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Black TiO_2 Nanotubes: Cocatalyst-Free Open-Circuit Hydrogen Generation

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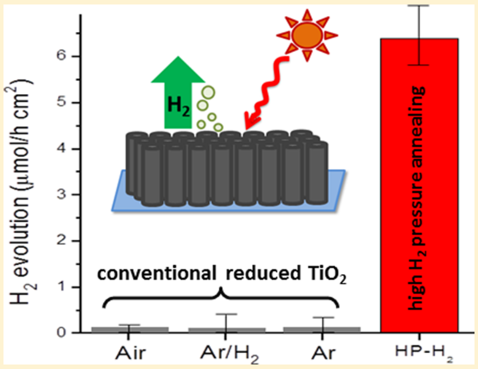
Ⓢ *Supporting Information*

ABSTRACT: Here we report that TiO_2 nanotube (NT) arrays, converted by a high pressure H_2 treatment to anatase-like "black titania", show a high open-circuit photocatalytic hydrogen production rate without the presence of a cocatalyst. Tubes converted to black titania using classic reduction treatments (e.g., atmospheric pressure H_2/Ar annealing) do not show this effect. The main difference caused by the high H_2 pressure annealing is the resulting room-temperature stable, isolated Ti^{3+} defect-structure created in the anatase nanotubes, as evident from electron spin resonance (ESR) investigations. This feature, absent for conventional reduction, seems thus to be responsible for activating intrinsic, cocatalytic centers that enable the observed high open-circuit hydrogen generation.



KEYWORDS: *TiO_2 nanotube arrays, water-splitting, hydrogenation, photocatalysis, cocatalyst, black titania*

In 2011, Chen and Mao reported on the remarkable visible light, photocatalytic water splitting performance of so-called "black titania". The black powder was obtained from TiO_2 anatase nanoparticles that were treated in a H_2 atmosphere at 20 bar at 200 °C for 5 days.[1] These nanoparticles were found to have virtually identical XRD data to anatase, but a high light absorption in the visible range, and provided a stable water splitting rate of 10 mmol h^{-1} g^{-1} H_2 under open-circuit-potential conditions (OCP) in a methanol solution and under AM 1.5 illumination (about 1 sun power). This very high hydrogen production rate was obtained using a Pt cocatalyst decoration on the TiO_2 particles to enable H_2 evolution. The effect of the high pressure H_2-treatment was attributed to a thin amorphous TiO_2 hydrogenated layer encapsulating the anatase core of the nanoparticles, leading to a considerable narrowing of the optical band gap of the treated material.

Not surprisingly, the work triggered a large amount of follow-up studies where TiO_2 in anatase (e.g., refs 2−5) or rutile (e.g., refs 2 and 6) form was exposed to various reductive treatments, mostly using a H_2 containing environment at elevated temperatures, but to a large extent, this work was carried out under atmospheric pressure, using Ar/H_2, or using chemical or electrochemical reduction treatments.[2−6] In the literature, however, for a large number of such "conventional" reductive treatments (including vacuum), a color change from transparent to blue has been well investigated over a number of years and has been ascribed to oxygen vacancy/Ti^{3+} formation,[7] with an according change in the electronic and optical properties of the material.[8,9]

Except for powders, especially interesting in view of water splitting, is the treatment of 1D or quasi-1D TiO_2 structures, such as nanowire and nanotube arrays, as they can provide orthogonality to light absorption and carrier separation.[10] Atmospheric pressure reductive treatments in H_2 at different temperatures were explored for rutile nanowires (hydrothermal) and anatase nanotubes (anodic).[2] This treatment showed in a classic two electrode photoelectrochemical cell (using a Pt counter electrode for H_2 evolution) a considerable photoelectrochemical performance for the hydrogenated black wire array. Further work by Hoang et al. that used a H_2/Ar atmospheric pressure treatment confirmed the beneficial effect on the photoelectrochemical performance of TiO_2 rutile-nanowire arrays. Additionally the authors showed a further beneficial effect on the photoelectrochemical behavior for samples codoped with nitrogen.[6] In comparison with the rutile nanowire array, the anatase nanotube arrays that were exposed to the same atmospheric pressure Ar/H_2 reduction treatment performed significantly weaker in photoelectrochemical water-splitting tests.[2]

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However, in spite of a wide range of investigations, hardly any of the follow-up work used the original H_2 high pressure approach of Chen and Mao, and most of the work used two electrode photoelectrochemical geometries to assess the performance of the material for photocatalytic H_2 generation. In every case, a Pt cocatalyst (or counter electrode) was used for enabling substantial H_2 evolution.

