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20. We measured a_{BF} by studying the damping of relative oscillations of the two species in the magnetic trap. This value is somewhat larger than the one previously measured with a different technique (8), though consistent also with our original prediction (15).
21. For $N_{\text{Rb}} = 10^5$ and $N_{\text{K}} = 3 \times 10^4$, the peak densities for the two noninteracting gases are $n_{\text{Rb}} = 2 \times 10^{14} \text{ cm}^{-3}$ and $n_{\text{K}} = 8 \times 10^{12} \text{ cm}^{-3}$.
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Efficient Photochemical Water Splitting by a Chemically Modified n-TiO₂

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Although n-type titanium dioxide (TiO₂) is a promising substrate for photogeneration of hydrogen from water, most attempts at doping this material so that it absorbs light in the visible region of the solar spectrum have met with limited success. We synthesized a chemically modified n-type TiO₂ by controlled combustion of Ti metal in a natural gas flame. This material, in which carbon substitutes for some of the lattice oxygen atoms, absorbs light at wavelengths below 535 nanometers and has a lower band-gap energy than rutile (2.32 versus 3.00 electron volts). At an applied potential of 0.3 volt, chemically modified n-type TiO₂ performs water splitting with a total conversion efficiency of 11% and a maximum photoconversion efficiency of 8.35% when illuminated at 40 milliwatts per square centimeter. The latter value compares favorably with a maximum photoconversion efficiency of 1% for n-type TiO₂ biased at 0.6 volt.

Since the discovery (1) of photoelectrochemical splitting of water on n-TiO₂ electrodes, semiconductor-based photoelectrolysis of water to hydrogen and oxygen has received much attention (2–7). Some applications include the use of n-TiO₂ in wet solar cells (8–10) and for the photodegradation of organics present in polluted water and air (11, 12) under ultraviolet (UV) light (wavelength $\lambda < 400 \text{ nm}$) illumination, the energy of which exceeds the band-gap energy of 3.0 eV in the rutile crystalline form of n-TiO₂. Efficient photosplitting of water to hydrogen, a source of abundant clean energy, requires photoelectrodes that (i) are highly stable, (ii) are inexpensive, (iii) have a conduction band minimum that is higher than the H₂/H₂O level and a valence band maximum that is lower than the H₂O/O₂ level, and (iv) can absorb most of the photons of the solar spectrum. Although both the anatase and rutile forms of n-TiO₂ meet the first three of these conditions, they are poor absorbers of photons in the solar spectrum. Several attempts have been made to lower the band-gap energy

of n-TiO₂ by transition metal doping (13–16) and reduction by hydrogen (17, 18), but no noticeable change in band-gap energy of n-TiO₂ was observed. Recently, Asahi *et al.* (19) reported that nitrogen doping of n-TiO₂

to n-TiO_{2-x}N_x shifted its optical absorption and photodegradation of methylene blue and gaseous acetaldehyde in the visible region of $\lambda < 500 \text{ nm}$.

We therefore synthesized a chemically modified (CM) n-TiO₂ by flame pyrolysis of Ti metal sheet in an attempt to lower its band-gap energy so that it could absorb the UV and most of the visible light of the solar spectrum while retaining its stability. We thermally pyrolyzed a Ti metal sheet 0.25 mm thick (Strem Co.) in the presence of combustion products [CO₂ and steam (H₂O)] in a natural gas flame with controlled amounts of oxygen added at a flow rate of $\sim 350 \text{ ml min}^{-1}$. The flame temperature, measured with a digital pyrometer (Thermolyne Co.), was maintained close to 850°C by controlling the flow rates of natural gas and oxygen. The best photoresponse was obtained with a pyrolysis time of 13 min. The CM-n-TiO₂ films were dark gray, whereas the n-TiO₂ films prepared in an electric tube furnace under the same oxygen flow rate, at the same temperature and time of pyrolysis (considered here as a reference sample of n-TiO₂ film), were very light gray.

