Abstract: A high-throughput method has been developed for screening and optimization of colloidal water oxidation catalysts. The catalysts are irradiated in parallel by visible light from an overhead projector in solutions containing tris(2,2′-bipyridyl)ruthenium(II) (Ru(bpy)32+) and persulfate. The array of reaction solutions is held in a 96-well plate, and absorbance readings are taken intermittently using a bioassay plate reader. The absorbance at 430 nm is indicative of the amount of Ru(bpy)32+ remaining in solution. The best catalysts give the most persistent absorbance, because the oxygen evolution reaction is kinetically competitive with decomposition of Ru(bpy)32+. Reagent concentrations were varied using a factorial design-of-experiment approach in order to optimize reaction conditions for a IrO2•xH2O colloidal catalyst. A higher colloid concentration, a lower Ru(bpy)32+ concentration, and a higher pH buffer doubled the number of turnovers relative to the original conditions. Metal oxide colloids consisting of IrO2•xH2O doped with varying amounts of Pt, Ru, and Os were made using a parallel microwave synthesis technique and were tested both by the parallel screening method and by direct measurement of oxygen evolution. The correlation between the two methods was good, with Ir–Pt–Os oxide compositions showing the highest activity. The effect of adding small amounts of Pt and Os to IrO2•xH2O appears to be predominantly to reduce the particle size of the colloids.

Introduction

Photochemical water splitting is one of the most attractive potential means of converting sunlight to usable chemical energy. In principle, light of both visible and near-infrared wavelengths is sufficiently energetic to drive the water-splitting reaction. However, the search for a robust and efficient photocatalyst for this reaction has been very challenging. The problem has been actively pursued for approximately 30 years, and only recently has the first visible light water-splitting catalyst been reported. While this is an important milestone in the field, the efficiency is low, and it is not immediately apparent how one could improve upon the visible light absorbing metal oxides that have been tested so far as photocatalysts.

Another approach to the problem is to design composite systems that consist of molecular photosensitizers coupled to colloidal or solid catalysts. In this case the problem is simplified by studying the hydrogen and oxygen half-reactions separately. The catalysts and reaction conditions are optimized for each in the hope of combining them for the overall water-splitting reaction. One of the difficulties in this work has been the search for oxygen-evolving catalysts. Harriman et al. studied a variety of metal oxide powders, using tris(2,2′-bipyridyl)ruthenium(II) (Ru(bpy)32+) as the photosensitizer, and found the highest rates of oxygen evolution with IrO2 and Co3O4. Other powders that performed moderately well included RuO2, Rh2O3, Mn3O4, and NiCo2O4. Among colloidal catalysts, IrO2•xH2O14 and RuO2•2H2O15 have been the most thoroughly studied. However, RuO2•2H2O is unstable under photochemical conditions. The highest quantum yields and number of turnovers for oxygen evolution from Ru(bpy)32+ using persulfate as a sacrificial electron acceptor, have been achieved using IrO2•xH2O.16

In general, the photochemical oxygen evolution half reaction is carried out as shown in Scheme 1. A sensitizer molecule or polymer (Ru(bpy)32+) is shown here as the most widely used...
example) absorbs visible light. In the case of Ru(bpy)$_3^{2+}$, a metal-to-ligand charge-transfer (MLCT) excited state is formed. The MLCT state is quenched by reaction with persulfate ion ($\text{S}_2\text{O}_8^{2-}$), forming Ru(bpy)$_3^{3+}$, $\text{SO}_4^{2-}$, and $\text{SO}_4^{2-}$. In the absence of a catalyst, Ru(bpy)$_3^{3+}$ rapidly and irreversibly decomposes to inactive products, and the solution turns colorless. On the surface of a suitable catalyst, however, oxygen is evolved, and the reduced form of the sensitizer is regenerated. After four turnovers of the Ru(bpy)$_3^{3+}$ couple, which requires two photons in this sacrificial system, one molecule of O$_2$ is produced.