In the present work, we demonstrate that the treatment of anodic TiO_2 nanotube layers in a high pressure H_2 atmosphere leads to a strong and persistent open-circuit photocatalytic hydrogen production without the need of a cocatalyst. In contrast, a classic reduction treatment such as reduction in H_2/Ar under atmospheric pressure, without cocatalyst, does not provide any significant effect. Figure 1a compares the amount of H_2 produced under open-circuit conditions from an aqueous methanol solution (50 vol %) under AM 1.5 (100 mW/cm^2) solar simulator illumination for (i) an anatase TiO_2 nanotube layer (air); (ii) this layer converted with Ar (Ar) or H_2/Ar (H_2/Ar) to black titania under atmospheric pressure; (iii) the anatase layer converted with a high pressure H_2 treatment (20 bar, 500 °C for 1 h) (HP-H_2); and (iv) using the high pressure conditions of Chen and Mao (H_2, 20 bar, 200 °C for 5 d) to hydrogenate the anatase nanotube layer (Sci ref).[1] Clearly, for the high pressure annealed samples under both conditions a significant amount of photocatalytic H_2 production can be observed, while neither the simple air annealed sample to anatase nor the Ar/H_2 reduced sample shows H_2 evolution, although the latter shows, as expected, a deep blue/black color even darker than the H_2 treated samples (inset in Figure 1a). For reference (and discussed later), also results for annealing the nanotube layers in pure Ar under atmospheric conditions and rutile nanorods annealed under high pressure H_2 conditions are included; both do not show significant H_2 evolution. Our optimized treatment (500 °C, 1 h) shows a H_2 evolution rate of 7 μmol/(h cm^2), which was found to be stable over several days, and for experiments after one and two months of storage of the electrodes.

