This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
We report the direct production of H$_2$O$_2$ from O$_2$ and H$_2$O by a heterogeneous catalyst made from non-toxic materials using light as the sole energy source for the process. Photocatalytic production of H$_2$O$_2$ is demonstrated using light energy without the need for additional chemical energy (sacrificial compounds) or applied electrical potential. Fine-tuning of catalyst architecture and interface design enables the exceptional photocatalytic activity.

Broader Context

H$_2$O$_2$ is a useful chemical reagent with numerous uses in the chemical industry, as a disinfectant, and as an environmentally friendly chemical fuel. Ideally, the production of H$_2$O$_2$ would utilize environmentally compatible materials throughout the process including the preparation of the catalyst and the reagents consumed. Furthermore, it is desirable to use sustainable energy resources such as available light energy for driving the process without additional energy required in the form of external electrical potential or chemical fuels. Namely, the ideal process may rely on photocatalytic producing of H$_2$O$_2$ by directly harnessing the excited hole-electron pair (exciton) for reducing molecular oxygen and oxidizing water molecules without the need for additional energy sources, such as externally applied electrical potential or chemical fuel. Metal oxides (MOs) and TiO$_2$-Au hybrid systems in particular have been widely studied as promising candidates in the context of photocatalytic production of H$_2$O$_2$ owing to their high stability and low toxicity.$^{6,7,8,9}$ However, until now all studies where direct photocatalytic production of H$_2$O$_2$ by MOs was attempted without the use of hole scavengers showed negligible concentrations.$^{5,10}$ Namely, despite the vast ongoing research activity in this field there are no studies reporting the direct photocatalytic production of H$_2$O$_2$ by MOs without the consumption of organic compounds that act as sacrificial electron donors or the application of external electric field that provide the additional energy required for completing the photocatalytic reaction. Recently, a homogeneous photocatalytic system exhibiting direct generation of H$_2$O$_2$ from O$_2$ and H$_2$O was demonstrated using a Ru complex with the additional use of iridium oxide and rare earth metals ions as cocatalysts.$^{11}$ Here we report the direct production of H$_2$O$_2$ from O$_2$ and H$_2$O by a heterogeneous catalyst made from non-toxic materials such as TiO$_2$, silicon and gold without using any external source of energy except for light. While the materials used are conservative, the catalyst structure exhibits a unique architecture resulting in the exceptional photocatalytic activity. Molecular layer deposition (MLD) of titanium ethylene glycol (Ti-EG) shell and subsequent thermal activation is used to produce the photoactive layer.$^{12}$ Addition of rare earth metal ions function as co-
catalysts further increasing the levels of \( \text{H}_2\text{O}_2 \) photocatalytically produced from \( \text{O}_2 \) and \( \text{H}_2\text{O} \) without using sacrificial compounds.

Briefly, the catalyst was synthesized using silicon nanowires (SiNWs) scaffolds prepared by chemical vapor deposition (CVD) and coated with titanium ethylene glycol (Ti-EG) shell by MLD to form core-shell structures (SiNW-Ti-EG). A thermal anneal step was applied for activating the Ti-EG layer resulting in a highly photocatalytic and molecularly permeable \( \text{TiO}_2 \) shell.

The thermal anneal of the Ti-EG layer results in decomposition of the organic components of the Ti-EG film and formation of \( \text{TiO}_2 \) nanocrystals with an anatase phase embedded in an amorphous layer, in agreement with our previous work (see ESI for additional details and Table S1 for electron diffraction data).

Finally, the annealed core-shell structures were modified in solution for depositing gold clusters yielding SiNW-(Ti-EG)\text{anneal} Au structures. Quartz slides were used as UV transparent substrates for preparing catalyst films used for photocatalysis experiments (Fig. 1).

The photoactive \( \text{TiO}_2 \) shell preparation relies on thin Ti-EG films prepared by MLD followed by thermal activation step. This route provides an initially metastable organic-inorganic titanicone film as source for the \( \text{TiO}_2 \) shells that can be further tuned by annealing and chemically modifying steps while controlling critical properties such as the overall catalyst architecture, shell permeability, crystallinity and surface composition as will be discussed and demonstrated here (vide infra). This approach delivers fine control over a number of the critical factors that determines the overall photoreactivity of the hybrid catalyst resulting in the enhanced reactivity reported here. Most importantly, direct production of \( \text{H}_2\text{O}_2 \) from \( \text{O}_2 \) and \( \text{H}_2\text{O} \) require that the excited electron energy level is sufficient to promote electron transfer from the photocatalyst conduction band (CB) to the oxygen molecule. In addition, the hole oxidative potential, determined by the valence band (VB) position, should exceed the water oxidation potential.\(^{13-15}\)

The photoinduced reduction and oxidation processes are linked, so hampering any one of the processes result in charge accumulation and halting of the whole photocatalytic process. When both processes occur in tandem with sufficient efficiency, direct photocatalytic production of \( \text{H}_2\text{O}_2 \) can occur. Most studies related to photocatalytic generation of \( \text{H}_2\text{O}_2 \) report the use of hole scavengers that function as electron donors for completing the photocatalytic cycle or utilize externally applied electric potential.\(^{16,17}\)

Typically, the electron donors are sacrificial organic molecules that are consumed in the process and function as chemical fuel generating by-products. Additionally, the sacrificial compounds often results in partially or fully oxidized organic compounds and intermediates that are both environmentally unwanted and negatively interfere with the catalyst by adsorption to the catalyst surface and often result in catalyst passivation.\(^{18}\)

Such processes are less attractive as compared to a purely photocatalytic process that consumes only light, water and oxygen.