Under optimized conditions, the quantum efficiency of photochemical oxygen evolution from IrO$_2\cdot$xH$_2$O, as shown in Scheme 1, can exceed 70%. While this sounds impressive, substantial improvement in the colloidal catalyst is needed for two reasons. First, the photosensitizer survives for, at best, a few hundred turnovers before it is decomposed by nucleophilic attack of water or OH$^-$ on Ru(bpy)$_3^{3+}$. Because this reaction occurs in competition with hole transfer from Ru(bpy)$_3^{3+}$ to the colloidal catalyst, it follows that a better catalyst will increase the lifetime of the sensitizer. Second, the oxygen-evolving reaction should outpace any charge-recombination reactions that occur in a full (nonsacrificial) water-splitting cycle. Typically, charge recombination occurs on a microsecond to millisecond time scale in molecular and dye/semiconductor donor–acceptor systems.

The search for better oxygen evolution catalysts is complicated by the many factors that influence the reaction kinetics. Apart from the composition of the colloidal catalyst itself, the method of colloid preparation, as well as the presence of different buffers, stabilizers, and supports, all affect the catalyst turnover rate. Decomposition of the sensitizer occurs more rapidly if the sensitizer molecules are not in physical contact with the catalyst, or if the catalyst itself is not efficient at reducing the oxidized form of adsorbed sensitizer molecules.

To date, these factors have been optimized empirically and in a serial fashion. Catalysts are tested by continuous photolysis, in which oxygen evolution is monitored by periodically withdrawing headspace samples and analyzing them by gas chromatography (GC). This process takes 1–2 h per sample and is unwieldy for comparison of large numbers of catalysts because it requires, for each one, a steady light source, a reaction vessel purged with inert gas (to eliminate interference from atmospheric O$_2$), and frequent GC injections. If serial tests are performed on different days, then fresh colloids and buffers must be prepared, and this introduces another source of error in the comparison.

One of the most convenient ways of adapting a catalysis problem to rapid, parallel screening is to detect the products or byproducts of the reaction optically, as a change in absorbance or emission. We report here a new parallel, high-throughput method for testing large numbers of colloidal oxygen-evolving catalysts. The method uses optical, indirect detection of the reaction and is based on the idea that sensitizer turnover/sensitizer decomposition represents a kinetic branch point in Scheme 1. The method—which involves detecting the absorbance or emission of residual Ru(bpy)$_3^{3+}$—relies on the fact that poorer catalysts give more rapid decomposition of the sensitizer, because the catalytic cycle is not kinetically competitive with nucleophilic attack on Ru(bpy)$_3^{3+}$. Because oxygen is not detected directly, the requirement for a sealed, inert-gas-filled reaction vessel is removed. As an optical method, it also avoids interferences associated with electrochemical detection of reaction products. When the reaction volume is scaled down to a microwell format, then an entire array of catalysts can be irradiated simultaneously (using light from an overhead projector) and periodically interrogated during the photolysis by means of an automated plate reader. We show here that this method allows one to optimize, in a rapid and straightforward manner, both the reaction conditions and the composition of colloidal catalysts for photochemical oxygen evolution.

**Experimental Section**

Conventional Synthesis of Colloidal IrO$_2$$\cdot$3H$_2$O A 6.2 $\times$ 10$^{-4}$ M colloidal IrO$_2$$\cdot$3H$_2$O solution was made by adding 0.3 g of K$_3$IrCl$_4$ to a 50 mL aqueous solution of 0.5 g of sodium hydrogen citrate to 95 °C for 30 min, and then removed from the heat and allowed to cool. The pH was adjusted to 7.0, and then an entire array of catalysts can be performed on different days, then fresh colloids and buffers must be prepared, and this introduces another source of error in the comparison.

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were heated for 2 h at 95 °C with oxygen bubbling through it. The IrO₂·
H₂O colloidal solution was removed from the heat and allowed to cool. The solution was split into two parts: one part was ion-exchanged
with chloride-exchanged Dowex 2×8-50 resin, and the other was
dialyzed to remove excess citrate ions. The resulting solutions were
diluted to twice their initial volumes to make two nominally 6.2 × 10⁻⁴ M colloidal IrO₂·H₂O solutions.