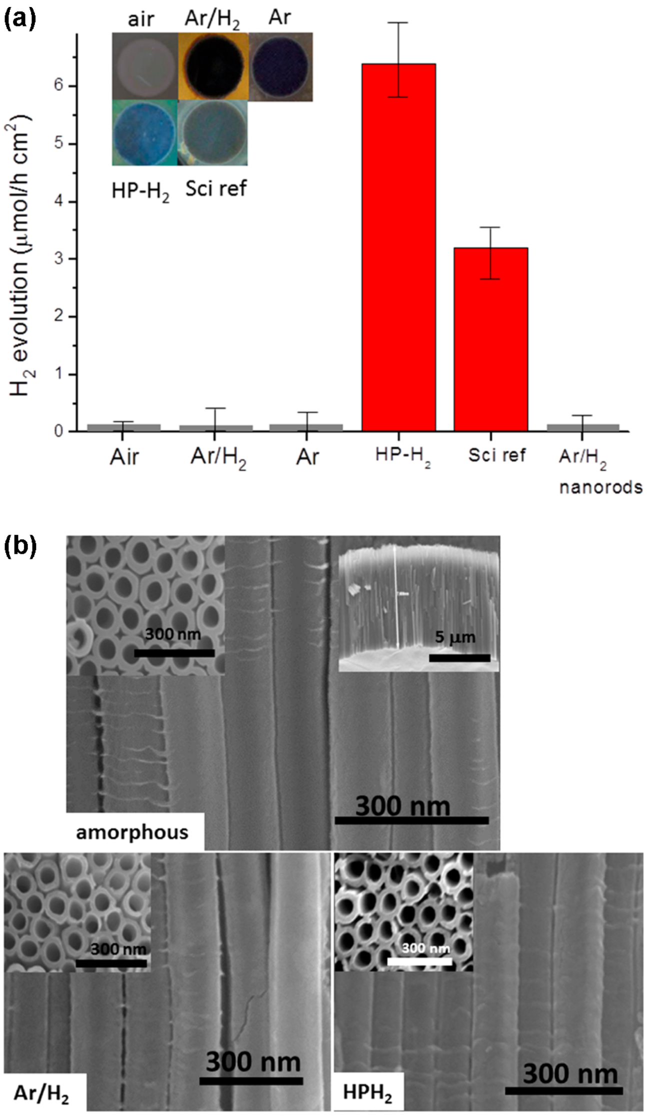


Figure 1. (a) Photocatalytic H_2 production under open circuit conditions in methanol/water (50/50 vol %) with TiO_2 nanotubes and nanorods treated in different atmospheres under AM 1.5 (100 mW/cm^2) illumination. Air, heat treatment in air at 450 °C; Ar, heat treatment in pure argon at 500 °C; Ar/H_2, heat treatment in H_2/Ar (5 vol %) at 500 °C; HP-H_2, heat treatment in H_2 at 20 bar at 500 °C; Sci ref, heat treatment in H_2 at 20 bar at 200 °C for 5 days (following ref 1) (inset: optical images for the differently treated samples). (b) SEM images of the TiO_2 nanotube layer as-formed and after hydrogenation treatments in Ar/H_2 and high pressure H_2.

For the main part of the experiments, TiO_2 nanotube layers as shown in Figure 1b were grown by anodic oxidation to a length of 7 μm using an ethylene glycol electrolyte containing 0.1 M NH_4F and 1 M H_2O as described in the experimental section in the Supporting Information. The samples were then annealed to anatase by a heat treatment at 450 °C for 1 h in air.

After all additional reduction treatments in H_2/Ar, pure Ar (500 °C for 1 h), or in pressurized H_2 as described in the experimental section, the tube layers turn blue to black (inset in Figure 1a), but maintain their original geometry (Figure 1b). In every case, i.e., before and after any reduction treatment, X-ray diffraction (XRD) shows diffraction peaks corresponding to well crystallized anatase (Figure 2a). This is well in line with literature reports on a wide range of hydrogenation conditions.[1,2]

Also high-resolution transmission electron microscopy (HRTEM) investigation of tube walls (Figure 2b) and acquired selected area diffraction (SAD) patterns show an identical lattice spacing (d = 0.351 nm typical of anatase) and a very similar diffraction pattern for the H_2-treated sample and the sample annealed in air to anatase. Also further HRTEM investigation did not reveal a significant difference between air-annealed TiO_2-NTs and H_2-annealed tubes. Moreover, from XPS (Supporting Information) no significant variation in the composition of the samples treated in air, Ar/H_2, or high pressure H_2 could be observed. This confirms, together with the XRD, that not a massive conversion to a suboxide phase occurred and that in the surface-near region (penetration depth of XPS ≈ 5−10 nm) not a reduction to more than approximately 1% Ti^{3+} took place (detection limit of XPS).

Nevertheless, light reflectivity spectra (Figure 2c) show a strong visible light absorption for the Ar/H_2 and the H_2-treated nanotube layers, with an even much stronger light absorption for the Ar/H_2-treated samples; this is in line with the visual impression of the darkness of the samples (inset in Figure 1a). Please note that also samples annealed in plain Ar show a similar coloration as samples from Ar/H_2. These findings indicate that the magnitude in optical absorption (in visible or UV) does not correlate with the observed open-circuit photoactivity in Figure 1a.

