxide precursors can then be printed onto the substrates after they have been taped to a standard sheet of printer paper. To date, all of our metal oxide precursors have been metal nitrate salts. These compounds are prepared at a concentration of 0.35-M in the presence of 0.6-M NH_4NO_3 and 0.015-M HNO_3. The solution is injected into empty black printer cartridges and the printer's cleaning cycle is run before printing. The cartridges can be stored in a "cartridge humidor" (a dessicator that is filled with water at the bottom) and used again up to several months after they were originally made.

After printing multiple layers, each with a different metal species, the samples are fired in a tube furnace at 500°C for 24 hours. The metal nitrates are easily pyrolized to metal oxides at this temperature- an assertion that has been confirmed with EDS and X-ray diffraction. After cooling, materials testing can be performed in a variety of different electrolyte solutions. To this point we have screened materials in 0.50-M H_2SO_4, 0.50-M Na_2SO_4, 0.50-M NaOH, and buffers of pH 4, 7, and 10.

A virtual instrument program was designed with Labview software that rasters a visible wavelength laser over the printed and fired materials that are to be screened and simultaneously records the photocurrent generated by the materials at each point. The program generates a series of stepwise voltages that are applied to a two-mirror galvanometer. The two mirrors move the laser in a two dimensional pattern and the photocurrent signal is recorded by a Data Acquisition (DAQ) Board connected in series to a lock-in amplifier and potentiostat. The start and end points of the scan are completely adjustable, but typically a 140 × 140 array of photocurrent values are produced. A false color image that displays photocurrent as a function of Cartesian position can then be obtained by opening the data array with the ImageJ software program.

We currently have the capability to print, fire and screen three films per day. This equates to thousands of unique combinations being tested on a daily basis. Additional information about this process, and the identification and characterization of some other materials that have been found early on in the process, will soon be published elsewhere.[19]

Results and Discussion

A sample of a film of materials that have been printed, fired, and screened using our method are shown in Figure 1. Using the template shown in Figure 1(a), gradients of Cs, Cu, Fe, and La metal nitrates were printed in patterns that approximate ternary phase diagrams. A picture of the printed and fired film is shown in Figure 1(b). Using these templates one gets pure single-component metal oxides at each vertex, binaries along each edge, and ternary mixtures everywhere else. Pure Fe and Cu gradients are also printed onto each film to serve as "internal standards" from material to material as α-Fe_2O_3 has been demonstrated to be a consistent *n*-type material (has a photocurrent under positive applied bias) while CuO can function as a consistent *p*-type material (has a photocurrent under negative applied bias).[20] Assuming that the pure Fe_2O_3 and CuO compounds behave similarly for all printed films, this procedure gives a useful shortcut to compare the relative performances of materials that are tested.

A wealth of information can be gleaned from analyzing the scans. In these images, the brighter spots correspond to materials that produce the most photocurrent at the applied bias being studied. Black areas correspond to materials that produce current flowing in the direction opposite to the bright areas due to different current-voltage characteristics. The bright spot in the Fe-Cu-Cs triangle in the figure above is about 210% more photoactive than the brightest area in the pure Cu triangle when a bias of -0.500-V is applied. The alloying of iron with copper and cesium gives no discernable advantage over pure Fe when the positive bias is applied and some mixtures, notably those containing Lanthanum in this particular series, actually weaken the ability of iron to function as a photocatalyst. One can also see that the mixed compounds behave completely differently depending upon the molar ratios of the starting materials. For example, the Fe-Cu-Cs materials act as either *p*-type or *n*-type depending upon the relative amounts of copper and iron. That is, the brightest areas in the positive bias scan become the dark areas of the negative bias scan and vice versa.

Identifying potential materials is the first step in the process. After a certain material has reproducibly demonstrated photocatalytic activity in our screening system (as evidenced by multiple testing), the next question becomes how effective the material will be at harvesting the full solar spectrum. A determination of the bandgap of the material is also an important determination as the optimal single material for water splitting would have a bandgap around 2.0-eV. As an initial test for these properties, we scan promising materials over the visible wavelength spectrum and measure the incident photon-to-electron conversion efficiency (IPCE)- a measure directly proportional to the photogenerated current. From figure 2 we see that the onset of photoactivity occurs around 600-nm which corresponds to a band gap of about 2.1-eV. Although this material meets the requirements of visible wavelength response, further analysis such as Mott-Schottky and current-voltage analysis are necessary to determine if the the valence and conduction bands of this material straddle the water redox potentials. Furthermore, the material must be tested for stability of operation over long working times and the efficiency must be improved, for example, by draping the material over a Grätzel scaffold.