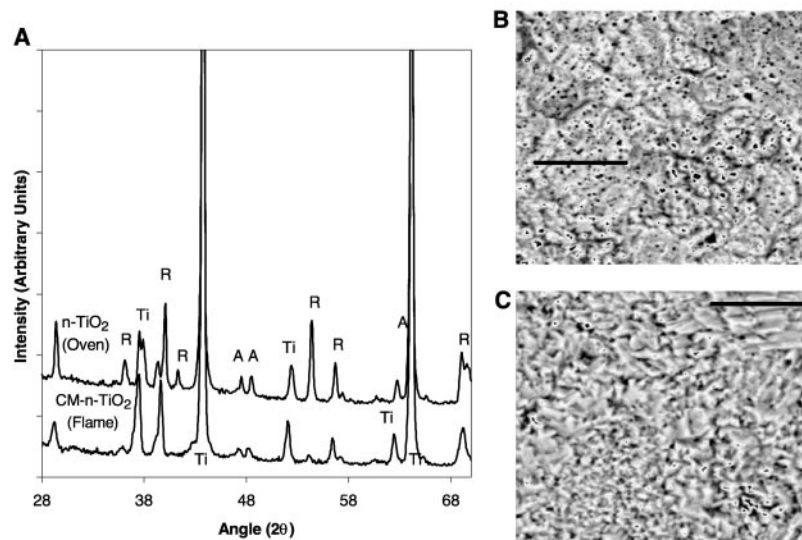


Fig. 1. (A) X-ray diffraction (XRD) pattern for a CM-n-TiO₂ (flame-made) and the reference n-TiO₂ (electric tube furnace- or oven-made) photoelectrodes. Ti, titanium metal; A, anatase peaks; R, rutile peaks. (B and C) SEM images of CM-n-TiO₂ (flame-made) sample (B) and reference n-TiO₂ (electric tube furnace- or oven-made) sample (C). Scale bars, 20 μm .

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The x-ray diffraction (XRD) of the CM-n-TiO₂ film showed mainly rutile structure (Fig. 1A). However, the reference n-TiO₂ film shows a mixture of rutile and anatase crystalline forms (Fig. 1A). The scanning electron microscopic (SEM) results indicate that CM-n-TiO₂ is more porous (represented by more dark spots) compared to a reference n-TiO₂ sample (Fig. 1, B and C). X-ray photoelectron spectroscopic (XPS) data indicate an average composition of CM-n-TiO₂ to be n-TiO_{2-x}C_x, where x is ~ 0.15 . The presence of CO₂, a combustion product in the natural gas flame at 850°C, facilitated the incorporation of carbon in the n-TiO₂ films. The presence of steam (H₂O) in the flame is expected to enhance the rate of titanium oxide film formation (20). The XPS analysis also showed the absence of N and H in both CM-n-TiO₂ and the reference n-TiO₂ films. The optical absorption spectra (Fig. 2) show that CM-n-TiO₂ films absorb appreciably at wavelengths less than 535 nm (which corre-

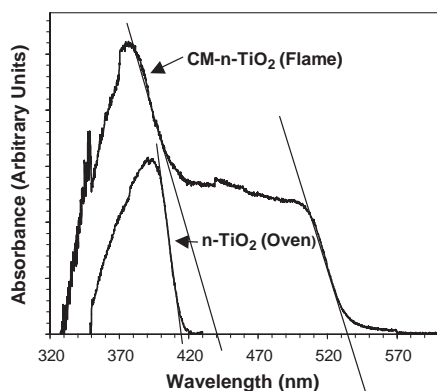


Fig. 2. The UV-visible spectra of CM-n-TiO₂ (flame-made) and reference n-TiO₂ (electric tube furnace- or oven-made). The flame-made sample shows threshold wavelengths of 535 nm (band gap of 2.32 eV) and 440 nm (band gap of 2.82 eV); the electric tube furnace- or oven-made sample shows a threshold wavelength of 414 nm (band gap of 3.0 eV).

sponds to a band-gap energy of 2.32 eV), whereas reference n-TiO₂ samples do not. The CM-n-TiO₂ films show two optical absorption thresholds at 535 and 440 nm (Fig. 2) in the visible range, whereas the reference n-TiO₂ shows only one at 414 nm, which corresponds to a band-gap energy of 3.0 eV (Fig. 2). These two absorption thresholds indicate two possible compositions of chemically modified n-TiO_{2-x}C_x.

The photoresponse of CM-n-TiO₂ films was evaluated by measuring the rate of water-splitting reaction to hydrogen and oxygen, which is proportional to photocurrent density j_p . We verified that H₂ and O₂ are the photoproducts by gas chromatographic (GC) analysis using a SRI 8610 chromatograph equipped with a thermal conductivity detector (TCD). Also, GC analysis using a Perkin Elmer 8500 chromatograph equipped with TCD showed the absence of CO and CO₂ in the photoproducts. Furthermore, we collected gaseous photoproducts and observed an exact 2:1 volume ratio of H₂ and O₂, which further confirmed water-splitting.

Photocurrents were measured with a CM-n-TiO₂ sample (area 0.2 cm²) under illumination from a 150-W xenon arc lamp (Hanovia) fitted with an infrared light filter (21). Photocurrent densities j_p (which correspond to rates of production of hydrogen and oxygen) from the water-splitting reaction at CM-n-TiO₂ under illumination of light of power density 40 mW cm⁻² from a 150-W xenon lamp are shown in Fig. 3 as a function of applied potential E_{app} . The observed dark current densities were found to be negligible (Fig. 3).