Most elusive information on the differently reduced samples is obtained from electron spin resonance (ESR) investigations at

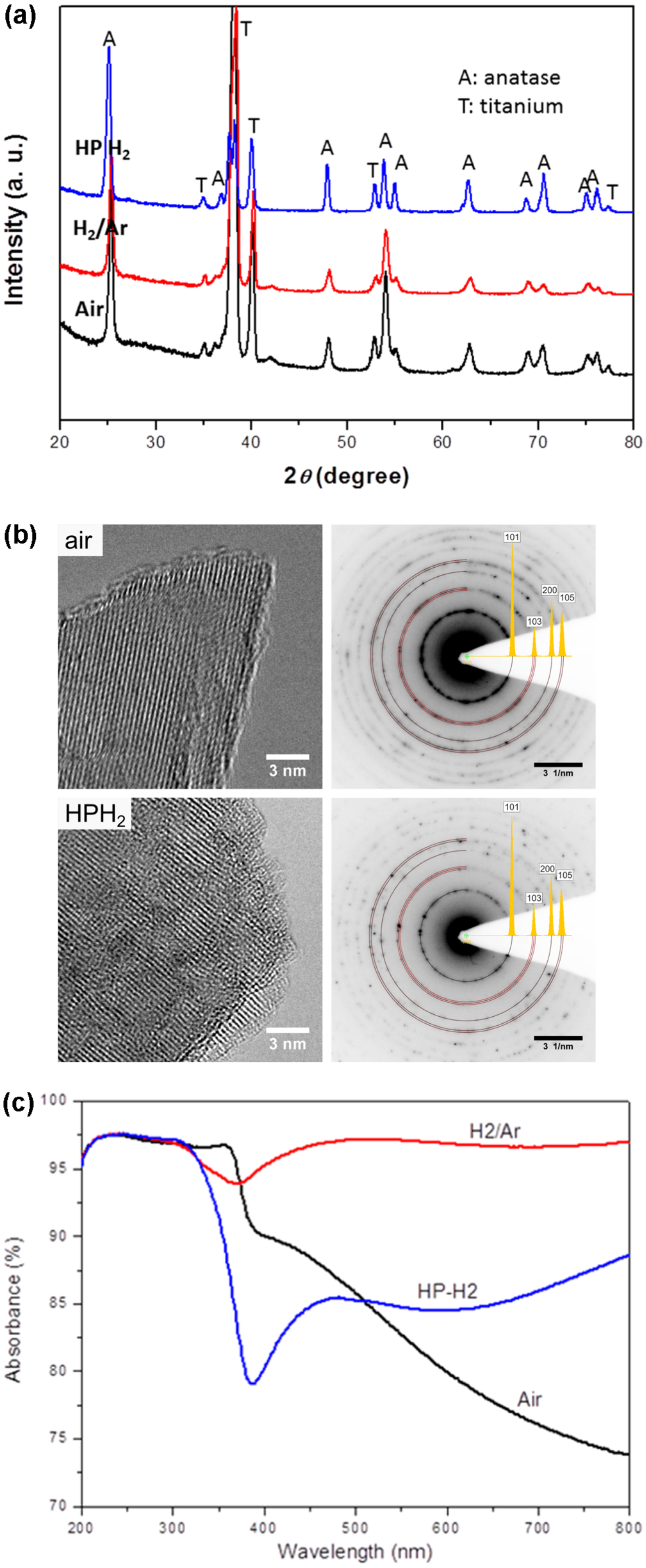


Figure 2. (a) XRD patterns of TiO_2 nanotubes annealed and treated in different atmospheres; (b) HRTEM images (left) and SAD patterns (right) of TiO_2 nanotubes annealed in air and high pressure H_2, respectively; (c) integrated light reflectance results of TiO_2 nanotubes annealed in air, Ar/H_2, and high pressure H_2, respectively.