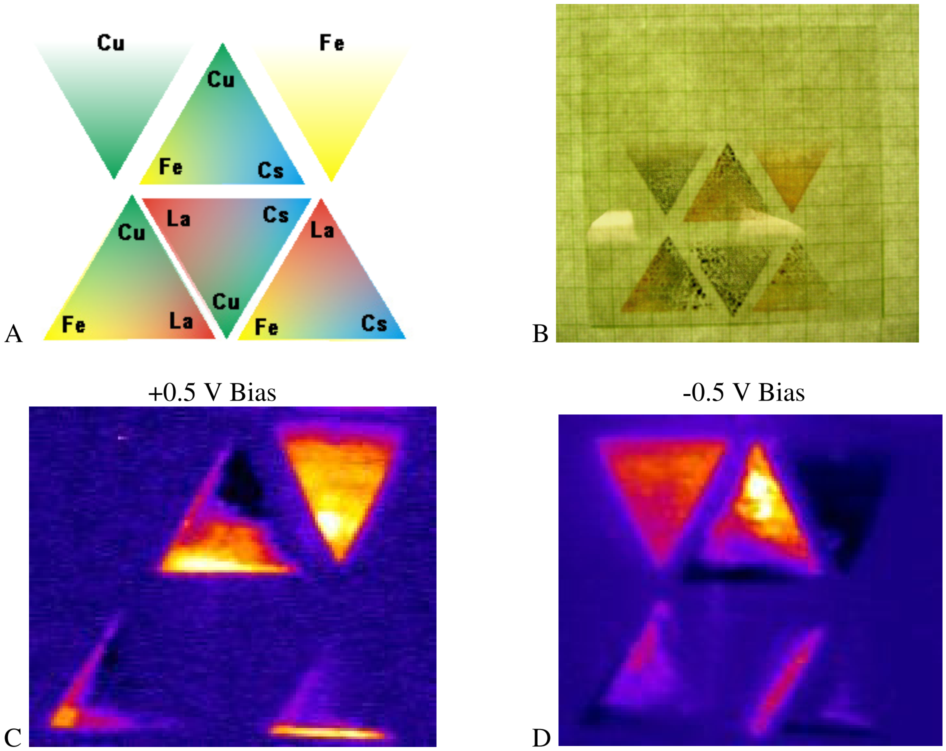

Figure 1. An example of screening for promising materials. Four unique ternary gradients and two internal standards were printed according to the template shown in (a). A picture of the printed materials is shown in (b). Subsequent screening of the compositions at two different applied biases shows different photoelectrochemical properties for the different materials. Refer to the text for a full interpretation of the results.

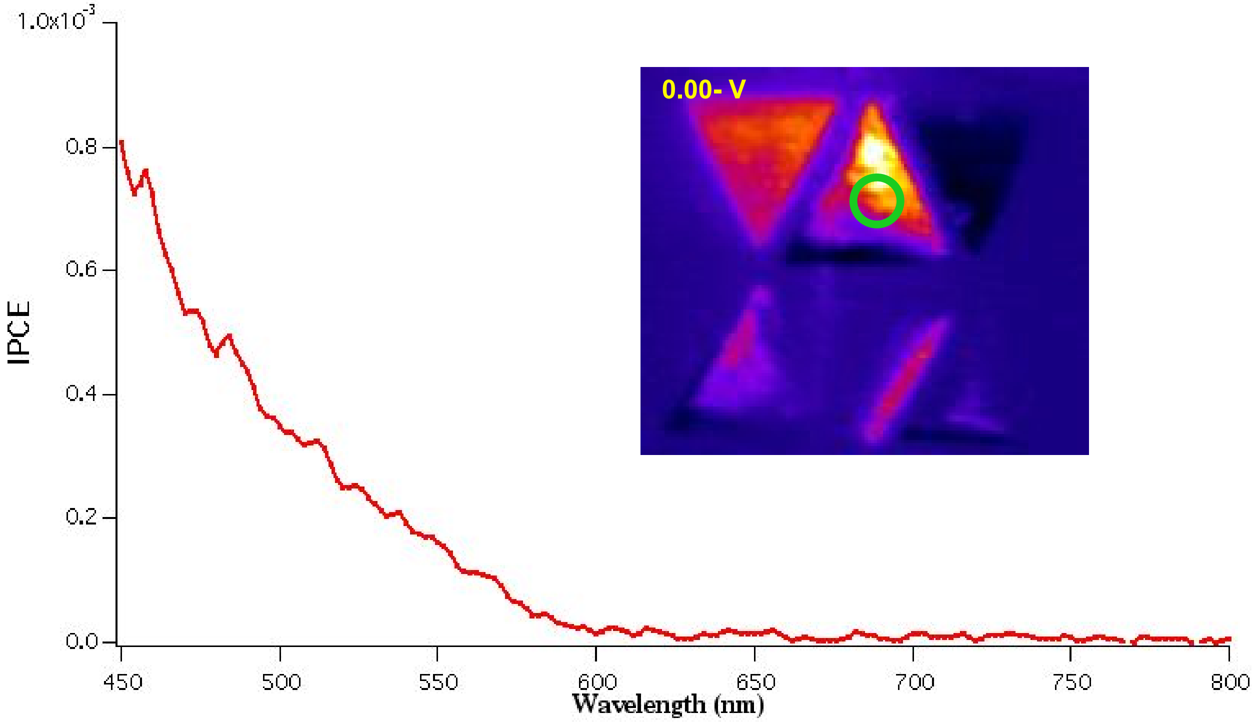

Figure 2. Action Spectrum of the bright spot seen in Figure 1(d) outlined above with a green circle. The spectrum was taken with no applied bias in a 0.500-M NaOH solution. Note that the thin films produce low IPCE values as the current configuration allows the majority of light to pass directly through. Better quantum yields could possibly be obtained by incorporating a Gratzel-type scaffold for the materials. This is not done in our initial combinatorial search as the additional substrate preparation time would lower our throughput.

Conclusion

The use of ink jet printing for materials deposition and discovery is a bourgeoning art. In the context of looking for novel materials to solve the world's energy problem, we have developed a method to rapidly and inexpensively combine and test potential materials for photoelectrolysis.

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Author Biography

Bruce Parkinson received his BS degree in chemistry at Iowa State University in 1972 and his PhD from Caltech in 1977 under the guidance of Professor Fred Anson. After a year of post-doctoral studies at Bell Laboratories with Adam Heller, he became a staff scientist at the Ames Laboratory. He then joined the Solar Energy Research Institute in Golden, Colorado in 1981 as a senior scientist. In 1985 he moved to the Central Research and Development Department of the DuPont Company where he worked until he became Professor of Chemistry at Colorado State University in 1991. His research covers awide range of areas including materials chemistry, surface chemistry and photoelectrochemistry.