Self-Doped Rutile Titania with High Performance for Direct and Ultrafast Assay of H$_2$O$_2$

Shu Sheng Pan,$^*$$^{†}$‡ Wei Lu,$^†$ Yi Hua Zhao,$^§$ Wei Tong,$^†$ Ming Li,$^‡$ Li Min Jin,$^†$ Jin Yuk Choi,$^†$ Fei Qi,$^#$ Shi Guo Chen,$^‡$ Lin Feng Fei,$^†$ and Siu Fung Yu*$^{†,‡}$

$^†$Department of Applied Physics, $^#$Department of Civil and Environmental Engineering, and $^§$Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

$^‡$Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanostructures, Institute of Solid State Physics, and $^*$Steady High Magnetic Field Facility, High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, Anhui, People’s Republic of China

$^§$Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

$^*$Supporting Information

ABSTRACT: Detection of H$_2$O$_2$ is important for the applications in environmental protection, pharmaceutical industries, food production, and clinical control. Current colorimetric assay of H$_2$O$_2$ based on enzyme or nanomaterials always needs TMB or other peroxidase substrate as coloration species. Furthermore, the corresponding response time including incubation process is in order of minute. In this study, we report on the synthesis of heavily Ti$^{3+}$-doped TiO$_2$ composed of spherelike nanoparticles by pulsed laser ablation method. This TiO$_2$ can directly detect H$_2$O$_2$ without using TMB or any other peroxidase substrate and is free from incubation process. In addition, the detection sensitivity is compatible with or better than that of the natural enzyme or other nanomaterials. Hence, the self-doped TiO$_2$ nanoparticles provide a novel, direct, ultrafast approach for H$_2$O$_2$ assay application.

KEYWORDS: H$_2$O$_2$ assay, Ti$^{3+}$ self-doping, titanium oxide, absorption, nanotechnology

1. INTRODUCTION

Hydrogen peroxide (H$_2$O$_2$) is an indispensable intermediate product in most of the environmental and biological circulation processes so that rapid and accurate detection of H$_2$O$_2$ is essential for environmental protection pharmaceutical industries, food production, and clinical control.$^{1,2}$ Therefore, the development of rapid, efficient and sensitive methodologies for H$_2$O$_2$ detection is of great interest and extensive attention has been concentrated on the realization of novel H$_2$O$_2$ assay. Horseradish peroxidase (HRP), which is a natural enzyme, has been utilized to assay H$_2$O$_2$. This is because HRP is sensitive to the presence of H$_2$O$_2$ and selectively in catalyzing H$_2$O$_2$ reduction in biological solutions.$^3$ However, the reaction time of enzymes with H$_2$O$_2$ is usually very long (i.e., in tens of minutes) and the preparation/purification cost of enzymes is expensive. In addition, enzymes may malfunction in harsh environment and tend to denature under normal detection conditions. Hence, despite the high detection sensitivity of HRP, artificial enzyme mimics were developed to replace natural enzymes for the assay of H$_2$O$_2$.

Up to now, various nanomaterials including iron oxide-based nanocomposite,$^{1-5}$ carbon nanotubes,$^6$ graphene oxide,$^7$ BiFeO$_3$, NPs,$^8$ polymer-coated CeO$_2$ NPs,$^9$ Au NPs,$^{10}$ V$_2$O$_5$ nanowires,$^{11}$ and FeS sheet$^{1,2}$ had been developed for the assay of H$_2$O$_2$. However, there are major drawbacks for the current colorimetric detection of H$_2$O$_2$ by using either natural enzymes or nanomaterials: (1) The need of peroxidase substrate as the chromogenic reagent in acidic condition (i.e., 3,3,5,5-tetramethylbenzidine (TMB) at pH 4.0) renders all the available assay of H$_2$O$_2$ to be performed in an indirect way. (2) The incubation time of the coloration based on the nanomaterials is in a range of minutes. Therefore, new technology or materials are needed to achieve rapid, direct and facile assay of H$_2$O$_2$.