**Parallel Microwave Synthesis of Metal Oxide Colloids.** Metal oxide colloids with elemental proportions of Ir₂₇O₇₃ (two duplicates), IrO₃,
Os₂, Ir₉₀Pt₁₀R₁₀Os₅, Ir₉₁Ru₉₁Os₅, Ir₉₁Pt₉₁Ru₁₀, and Ir₉₁Pt₂₀Ru₁₀Os₅ were prepared. The metal salts used to
prepare the metal oxide colloids were K₂IrCl₆, K₂RuCl₆·H₂O, K₂PtCl₆,
and OsCl₆. Metal salt solutions were prepared by adding enough of
the appropriate salt to make the metal concentration 1.55 × 10⁻⁴ M in
a 4.75 × 10⁻³ M sodium hydrogen citrate sesquisilicate solution. The
pH of each solution was adjusted to 7.0 using 0.25 M NaOH. Different
colloid compositions were made by using metal salt solutions in the
correct proportions to make 20 mL total. Five milliliters of a 1.05 × 10⁻³ M Na₂SiF₆ solution was added to each reaction tube. The reaction solutions with varying proportions of Ir:Pt:Ru:Os were heated simultaneoulsly in a MARSS (CEM Corp., Matthews, NC) microwave digestion system at 95 °C for 2 h. The metal oxide colloids solutions
were then cooled to room temperature and dialyzed separately to remove excess citrate ions. The volumes were diluted to 50 mL each to make
6.2 × 10⁻⁴ M (based on total metal) metal oxide colloidal solutions. The solutions were then filtered through a 0.2 μm filter so that they
would not clog the tip of the robotic plotter used to dispense reagents
into multiwell plates for screening.

**Serial Testing of Oxygen Evolution Catalysis.** Typical reaction
conditions were the same as those described by Hara et al. The concentrations of Ru(bpy)₃²⁺, metal oxide colloid, Na₂SO₄, and Na₃SiO₃ were
1.1 × 10⁻⁴, 6.2 × 10⁻⁵, 0.05, and 0.01 M, respectively. The buffer was
made by taking 3.75 × 10⁻² M Na₂SiF₆ and adding enough NaHCO₃ to make the pH 5.7. The concentration of NaHCO₃ in the
buffer solution was approximately 8.0 × 10⁻² M. The buffer solution
was sonicated for 15 min and aged overnight. The aging step was
important since the actual buffer is a poly(silicate) hydrolysis product
of Na₂SiF₆. The buffer was filtered, and 2.9 mL was added to the reaction
solution along with the other reagents for a total of 5 mL of
reaction solution. The reaction solution was put in a scaled 26 mL test
tube. The test tube was placed in an outer vessel with argon flowing
through it to prevent contamination by air. After the solution was
purged with argon for 15 min, it was irradiated with light from a 450 W Xe/
Hg lamp filtered by a 450 nm bandwidth filter for the initial and
optimized experiments, and by a 420 nm cutoff filter for the microwave
experiments. Gas samples were removed from the test tube as the
reaction proceeded and analyzed for oxygen content by GC using a
thermal conductivity detector and room-temperature molecular sieve
5A columns (Supelco).

**High-Throughput Testing of Catalyst Arrays.** Unless otherwise
noted, the same concentrations of reagents were used as in the serial
oxygen evolution studies. Reagent aliquots were distributed into a 96-
well plate either by hand pipetting or by means of a robotic plotter
(Cartesian Technologies, PixSys 3200). The well plates were irradiated
on a Horizon 2 16000 Series (Apollo) overhead projector, and
absorbance and emission scans were done intermittently throughout
the course of the photolysis using an HTS 7000 Plus Bio Assay Reader
(Perkin-Elmer). The plate reader required approximately 25 s to measure
a 96-well array, after which it was returned to the overhead projector.

The light intensity from the overhead projector was highest at the center
(where the 96-well plate was placed) and varied about 25% between
the center and edges of the plate. Multiple samples (typically three or
four) were used for each composition and were randomly placed in
the array to compensate for variations in light intensity. The reported
absorbance readings represent an average of those measurements. The
standard deviation of the parallel screening method, obtained from the

![Figure 1](image-url)  
*Figure 1. Photochemical oxygen evolution using IrO₂·H₂O colloids with the excess citrate removed by ion exchange (■) and by dialysis (○).*