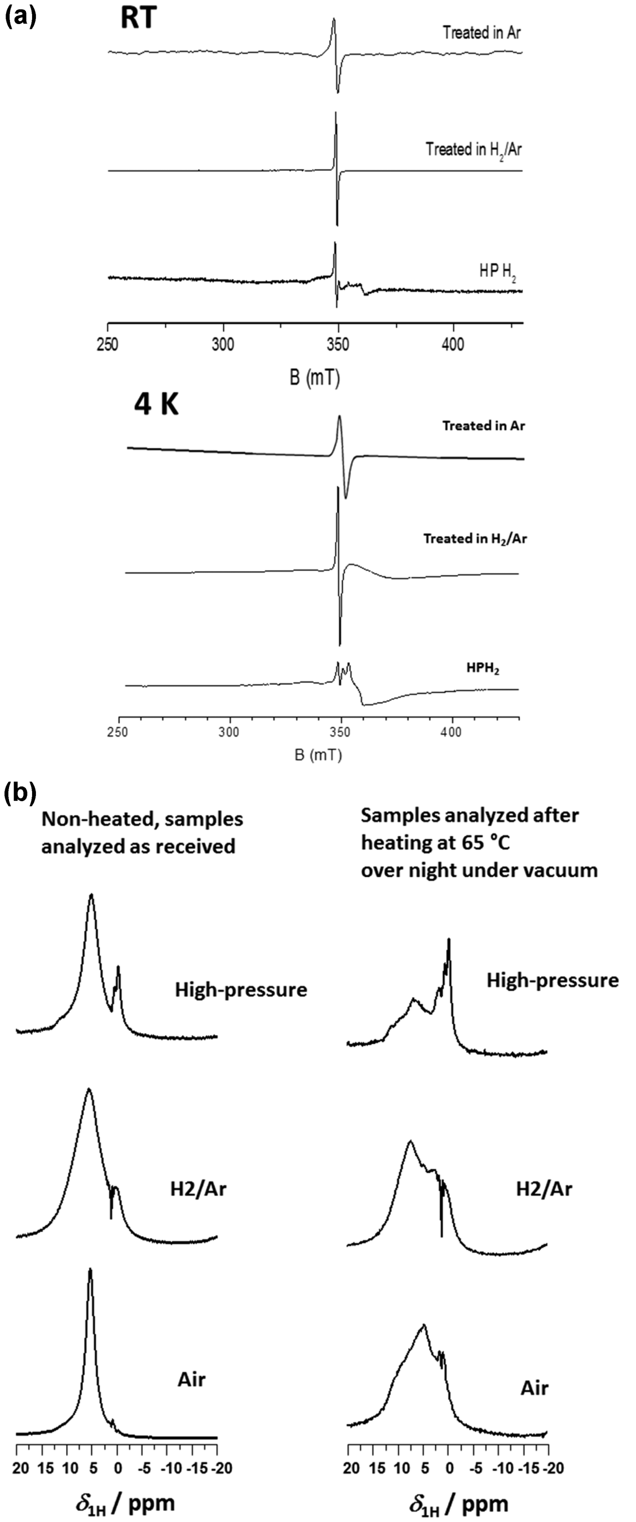


Figure 3. (a) ESR spectra of TiO_2 nanotubes annealed in Ar, Ar/H_2, and high pressure H_2 at room temperature and 4 K; (b) ^1H magic angle NMR spectra of TiO_2 nanotubes annealed in air, Ar/H_2, and high pressure H_2 before and after drying by heating.

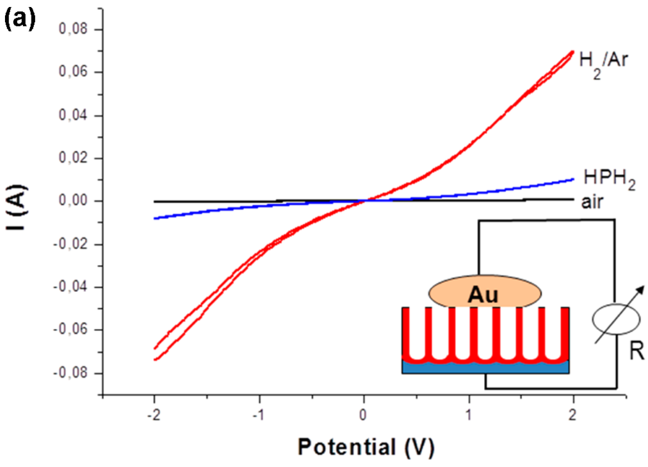
room temperature and at 4 K (Figure 3a). At 4 K, the samples treated in Ar or H_2/Ar show a pronounced oxygen vacancy signal ($g = 2.002$) and a broad line that can be attributed to Ti^{3+}.[11,12]