Because of high chemical and physical stability in ambient conditions, easy preparation, low fabrication cost, nontoxicity, excellent biocompatibility, and environmental friendliness, TiO$_2$ has been widely used in energy and environmental science and technologies, such as photocatalysis, self-cleaning, solar cells, etc.$^{13-18}$ Zuo and co-workers have shown that the Ti$^{3+}$-doped TiO$_2$ (i.e., self-doped titania) can enhance the performance of hydrogen generation.$^{19}$ This implies that the presence of Ti$^{3+}$ may transform TiO$_2$ as a reducing agent to directly assay H$_2$O$_2$. Here, we reported a one-step method to prepare heavily Ti$^{3+}$ self-doped TiO$_2$ NPs (herein after, TiO$_2$:Ti$^{3+}$ NPs), which unexpectedly possess rapid and high sensitivity for determining H$_2$O$_2$ without using any peroxidase substrate. The coloration response is instantaneous (<1 s), the sensitive concentration range is as large as 1 × 10$^{-6}$ to 1 M, and
the detection limitation can reach to $5 \times 10^{-7}$ M, even lower than that of the HRP.

2. RESULTS AND DISCUSSION

TiO$_2$:Ti$^{3+}$ NPs were fabricated by ablating rutile TiO$_2$ powder dispersed in deionized water (concentration: 10 mg/mL) via a 355 nm nanosecond pulsed Nd:YAG laser (6 ns, 10 Hz, typical laser fluence: $\sim 1$ J/(pulse cm$^2$)). Blue color was instantly appeared in the white emulsion containing TiO$_2$ powders after 355 nm laser irradiation for $\sim 1$ min. The emulsion eventually became transparent with blue color after $\sim 10$ min of irradiation.

The calculated laser fluence for anatase TiO$_2$ to heat an individual spherical particle (diameter: 60 nm) to full melting is $\sim 0.6$ J/(pulse cm$^2$). The rutile TiO$_2$ has similar physical parameters with anatase; we assume the laser fluence threshold is same to that of anatase. The 355 nm Nd:YAG laser fluence used in this study is about $\sim 1$ J/pulse-cm$^2$, which is high enough to fully melt the TiO$_2$ nanoparticles. During the ablation process, TiO$_2$ nanoparticles were generated by heat evaporation arisen from the absorption of laser light. After 10 min of irradiation, a blue and transparent solution without any precipitate was obtained. The zeta potential of the TiO$_2$ nanoparticles colloidal solution is about $-59$ mV. The as-prepared TiO$_2$ NPs is spherelike with average size of about 30 nm, as shown in Figure 1c. According to the electron diffraction, the TiO$_2$:Ti$^{3+}$ NPs is amorphous, as shown in Figure S1 in the Supporting Information. The atomic percentage of O and Ti determined from energy-dispersive X-ray spectrometer (EDX) is 67.84 and 32.16%, respectively. These values are consistent with the atomic constitution of TiO$_2$ as shown in Figure S1b in the Supporting Information. It is noted that the solution is stable in ambient conditions for more than 3 months without any evident color variation or deposition formation.

The high resolution Ti 2p X-ray photoelectron spectra (XPS) of the TiO$_2$ powders before and after laser irradiation are shown in Figure 1a. For the pristine TiO$_2$, the binding energy peaks at 458.9 and 464.7 eV are assigned to the 2p$_{3/2}$ and 2p$_{1/2}$ core levels of Ti$^{4+}$. After laser irradiation, the 2p$_{3/2}$ and 2p$_{1/2}$ peaks shift to a lower energy side. The fitting of the Ti 2p$_{1/2}$ peak reveals the presence of two peak energies at 463.7 and 464.5 eV. The Ti 2p$_{3/2}$ peak can also be resolved into two Gaussian peaks with peak energy at 458.2 and 458.7 eV. The binding energy of 458.2 and 462.5 eV can attribute to the 2p$_{1/2}$ and 2p$_{3/2}$ core level of Ti$^{4+}$ respectively. On the other hand, the peak energies at 458.7 and 463.7 eV are related to the 2p$_{1/2}$ and 2p$_{3/2}$ core level of Ti$^{3+}$ respectively. These resolutions of peaks are well consistent with the recently reported on the binding energy value of TiO$_2$ nanostructures containing Ti$^{3+}$ synthesized by chemical method. These quantitatively analysis of the XPS data indicates that the Ti$^{3+}$/(Ti$^{3+}+Ti^{4+}$) atomic ratio is about 49%, i.e., nearly half of the titanium species in TiO$_2$:Ti$^{3+}$ are presented in the form of Ti$^{3+}$. The existence of Ti$^{3+}$ can also be verified by the EPR spectrum, as shown in Figure 1b. The dried TiO$_2$:Ti$^{3+}$ blue powder gives rise to a very strong electron paramagnetic resonance (EPR) signal, while no evident signal is seen for the pristine rutile TiO$_2$ powder. The g-value signal can be attributed to originate from the surface and subsurface paramagnetic Ti$^{3+}$ centers, which has also been previously reported in Ti$^{3+}$-doped TiO$_2$ grown by chemical method.