**Results and Discussion**

**Proof-of-Concept Testing of the Optical Screening Method.**
To test the viability of the high-throughput optical screening method,
IrO₂·H₂O was prepared by conventional convection heating, with the excess citrate ions being removed by either
ion exchange or dialysis. Figure 1 shows plots of oxygen
evolution vs time for these catalysts. At early times, the reaction
rate is light-limited, and the apparent rate is the same for both
catalysts. However, after about 20 min the plots diverge, and
eventually both curves level off as the sensitizer is progressively
destroyed. As shown in Figure 1, the ion-exchanged colloid
produced slightly more than half the oxygen as the dialyzed
colloid under the same conditions. UV-visible spectra showed
that the ion-exchanged colloid had only 44% of the absorbance
of the dialyzed colloid at 580 nm, indicating that much of
the colloid was lost during the synthesis by adsorption to the ion-
exchange resin. These two colloidal catalyst solutions provided
benchmark “good” and “bad” catalysts for testing the optical
screening method.

Using similar reaction solutions in 96-well plates, a series of
16 wells were irradiated and tested. Each lane contained four
identical solutions: one set each of a solution with no colloid,
the “bad” ion-exchanged colloid, the “good” dialyzed colloid,
and one solution containing no sacrificial acceptor. In these
experiments, the wells containing no colloid were expected to
show the most rapid decomposition of the sensitizer, and those
with no sacrificial acceptor were expected to show little or no
decomposition. The “good” and “bad” catalysts represent inter-
mediate cases, in which the oxygen evolution cycle is kinetically
competitive with Ru(bpy)₃²⁺ decomposition.

As seen in Figure 2A, the 430 nm absorbance of the samples
with no colloid decreased abruptly, followed by the absorbance
of samples with the ion-exchanged colloid. Ru(bpy)₃²⁺ was
present in the sample with the dialyzed colloid for a longer
amount of time. In this experiment, the “good” and “bad”
catalysts are differentiated after about 10 min, and the absorbance
of the “bad” catalyst reaches a baseline level after about
The ranking of catalytic activity is the same as that shown in Figure 1; however, the difference is not apparent at early times in Figure 1 because the oxygen evolution rate is light-limited. Emission measurements were also taken, using an excitation wavelength of 430 nm and an emission wavelength of 635 nm as shown in Figure 2B. The emission plots are consistent with more rapid decomposition of the sensitizer in the presence of the “bad” ion-exchanged colloid. However, the rapid decay and reappearance of an emission signal in the “no colloid” sample shows that some emissive products are formed in the complex decomposition pathway of Ru(bpy)$_3^{2+}$. Finally, the same rank ordering of catalysts could be observed in emission snapshots of the array (Figure 3). Initially, all the wells show bright fluorescence, but the sensitizer is destroyed within 3 min in the lane with no colloid. The “good” and “bad” catalysts are easily differentiated from the control lanes, but not from each other, after 40 min of irradiation. This is quite consistent with the results shown in Figure 2B.

Optimization of Reaction Conditions. The parallel screening method was first used with a single IrO$_2$:H$_2$O colloid to identify the optimal reaction conditions for oxygen evolution. Factors that could be optimized easily using this method included the Ru(bpy)$_3^{2+}$, colloid, and added Nafion concentrations, as well as the buffer pH. It was found in a preliminary screening study that the sulfate and buffer concentrations had little effect on the absorbance response of the Ru(bpy)$_3^{2+}$ sensitizers.

With the aid of JMP Statistical Discovery Software (SAS Institute), an orthogonal central composite design of experiments was chosen to test these four factors. In an orthogonal central composite design (CCD), five levels (values) for each factor (concentration or pH) are studied in different combinations, allowing a response surface to be modeled effectively, even if

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**Figure 2.** (A) Absorbance at 430 nm of reaction solutions with no colloid (×), ion-exchanged colloid (■), and dialyzed colloid (○) vs irradiation time and (B) the emission (excitation at 430 nm and emission at 635 nm) of reaction solutions with no colloid (×), ion-exchanged colloid (■), and dialyzed colloid (○) vs irradiation time.

**Figure 3.** Emission snapshots of a well plate containing sensitizer—colloid—sacrificial acceptor reaction solutions: lane 1, no colloid; lane 2, ion-exchanged colloid; lane 3, dialyzed colloid; and lane 4, no sacrificial acceptor. Conditions were the same as those used in Figure 2. The emission images were acquired through a red filter by illuminating with 450 nm light.