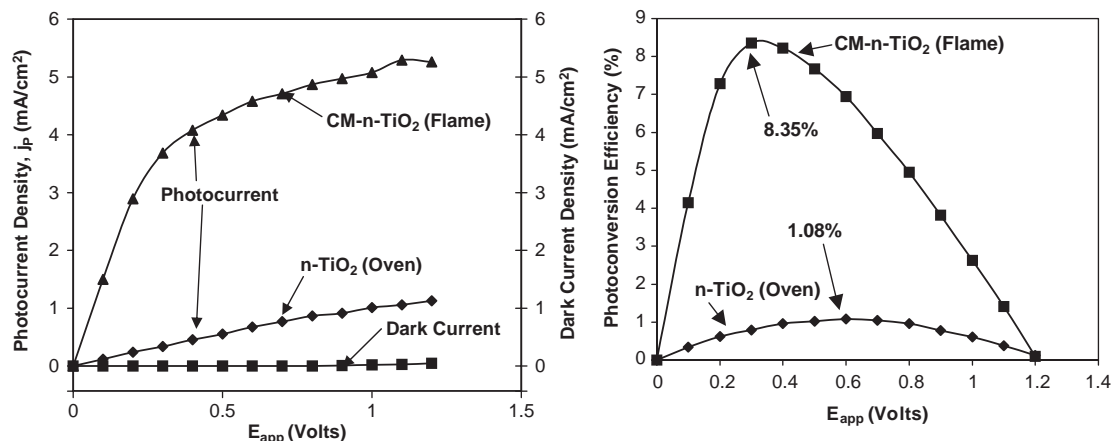
The maximum photoconversion efficiency ϵ_{eff} (photo) of 8.35% (which corresponds to a total conversion efficiency of 11.0%) was observed at a minimal applied potential of 0.30 V with a photocurrent density of 3.60 mA cm⁻² (Fig. 4) when ϵ_{eff} (photo) was calculated using an efficiency equation [Eq. 1 (22)] in which the contribution due to applied potential was subtracted from the total efficiency. How-

ever, under similar conditions of illumination, a maximum ϵ_{eff} (photo) of 1.08% was observed at a higher applied potential of 0.60 V for the reference n-TiO₂ samples under 150-W xenon lamp illumination (Fig. 4). These results confirm that flame pyrolysis chemically modified n-TiO₂ and lowered its band-gap energy to a minimum value of 2.32 eV to absorb visible light. Photoconversion efficiency did not decrease during successive tests with illumination intensity of 40 mW cm⁻² over a period of 6 months. Hence, the lowering of the band-gap energy did not affect the stability of CM-n-TiO₂.

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Fig. 3 (left). Photocurrent density j_p as a function of applied potential E_{app} at CM-n-TiO₂ (flame-made) and the reference n-TiO₂ (electric tube furnace- or oven-made) photoelectrodes under xenon lamp illumination at an intensity of 40 mW cm⁻². Dark current densities at CM-n-TiO₂ (flame-made) as a function of applied potential are also shown. **Fig. 4 (right).** Photoconversion efficiency as a function of applied potential E_{app} at CM-n-TiO₂ (flame-made) and the reference n-TiO₂ (electric tube furnace- or oven-made) photoelectrodes under xenon lamp illumination at an intensity of 40 mW cm⁻².



calomel electrode (SCE) as the working, counter, and reference electrodes, respectively. Photocurrents as a function of electrode potential were measured with an EG & G 362 scanning potentiostat and recorded with an X-Y recorder (Houston Instruments, model RE0092). The intensity of the light source (in mW cm^{-2}) was measured by a radiometer (International Light Co., model IL 1350). The electrolyte, 5 M KOH, was freshly prepared using double-deionized water with resistivity of 18 megohms cm^{-1} . All solutions were prepared from analytical-grade reagents.

22. The photoconversion efficiency ϵ_{eff} (photo) of light energy to chemical energy in the presence of an

external applied potential E_{app} can be expressed as

$$\% \epsilon_{\text{eff}}(\text{photo}) = [j_p(E_{\text{rev}}^0 - |E_{\text{app}}|) \times 100 / (I_0)] \quad (1)$$

(3–5), where j_p is the photocurrent density, E_{rev}^0 is the standard state-reversible potential (which is 1.23 V for the water-splitting reaction), I_0 is the intensity (power density) of the incident light, and $|E_{\text{app}}|$ is the absolute value of the applied potential E_{app} , which is obtained as

$$E_{\text{app}} = (E_{\text{meas}} - E_{\text{aoc}}) \quad (2)$$

(3–5), where E_{meas} is the electrode potential at which j_p was measured, and E_{aoc} is the electrode potential

at open circuit in the same electrolyte solution and under the same illumination of light at which j_p was measured. For the CM-n-TiO₂ electrode, $E_{\text{aoc}} = -1.0$ volt/SCE was observed at illumination intensity of 40 mW cm^{-2} in 5 M KOH solution; E_{meas} and E_{doc} were with respect to the same reference electrode (SCE). Note that the total conversion efficiency of light and electrical energy to chemical energy, ϵ_{eff} (total), was calculated by neglecting E_{app} in Eq. 1.