The blue coloration was also reported previously in the reduced TiO$_2$ (TiO$_2$-x), nonaqueous-synthesized TiO$_2$ nanocrystals, and raw TiO$_2$ irradiated by ultraviolet light in an inert atmosphere. The observation of blue coloration can be attributed to the Ti$^{3+}$ species formed in TiO$_2$. In the reduced TiO$_2$ (TiO$_2$-x), additional electrons (i.e., blue color) are resulted from the titanium interstitials or oxygen vacancies arisen during the synthetic process. In the nonaqueous-synthesized TiO$_2$ NPs, the blue coloration is stable in air for several months without any noticeable change in the absorbance. For the TiO$_2$ under ultraviolet light irradiation, bandgap absorption produces conduction band electrons which localize on the surface of Ti atoms, and this coloration can be rapidly extinguished upon exposure to oxygen. In this study, the dried TiO$_2$:Ti$^{3+}$ blue powder can be stable in air more than 1 month.

Figure 2a shows the typical absorption spectra and photo images of the TiO$_2$:Ti$^{3+}$ NPs with and without adding H$_2$O$_2$. The spectrum of the TiO$_2$:Ti$^{3+}$ NPs (without H$_2$O$_2$) shows a sharp absorption edge at 390 nm (3.18 eV) corresponding to band-to-band transition. As the particle size ($\sim 30$ nm) is much shorter than the wavelength of visible light (400–800 nm), light scattering caused by the NPs do not contribute to any absorbance in the absorption spectrum. The weak absorption in the visible region may be due to the Ti$^{3+}$-ion-related level in the band gap. The TiO$_2$:Ti$^{3+}$ NPs have negligible light absorption over the wavelength between 440 and 530 nm. As shown in Figure 2b, the TiO$_2$:Ti$^{3+}$ NP solution produces an orange-yellow color after introducing H$_2$O$_2$. The solution remained transparent, and there is no deposition formed even adding excessive H$_2$O$_2$. The absorbance of the TiO$_2$ NP–H$_2$O$_2$ system in the visible light and near UV ranges is dramatically enhanced when compared to the TiO$_2$:Ti$^{3+}$ NPs. The resulting solution shows a maximum absorbance at 450 nm, which corresponds to
the orange-yellow color of the systems. It should be pointed out that the blue solution instantly produce orange-yellow color after mixing the TiO2 NPs with H2O2, as shown in the Supporting Information (video).

For H2O2 detection based on other nanomaterials, such as V2O5,11 Fe3O4,1,2 and Au,10 the coloration reaction needs TMB as the peroxidase substrate, the mixture of nanomaterials, TMB substrate and H2O2 is generally required to be incubated for some “time interval” in acidic environment at about 45 °C before the corresponding absorption spectra are recognized as a valid measurement.1,2,4 See Table 1 for the required “time interval” for different types of nanomaterials for the detection of H2O2. In our case, no chemical is added to the mixture TiO2:Ti3+ NPs and H2O2 so that incubation process is not required to detect H2O2 and the “time interval” is zero. Figure 2b illustrates the variation of absorbance at wavelength of 450 nm with time after the TiO2:Ti3+ NPs and H2O2 were mixed together. The absorbance at ∼450 nm quickly increases with time and becomes stable after ∼30 s.