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The response is nonlinear or has strongly interacting parameters. An orthogonal CCD for three factors is shown schematically in Figure 4A. The number of factorial points amounts to $2^k$, where $k$ is the number of factors. There were 16 factorial points in the four-factor design for this series of experiments. Factorial points test high and low values for each factor in all possible combinations. Axial points test a high or low extreme value for one factor while the remaining factors are held at an average value. The number of axial points is $2^k$, or eight in this experiment. Finally, several replicate experiments are done at the central point, an average value for all factors. Seven replicate experiments were performed using the central point conditions.

These 31 sets of reaction conditions were tested in triplicate in a 96-well plate, and average absorbance values were used in the calculations that generated the response surface. The levels of each factor tested were the following: colloid concentration, $(2.7-9.7) \times 10^{-5}$ M IrO$_2$·xH$_2$O; Nafion concentration, 0–0.05 g/L; Ru(bpy)$_3^{2+}$ concentration, $(0.75-1.45) \times 10^{-4}$ M; and buffer pH, 4.5–8.1. The number of moles of Ru(bpy)$_3^{2+}$ in each well was held constant, even though the concentrations were different, meaning that different wells contained different volumes of reaction solution. Because the amount of Ru(bpy)$_3^{2+}$ was constant, the initial absorbance was comparable for all wells. The buffer and sacrificial acceptor concentrations were held constant in each well. Absorbance data were acquired, and the averaged data at 30 min irradiation time (where the absorbance values of samples in the array were well differentiated) were used to calculate the response surface.

From the array absorbance data, an initial polynomial least-squares fit to the response surface was generated in the form

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_{12} x_1^2 + b_{22} x_2^2 + b_{33} x_3^2 + b_{44} x_4^2 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{14} x_1 x_4 + b_{23} x_2 x_3 + b_{24} x_2 x_4 + b_{34} x_3 x_4$$

Here, $y$ is the absorbance and $b_i$ is the coefficient for the $i$th factor, $x_i$. This equation allows for single-parameter and two-parameter cross terms in the response surface but neglects higher order interactions. An initial 15-parameter fit to the 31 independent data points yielded an $R^2$ value of 0.92. However, it was found that the addition of Nafton, within this concentration range, had no significant effect on the absorbance values. This

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**Figure 4.** (A) Three-factor orthogonal central composite design (CCD) of an experiment in which each axis corresponds to a factor, the center point represents an average value for each factor, and the circles represent the values at which the experiment is conducted. (B) Plot of experimental absorbance values after 30 min of irradiation vs absorbance predicted from a least-squares fit to the four-factor orthogonal CCD data. The horizontal line indicates the average response, and the curved lines on either side of the best-fit line show the 95% confidence interval. (C) Contour profiles of the response surface showing the factor levels that give the maximum predicted absorbance (vertical lines). Error bars show the 95% confidence interval.
Optimization of Colloidal Water Oxidation Catalysts

The availability of a rapid screening method opens the possibility of testing colloid compositions beyond simple binary oxides. Because IrO$_2$·H$_2$O is known to be the best of these oxides, we investigated compositions containing primarily Ir with small added amounts of other transition elements. Pt, Ru, and Os were chosen because together they have been found to give good electrochemical water oxidation catalysts. These dopants were used in small quantities so that the same preparation method could be used for each colloid. Colloid preparation by microwave heating was chosen because it presented advantages of speed and parallel synthesis, although in general it gave catalysts that were inferior to those produced by the convective heating method. Identical heating cycles were ensured since all samples could be used in small quantities so that the same preparation method could be used in one batch.