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The Origin of Aluminum Floccs in Polluted Streams

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About 240,000 square kilometers of Earth's surface is disrupted by mining, which creates watersheds that are polluted by acidity, aluminum, and heavy metals. Mixing of acidic effluent from old mines and acidic soils into waters with a higher pH causes precipitation of amorphous aluminum oxyhydroxide floccs that move in streams as suspended solids and transport adsorbed contaminants. On the basis of samples from nine streams, we show that these floccs probably form from aggregation of the ϵ -Keggin polyoxocation $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}(\text{aq})$ (Al_{13}), because all of the floccs contain distinct $\text{Al}(\text{O})_4$ centers similar to that of the Al_{13} nanocluster.

In studies of the aluminum geochemistry of acid mine drainage (1, 2), solids were identified that precipitate at $4.2 < \text{pH} < 4.9$ as either x-ray-amorphous $\text{Al}(\text{OH})_3$ or microcrystalline gibbsite. These floccs are fluffy (Fig. 1) and form as acidic effluent enriched in dissolved aluminum mixes with near-neu-

tral surface water. A similar phenomenon occurs in watersheds where the load of acid rain critically exceeds the buffering capacity of the soil and parent rock (3). It is thought (4) that the floccs form by aggregation of monomeric aluminum complexes into a $\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}^{6+}$ multimer that is structurally similar to dioctahedral sheets of gibbsite. Dissolved $\text{Al}_6(\text{OH})_{12}(\text{H}_2\text{O})_{12}^{6+}$, however, has never been detected, and this model has been challenged (5).

Here we propose an alternative explanation. We examined floccs from nine polluted streams in Germany and California (Table 1) (table S1 and figs. S2 to S4) with ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy, which resolves aluminum atoms with different coordination environments. The ^{27}Al NMR spectra of all field samples exhibit signals near +63 and +35 parts per

million (ppm), which indicate the presence of substantial amounts of aluminum in tetrahedral form $[\text{Al}(\text{O})_4]$ and in coordination to five oxygen atoms $[\text{Al}(\text{O})_5]$ (6), in addition to the dominating $\text{Al}(\text{O})_6$ peak near +7 ppm. Because the spectra of all samples were similar, we selected three samples to show the range in relative intensities (Fig. 2A). The first and last samples (Fig. 2A, top and bottom) have the most and least amounts of $\text{Al}(\text{O})_4$, respectively. The sec-



Fig. 1. Aluminum oxyhydroxide flocc on a streambed in Yuba County, California. The white aluminum oxyhydroxide flocc overlies orange iron oxyhydroxide solids. Image width, ≈ 30 cm.

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Table 1. Characterization of the selected field samples of representative aluminum oxyhydroxide floccs, collected from 1996 to 2001. Some samples were centrifuged immediately after collection and then dried under ambient conditions. Other samples (e.g., those from Spenceville) were analyzed both as a wet paste and as an air-dried gel. The aluminum concentrations were

measured in the 0.45 μm -filtered water samples from the mixing zones. For the sample shown in Fig. 2A, middle, values are not available from direct in situ measurements in the mixing zone because the acid mine effluent ($\text{pH} = 2.3$; $1 \text{ mM} < \Sigma \text{Al} < 15 \text{ mM}$) enters the pristine stream water [$\text{pH} = 7.7$; $\Sigma \text{Al} < \text{detection limit (d.l.)}$] from the hyporheic zone.

Sample spectrum	Geographic region	Geology	Vegetation	Type of pollution	Sampling date	pH in mixing zone	Aluminum concentration
Fig. 2A, top	East Thuringian, Slate Mountains, Germany	Carboniferous blue slate	Mixed forest	Acid mine drainage	22 May 1998	5.0 to 6.5	20 to 180 μM
Fig. 2A, middle	Spenceville, Yuba County, California	Metavolcanic rocks	Mixed forest	Acid mine drainage	4 Jan 2001	—	0 to 16 mM
Fig. 2A, bottom	Ore Mountains, Saxony, Germany	Mica slate, gneisses	Spruce	Acid rain	25 Mar 1999	5.0 to 5.5	18 to 60 μM