It was reported that similar yellow color solution was also produced in the hydrogen peroxide solution treated with titanium(IV) sulfate reagent with the presence of dilute sulphuric acid32 or gray TiH2 powders.33 The yellow species were tentatively attributed to the formation of pertitanic acid, TEM shows that the atomic ratio of O to Ti is about 4.8/1, which is close to the Ti and O elemental constitution in H2TiO4. See also the measured data of H2TiO4 given in the Supporting Information. Hence, a possible chemical reaction is tentatively proposed below to explain the reaction between TiO2:Ti3+ NPs and H2O2:34,35

\[
\text{Ti}^{3+} + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{TiO}_4 + 3\text{H}^+ \\
\text{blue} \rightarrow \text{yellow}
\]

The presence of Ti3+ ions and high surface-to-volume area of NPs greatly enhance the reducibility of TiO2:Ti3+ NPs, and can be directly oxidized by H2O2. As a result, the Ti3+ ions in TiO2:Ti3+ NPs can directly react with H2O2 and the resultant pertitanic acid is orange-yellow. Furthermore, the small size NPs with high surface-to-volume ratio accelerate the above chemical reaction. The pertitanic acid can be written as TiO2: H2O2, showing a true peroxide structure. As a comparison, the precursor of white rutile TiO2 powders without Ti3+ ions was also treated with H2O2 solution, however, there is no evident change of color, as shown in Figure S3 in the Supporting Information.

To investigate the reduction capability of H2O2 by TiO2:Ti3+ NPs, H2O2 with different concentration was added to the TiO2:Ti3+ NPs solution with concentration of 10 mg/mL, as shown in Figure 3 and Figure S6 in the Supporting Information. The absorbance at 450 nm was selected as the calibration wavelength. The absolute absorbance ∆A is defined as ∆A = A(TiO2−H2O2) – A(TiO2), where A(TiO2−H2O2) and A(TiO2) are the absorbance at 450 nm of TiO2:Ti3+ NP-H2O2 system and the corresponding TiO2:Ti3+ NPs solution with same concentration respectively. The ΔA of the system (TiO2−H2O2) increases with the increase of H2O2 concentration. As shown in Figure 3a, the absorbance at 450 nm versus H2O2 concentration can be well fitted by logarithmic function (with the R value is equal to 0.998) over a wide range of H2O2 concentration between 1 × 10−6 and 1 M. The detection limit is as low as 5 × 10−7 M. In a small concentration range of 1 mM to 10 mM, the ΔA has a linear relationship (R = 0.989) with H2O2 concentration.

HCl, NaClO, ethanol, and acetone were selected as the control reagents to verify the coloration of TiO2:Ti3+ NPs solution. The blue transparent solutions became muddy white after adding with HCl and NaClO. This observation is different to that from adding H2O2 to the TiO2:Ti3+ NPs solution (i.e., formation of orange-yellow transparent solution; see the inset of Figure 4, the absorption spectra are shown in Figure S5 in the Supporting Information). On the other hand, the adding of ethanol and acetone has shown no evidence of changing in TiO2:Ti3+ NPs solution except the blue color turn light. The absorbance of TiO2:Ti3+ NPs solution with H2O2 is much

![Figure 3](https://example.com/figure3)

**Figure 3.** (a) Relationship between absolute absorbance ∆A at 450 nm and concentration of H2O2 over a range between 1 × 10−6 and 1 M. The blue solid line is the fitted curve. (b) Linear fitting of absolute absorbance at 450 nm versus H2O2 concentration over a range between 1 and 10 mM. Error bar: standard deviation.

Information. The absorbance at 450 nm was selected as the calibration wavelength. The absolute absorbance ∆A is defined as ∆A = A(TiO2−H2O2) – A(TiO2), where A(TiO2−H2O2) and A(TiO2) are the absorbance at 450 nm of TiO2:Ti3+ NP-H2O2 system and the corresponding TiO2:Ti3+ NPs solution with same concentration respectively. The ΔA of the system (TiO2−H2O2) increases with the increase of H2O2 concentration. As shown in Figure 3a, the absorbance at 450 nm versus H2O2 concentration can be well fitted by logarithmic function (with the R value is equal to 0.998) over a wide range of H2O2 concentration between 1 × 10−6 and 6 × 10−5 M as well as 1 × 10−4 and 1 M. The detection limit is as low as 5 × 10−7 M. In a small concentration range of 1 mM to 10 mM, the ΔA has a linear relationship (R = 0.989) with H2O2 concentration.