Twelve different colloid compositions were chosen, and both serial oxygen evolution tests and parallel optical screening were performed. It should be noted that the highest reported number of turnovers for this reaction, using colloids made by convection heating, is about 290, corresponding to 40 μmol of O$_2$ evolved. Under similar conditions, 125 turnovers are more typical with microwave colloids. The number of Ru(bpy)$_3^{2+}$ turnovers was calculated by taking the moles of oxygen evolved multiplied by 4 and divided by the moles Ru(bpy)$_3^{2+}$ used. Four turnovers of Ru(bpy)$_3^{2+}$ corresponds to one oxygen molecule, as shown in the following reaction sequence:

\[
\text{Ru(bpy)}_3^{2+} + \text{hv} \rightarrow \text{Ru(bpy)}_3^{2+*} \quad (3)
\]
\[
\text{Ru(bpy)}_3^{2+*} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Ru(bpy)}_3^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad (4)
\]
\[
\text{Ru(bpy)}_3^{2+} + \text{SO}_4^{2-} \rightarrow \text{Ru(bpy)}_3^{3+} + \text{SO}_4^{2-} \quad (5)
\]
\[
4\text{Ru(bpy)}_3^{3+} + 2\text{H}_2\text{O} \rightarrow 4\text{Ru(bpy)}_3^{2+} + 4\text{H}^{+} + \text{O}_2 \quad (6)
\]

The numbers of turnovers obtained using the various colloids are shown in Table 1 and are plotted in Figure 6, along with

### Table 1. Number of Ru(bpy)$_3^{2+}$ Turnovers for 10 Different Colloid Compositions Calculated from Oxygen Evolution Data and from Absorbance Measurements from the 96-Well Plate after 22 min of Irradiation

<table>
<thead>
<tr>
<th>metal oxide colloid</th>
<th>no. of Ru(bpy)$_3^{2+}$ turnovers</th>
<th>absorbance at 430 nm after 22 min of irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir$<em>{80}$Pt$</em>{10}$Os$_5$</td>
<td>145</td>
<td>0.405</td>
</tr>
<tr>
<td>Ir$_{90}$Os$_5$</td>
<td>144</td>
<td>0.398</td>
</tr>
<tr>
<td>Ir$<em>{90}$Pt$</em>{10}$</td>
<td>138</td>
<td>0.371</td>
</tr>
<tr>
<td>Ir$<em>{90}$Pt$</em>{10}$</td>
<td>135</td>
<td>0.374</td>
</tr>
<tr>
<td>Ir$_{100}$a</td>
<td>127</td>
<td>0.352</td>
</tr>
<tr>
<td>Ir$_{100}$b</td>
<td>125</td>
<td>0.322</td>
</tr>
<tr>
<td>Ir$<em>{100}$Ru$</em>{10}$</td>
<td>123</td>
<td>0.300</td>
</tr>
<tr>
<td>Ir$<em>{2}$Pt$</em>{10}$Ir$_{90}$Os$_5$</td>
<td>122</td>
<td>0.374</td>
</tr>
<tr>
<td>Ir$_{100}$c</td>
<td>122</td>
<td>0.361</td>
</tr>
<tr>
<td>Ir$<em>{90}$Ru$</em>{10}$</td>
<td>114</td>
<td>0.266</td>
</tr>
<tr>
<td>Ir$<em>{90}$Ru$</em>{10}$Os$_5$</td>
<td>110</td>
<td>0.257</td>
</tr>
<tr>
<td>Ir$<em>{90}$Ru$</em>{20}$</td>
<td>86</td>
<td>0.251</td>
</tr>
</tbody>
</table>


Figure 5. Oxygen evolution data testing the performance of a conventional IrO$_2$ colloid under original (■) and optimized (○) conditions.

Parameter and the relevant cross terms were left out of the final fit. Additionally, most of the other cross terms were found to be insignificant within the margin of error of the data. The final least-squares fit included only five coefficients: three single-factor terms, one quadratic term (pH), and a baseline value, $b_0$. The final response surface had the form

\[
y = b_0 + b_1(\text{buffer pH}) + b_2[\text{Ru(bpy)}_3^{2+}] + b_3[\text{IrO}_3] + b_4(\text{buffer pH})^2 \quad (2)
\]

The correlation between the fit and the experimental absorbance at 30 min is shown in Figure 4B. The $R^2$ value is 0.89, indicating a good correlation between the absorbance data and that predicted from eq 2. Figure 4C shows a contour profile of the response surface along each of the variable axes and indicates that the best conditions within the range tested represent the high values of pH and colloid concentration, and the low value of Ru(bpy)$_3^{2+}$ concentration. A higher absorbance of the solution indicates a longer lifetime of the Ru(bpy)$_3^{2+}$ sensitizer during the reaction. Barring any great differences in the rate of the Ru(bpy)$_3^{3+}$ decomposition reaction, this implies a higher number of turnovers for these reaction conditions.