The sample treated at high pressure with H_2 shows a strong signal corresponding to Ti^{3+} with $[g_{xx}\ g_{yy}\ g_{zz}] = [1.991\ 1.974\ 1.939]$,[13] with a large distribution in g_{zz} values as obtained from the simulation of the experimental EPR spectrum at 4 K, performed using the Easyspin simulation package[14] (see Figure S5, Supporting Information), while the signal assigned to the oxygen vacancy is small compared to the Ar/H_2 sample. Even more striking is the difference in the ESR spectra recorded at the room temperature. For Ar/H_2 only low-intensity lines at $g = 2.002$ typically ascribed to trapped electrons on oxygen vacancies (e.g., O^{-2}) are observed. The high pressure sample, however, still shows a distinct signature of Ti^{3+} at $g_{\|} = 1.99$ and $g_{\perp} = 1.97$; i.e., at room temperature the Ti^{3+} features remain still apparent as separated lines (indicating the presence of isolated Ti^{3+} centers[15]). This is in contrast to most other ESR investigations of TiO_2, where clear Ti^{3+} states are usually only visible at sufficiently low temperature, similar to our Ar/H_2 sample in Figure 3a.[4,16]

We further conducted solid-state ^1H MAS NMR measurements to examine the role of hydrogen in TiO_2 (Figure 3b). Experiments were performed for the as-produced samples and after gentle heating to 65 °C as described in the Supporting Information. A strong peak at 5.7 ppm is observed for the three samples prior to heating, which is probably associated with crystallographic water or physically adsorbed water molecules.[17−21] Drying of the sample at 65 °C removes most of the physically adsorbed water, and several lines typically assigned to Ti−OH groups located at different crystallographic positions in the anatase structure remain.[17] Additionally, a peak around 0 ppm is apparent, which is very pronounced for the sample treated at high H_2 pressure, and becomes even more pronounced after drying the samples. These peaks are in line with the report from Chen and Mao,[21] where these sharp peaks at $\delta \approx 0$ ppm were attributed to the presence of interstitial hydrogen with a high dynamic exchange between hydrogen in different environments. In the context of the present findings, it is, however, noteworthy that peaks around 0 ppm were also reported for H_2-treatments under atmospheric pressure;[22] i.e., the presence of this type of hydrogen alone seems not a sufficient explanation for the observed catalytic activity after the high pressure treatment. Furthermore, literature reports on the formation built-in field effect upon TiO_2 reduction[23] seem to be generally true for any reduction treatment and therefore neither is a sufficient explanation for the observed effect. A direct way to generate and simultaneously defect classic Ti^{3+} state is ion bombardment of TiO_2 in an XPS as shown in the Supporting Information Figure S4a; but also surfaces modified in this way do not show significant photocatalytic H_2 evolution (Supporting Information Figure S4b).

Overall, the ESR/NMR findings show that the main effect of the high pressure H_2 treatment on anatase nanotubes is the formation of distinct Ti^{3+} defect sites with clearly different characteristics from defects formed by classic reduction treatments. The results suggest that these sites represent an active catalytic center for the evolution of H_2; they thus may be perceived as an intrinsic cocatalyst on the TiO_2 nanotube surface. In order to successfully form these centers, clearly an adequate H_2 treatment is needed and the detailed experimental procedure seems to be crucial.[24,25]