HCl, NaClO, ethanol, and acetone were selected as the control reagents to verify the coloration of TiO2:Ti3+ NPs solution. The blue transparent solutions became muddy white after adding with HCl and NaClO. This observation is different to that from adding H2O2 to the TiO2:Ti3+ NPs solution (i.e., formation of orange-yellow transparent solution; see the inset of Figure 4, the absorption spectra are shown in Figure S5 in the Supporting Information). On the other hand, the adding of ethanol and acetone has shown no evidence of changing in TiO2:Ti3+ NPs solution except the blue color turn light. The absorbance of TiO2:Ti3+ NPs solution with H2O2 is much

![Figure 4](https://example.com/figure4)

**Figure 4.** Selectivity analysis for H2O2 detection by monitoring the relative absorbance. Inset: the analyte concentrations are as follows: 1 M sodium hypochlorite (NaClO), 2 M hydrochloric acid (HCl), 1 M ethanol, 1 M acetone, 0.5 M hydrogen peroxide (H2O2). Error bar: standard deviation.

### Table 1. Comparison of Typical Nanomaterials for H2O2 Detection

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>Chromogenic Peroxidase Substratesa</th>
<th>Incubation Time (s)</th>
<th>pH</th>
<th>Detection Limit (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2:Ti3+ Nanowires</td>
<td>ABTS, TMB</td>
<td>60</td>
<td>4.0</td>
<td>7.0</td>
</tr>
<tr>
<td>PtPd-Fe3O4 Nanoparticles</td>
<td>TMB</td>
<td>300</td>
<td>5.2</td>
<td>2</td>
</tr>
<tr>
<td>Fe3O4 Nanoparticles</td>
<td>DAB, OPD</td>
<td>600</td>
<td>3.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Au Nanoparticles</td>
<td>TMB</td>
<td>600</td>
<td>4.0</td>
<td>0.05</td>
</tr>
<tr>
<td>Graphene Oxide</td>
<td>TMB</td>
<td>none</td>
<td>none</td>
<td>7.0</td>
</tr>
<tr>
<td>Ti3+-Doped TiO2</td>
<td>none</td>
<td>7.0</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

aABTS, 2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid; TMB, 3,3,5,5-tetramethyl-benzidine; DAB, diazo-aminobenzene; OPD, o-phenylenediamine.
higher than that with HCl, NaClO, ethanol, and acetone, as shown in Figure 4. This control experiment indicates that the TiO\textsubscript{2}:Ti\textsuperscript{3+} NPs shows high selectivity in detection of H\textsubscript{2}O\textsubscript{2}.

3. CONCLUSIONS

In conclusion, we reported that the fabrication of TiO\textsubscript{2}:Ti\textsuperscript{3+} composed of uniform nanospheres grown by a one-step method. The TiO\textsubscript{2}:Ti\textsuperscript{3+} NPs exhibit excellent detection behavior of H\textsubscript{2}O\textsubscript{2} with high selectivity and required the usage of no peroxidase substrate, such as TMB. Detection sensitivity of TiO\textsubscript{2}:Ti\textsuperscript{3+} NPs on H\textsubscript{2}O\textsubscript{2} is much faster than currently used materials. Photos and the corresponding absorbance at 450 nm of TiO\textsubscript{2}:Ti\textsuperscript{3+}, raw rutile TiO\textsubscript{2} after adding H\textsubscript{2}O\textsubscript{2}; absorption spectrum of TiO\textsubscript{2}:Ti\textsuperscript{3+} NPs solution after adding NaClO, HCl, ethanol, and acetone. Images of TiO\textsubscript{2}:Ti\textsuperscript{3+} solution with different H\textsubscript{2}O\textsubscript{2} concentration. Linear rinse point of absorbance at 450 nm and H\textsubscript{2}O\textsubscript{2} concentration in a narrow range of 1 × 10\textsuperscript{-3} to 0.06 mM. The live video of the TiO\textsubscript{2}:Ti\textsuperscript{3+} colloidal solution mixing with H\textsubscript{2}O\textsubscript{2}. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: sfyu21@hotmail.com.

*E-mail: sspan@issp.ac.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by “Hong Kong Scholars Program” (Grant XJ2011039, 201104336), Hong Kong Polytechnic University Central Research Grant (Grant G-YZ01), National Natural Science Foundation of China (Grants 11004197, 11374309, 51108030), China Postdoctoral Science Foundation (Grants 2013MS41847). We acknowledge the Steady High Magnetic Field Facility in High Magnetic Field Laboratory, Chinese Academy of Sciences for the EPR measurement. Dr. H.Q. Wang (Max Planck Institute of Colloids and Interfaces) is acknowledged for helpful discussion.

■ REFERENCES