Oxygen evolution tests were performed under both the original conditions (Figure 1) and the optimized conditions obtained by analysis of the absorbance data. Optimal concentrations tested were 0.7 × 10$^{-4}$ M Ru(bpy)$_3^{2+}$, 1.0 × 10$^{-4}$ M metal oxide colloid, 0.05 M Na$_2$SO$_4$, and 0.010 M Na$_2$S$_2$O$_8$. The buffer was made by taking 3.75 × 10$^{-2}$ M Na$_2$SiF$_6$ and adding enough NaHCO$_3$ to make the pH 6.7. The buffer solution was sonicated for 15 min, and the pH was rechecked. After sonication, the pH increased considerably. If the pH was lower than 8.1, more NaHCO$_3$ was added, and the buffer was again sonicated. If the pH was too high, 3.75 × 10$^{-2}$ M Na$_2$SiF$_6$ was added to adjust to the correct pH. The buffer was filtered and aged for 3 h, and 4.55 mL of buffer was added to the reaction solution along with the other reagents for a total of 7.86 mL of reaction solution.

The larger volume was needed to retain the same number of moles of Ru(bpy)$_3^{2+}$ as was in the reaction under the original conditions. Figure 5 shows a 2-fold increase in number of turnovers using these optimized conditions. It should be noted that the initial (light-limited) rate of oxygen evolution is lower, because less light is absorbed by the more dilute sensitizer solution; however, the total amount of oxygen evolved is greater. Under the optimized conditions (where the pH is considerably higher), the colloid also flocculates midway through the reaction but continues to evolve oxygen photochemically.

Optimization of the Catalyst Composition. The availability of a rapid screening method opens the possibility of testing colloid compositions beyond simple binary oxides. Because IrO$_2$·H$_2$O is known to be the best of these oxides, we investigated compositions containing primarily Ir with small added amounts of other transition elements. Pt, Ru, and Os were chosen because together they have been found to give good electrochemical water oxidation catalysts. These dopants were used in small quantities so that the same preparation method could be used for each colloid. Colloid preparation by microwave heating was chosen because it presented advantages of speed and parallel synthesis, although in general it gave catalysts that were inferior to those produced by the convective heating method. Identical heating cycles were ensured since all samples could be prepared simultaneously in one batch.

Twelve different colloid compositions were chosen, and both serial oxygen evolution tests and parallel optical screening were performed. It should be noted that the highest reported number of turnovers for this reaction, using colloids made by convection heating, is about 290, corresponding to 40 μmol of O$_2$ evolved. Under similar conditions, 125 turnovers are more typical with microwave colloids. The number of Ru(bpy)$_3^{2+}$ turnovers was calculated by taking the moles of oxygen evolved multiplied by 4 and divided by the moles Ru(bpy)$_3^{2+}$ used. Four turnovers of Ru(bpy)$_3^{2+}$ corresponds to one oxygen molecule, as shown in the following reaction sequence:

\[
\text{Ru(bpy)}_3^{2+} + \text{hv} \rightarrow \text{Ru(bpy)}_3^{2+*} \quad (3)
\]
\[
\text{Ru(bpy)}_3^{2+*} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Ru(bpy)}_3^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad (4)
\]
\[
\text{Ru(bpy)}_3^{2+} + \text{SO}_4^{2-} \rightarrow \text{Ru(bpy)}_3^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad (5)
\]
\[
4\text{Ru(bpy)}_3^{3+} + 2\text{H}_2\text{O} \rightarrow 4\text{Ru(bpy)}_3^{2+} + 4\text{H}^{+} + \text{O}_2 \quad (6)
\]

The numbers of turnovers obtained using the various colloids are shown in Table 1 and are plotted in Figure 6, along with

absorbance values taken from the plate reader at 22 min. After 22 min of irradiation (approximately midway through the reaction), the highest and lowest absorbance values were best separated. The correlation coefficient relating the two was 0.87. There are several factors that could negatively affect this correlation. If a given colloid accelerates the decomposition of adsorbed Ru(bpy)$_3^{2+}$ ions, then the number of turnovers would be low even if the oxygen evolution rate is high. Another factor is the absorbance of the colloid itself, since additives such as ruthenium make the colloids darker than those that contain only iridium. Despite these factors, it appears that the high-throughput method is well correlated with the oxygen evolution rates of different colloids.