Remarkable is also that reference experiments using rutile nanowire arrays did not yield significant open circuit H_2 production neither after the H_2 high pressure nor when treated with H_2/Ar (Figure 1a and Supporting Information Figure S2). In fact, the different polymorphs anatase and rutile are reported to have a very different defect formation behavior upon reductive treatments.[7,26,27] In both cases, treatment of TiO_2 (thermal, reductive gas, and vacuum) leads to oxygen or water loss from the surface and the formation of oxygen vacancies and Ti^{3+} states. It is reported, however, that the formed oxygen vacancies tend to remain located at the surface for rutile,[7] whereas for anatase they tend to switch to a subsurface configuration.[26,27] This difference has been found to strongly affect the effect of defects on the reactivity for the two crystal polymorphs.[7] This suggests that the two polymorphs anatase and rutile behave distinctly different in regard to activation under open-circuit conditions. Indeed reference experiments using anatase and rutile powder (Supporting Information Figure S2b) show a considerable H_2 evolution activity for high pressure treated anatase, while for rutile no significant activity could be found. Nevertheless, in photoelectrochemical water splitting experiments (see Supporting Information Figure S3), using a Pt counter electrode, rutile nanowire electrodes treated in Ar/H_2 atmospheric pressure were found (in line with the literature[2]) to show a somewhat



samples	resistance Ω cm
Air	30000
H_2/Ar	4000
HP-H_2	600

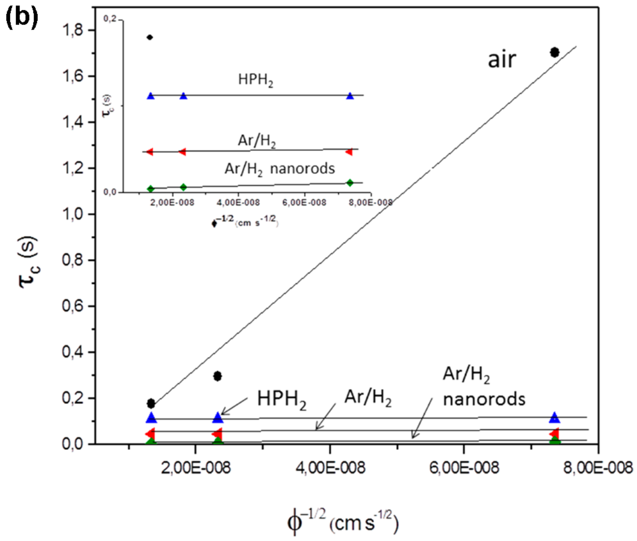


Figure 4. (a) Comparison of electrical resistance of nanotube layers annealed in different atmospheres (measured *I*−*V* curves at room temperature); (b) log−log graph of transport time constants for TiO_2 nanotubes annealed in air, Ar/H_2, and high pressure H_2 and nanorods annealed in Ar/H_2 calculated from photocurrent impedance (IMPS) measurements at different light intensities.

better performance than nanotubes treated under high pressure H_2 conditions. This effect may be ascribed to change in the electronic conductivity induced by any reduction treatment. In photoelectrochemical experiments, generated electrons have to travel through the 1D structure to the back contact before they are collected and can generate H_2 at the counter electrode; therefore, plain electron conductivity is important in these experiments. In fact, two-point conductivity (Figure 4a) and photocurrent impedance (IMPS) measurements (Figure 4b) show that nanotubes treated in Ar/H_2 show an even stronger improvement in conductivity and photoconductivity than samples exposed to the high pressure H_2 treatment and that reduced rutile nanorods (due to their single crystal nature) outperform the polycrystalline anatase tubes in electrical and photoelectrical conductivity.

In summary, the above results show that the surface of high pressure H_2-treated anatase TiO_2 nanotubes can, without the need of a cocatalyst (such as Pt, Pd, or Au), be intrinsically activated to show a high H_2 evolution rate in photocatalytic experiments. The results illustrate that a considerable difference in reactivity exists, if tubes are treated under high pressure H_2 conditions or under conventional reduction treatment in Ar/H_2 or Ar, as well as that the TiO_2 polymorph (anatase or rutile) can play a decisive role on the ability to activate such catalytic centers. In the light of the wide use of black titania nanostructures, the present work shows the need of differentiating classic effects such as conductivity/light absorption vs surface photocatalytic effects. In general, the present findings imply that an optimal H_2 treatment of TiO_2 nanotubes can trigger considerable intrinsic catalytic activity, which possibly can be exploited not only for H_2 evolution but for much wider applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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