In Figure 7, the variation in number of turnovers with the metal dopant concentration is evident. Colloids containing Os and Pt dopants are more active than those containing only Ir, and those with Ru are less active. Because the area of highest activity in the initial screening of these four metals was found at the upper limit of osmium and platinum used, a second experiment was done to examine the Ir–Pt–Os ternary compound more completely. The response surface obtained by ranking 21 compositions (Figure 7) shows a single optimal region within this ternary composition diagram at ca. 5% Os and 30–50% Pt. TEM images of selected colloids from these experiments showed that the most active Pt- and Os-containing colloids contained uniform particles with diameters in the 10–15 nm range, whereas those without these elements had larger particles. This suggests that the primary effects of these “dopants” is to increase the number of surface Ir atoms.
available for catalysis. These observations are worthy of further study in the search for a better water oxidation catalyst. Other metals performing well in Harriman’s experiments as powders that could also be tested as additives include Rh, Mn, and Co.13

The bottleneck that prevents this optical screening method from broad-range combinatorial screening of catalyst compositions is the preparation and dialysis of the colloidal catalysts. The microwave preparation method used here reduces preparation time substantially: the per-colloid preparation time is about 15 min (when 14 colloids are made in parallel), compared to 5 h for the conventional convective heating approach. Unfortunately, the average particle diameter of IrO$_2 \cdot x$H$_2$O prepared by the microwave method is about 50 nm, and therefore the particles have relatively low activity. The dialysis process is also unwieldy for combinatorial synthesis, although again this step can be done in parallel. Using the design-of-experiment approach, it is possible to optimize reaction conditions and compositions using a minimum number of unique samples. Thus, it should be possible to combine parallel synthesis, design of experiments, and optical screening in an iterative manner to test a wide range of catalyst compositions.

Conclusions

The parallel optical screening method, combined with reaction surface modeling, has proven effective in optimizing the conditions for photocatalytic oxygen evolution. Perhaps the most surprising finding from this study is that relatively basic solutions (pH 8) give higher numbers of turnovers than those at pH 5–6, at which the reaction has previously been optimized.16 Although the driving force for oxygen evolution from Ru(bpy)$_3$$^{2+}$ increases at higher pH, one expects that the rate of nucleophilic attack by OH$^-$ (see Scheme 1) should also increase. Measurements of Ru(bpy)$_3$$^{3+}$ decomposition, using methanol to reduce photogenerated Ru$^{3+}$ as described in ref 16, give first-order rate constants of 1.34(2) $\times$ 10$^{-3}$ and 8.25(3) $\times$ 10$^{-4}$ s$^{-1}$ at pH 5.7 and 7.6, respectively. This shows that the increase in number of turnovers at higher pH is due predominantly to a decreased decomposition rate, rather than an increased oxygen evolution rate at the colloid surface.

The screening method has also led to the discovery of doped IrO$_2 \cdot x$H$_2$O colloids with moderately improved catalytic activity. In general, these microwave-prepared colloids have lower activity than those made by convective heating, but the enhancement found with Pt and Os dopants is interesting. A good correlation was found between the number of Ru(bpy)$_3$$^{2+}$ turnovers calculated from the oxygen evolution data and the absorbance readings obtained using the screening method. This suggests that the method could be useful in examining a broader range of catalyst compositions, provided that sufficiently high-throughput synthetic methods can be developed.

Finally, we note that a wide range of photocatalytic systems (involving zeolites, vesicles, clays, semiconductor nanoparticles, and other organizing media) use Ru(bpy)$_3$$^{2+}$ and its derivatives as photosensitizers. In principle, this high-throughput optical method could be adapted to the optimization of many of those systems by introducing a decomposition reaction (such as nucleophilic attack, as used here, or photoanation by halide ions) that competes kinetically with the photocatalytic cycle.

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