Illuminating the core-shell SiNW-(Ti-EG)\text{anneal}-Au catalyst films suspended in acidic water (pH~2, HCl) showed direct formation of \( \text{H}_2\text{O}_2 \) without the addition of sacrificial compounds. \( \text{H}_2\text{O}_2 \) production was studied for various catalyst preparation conditions spanning MLD layer thickness between 4.5±1 and 13±2 nm corresponding to 25 to 80 cycles, respectively, and for an anneal range of 380 to 780 °C. In addition, the photocatalytic process was studied using UV (365 nm) and sun simulator illumination (AM 1.5G), (Fig. 2).
Typical evolution of $\text{H}_2\text{O}_2$ for optimal catalyst preparation parameters at UV illumination (365 nm) is presented in Fig. 2b (SSC of 38 µM, $k_f = 10.5$ µM x h$^{-1}$ and $k_d = 0.27$ h$^{-1}$).

The addition of a rare earth co-catalyst ($\text{Y}^{3+}$) resulted in a dramatic increase in the SSC of $\text{H}_2\text{O}_2$ to 114 µM, ($k_f = 14.8$ µM x h$^{-1}$, and $k_d = 0.13$ h$^{-1}$). An even more dramatic increase in $\text{H}_2\text{O}_2$ concentration and change in the overall kinetics was obtained by adding $\text{Sc}^{3+}$ as co-catalyst resulting in a steady linear increase and overall zero order kinetics ($k_f = 5.7$ µM x h$^{-1}$), Fig. 2c. $\text{Sc}^{3+}$ cations have been shown to act as Lewis acid co-catalyst facilitating two-electron reduction of $\text{O}_2$ and effective inhibitors of disproportionation of $\text{H}_2\text{O}_2$. The same catalyst samples were used for studying the reactivity under visible light ($\lambda$$\geq$400nm) and simulated sun illumination (AM 1.5G) showing SSC of $\approx$5 µM and $\approx$15 µM, respectively (Fig. 2d) for $\text{Y}^{3+}$. Significantly higher concentrations of $\text{H}_2\text{O}_2$, above 40 µM, were obtained for AM 1.5G illumination in the presence of $\text{Sc}^{3+}$. Although the catalyst absorption spectra shows a clear plasmon band (Fig. S4) simultaneous catalyst illumination by UV and visible light sources showed no observable enhancement in the photocatalytic production rates or SSC of $\text{H}_2\text{O}_2$.

The role of gold clusters in the overall photocatalytic process was further studied by blocking the gold surface by a long-chain alkyl thiol (1-ocanadenecanethiol) resulting in significantly lower SSC of $\text{H}_2\text{O}_2$, similar to the levels measured for catalyst without the gold deposition step (Fig. 2e). Our combined results suggest that the deposited gold clusters effectively improve charge
separation and assist in avoiding recombination reactions.\textsuperscript{20-23} In addition to the electronic effects, some aspects regarding O\textsubscript{2} and H\textsubscript{2}O diffusion at the catalyst interface may have additional contributions as well. Photocatalysis experiments performed using deoxygenated solutions and measured under Ar did not result in significant SSC of H\textsubscript{2}O\textsubscript{2} pointing at dissolved O\textsubscript{2} as the source for oxygen in the reaction (Fig. S2). Previously we reported the enhanced photocatalytic activity of TiO\textsubscript{2} films obtained by annealing Ti-EG layers prepared by MLD which exhibit a molecularly permeable TiO\textsubscript{2} layer with unique properties distinct from TiO\textsubscript{2} films obtained by other preparation methods, such as atomic layer deposition (ALD).\textsuperscript{24-29} In addition, several studies demonstrated the enhanced photocatalytic activity of SiNW-TiO\textsubscript{2} core-shell structures;\textsuperscript{30-35} however direct photocatalytic production of H\textsubscript{2}O\textsubscript{2} from O\textsubscript{2} and H\textsubscript{2}O by a heterogeneous catalyst made from those materials, without the need for sacrificial compounds or externally applied potential was not reported. We suggest that the molecular permeability of the TiO\textsubscript{2} layer obtained by annealing the MLD film plays a significant role in the catalyst preparation and performance where gold is deposited onto the annealed SiNW-Ti-EG core-shell structure. The gold deposition step is performed in solution with both galvanic displacement (GD) and photocatalytic deposition (PD) taking place in the presence of HF and light. The simultaneous deposition by GD and PD resulted in mixture of full and hollow nanoarchitectures.

The filled nanoarchitectures comprise of SiNW core coated with permeable TiO\textsubscript{2} layer and decorated with gold clusters at the external surface (Fig. 3a,b). The hollow structures consist of a TiO\textsubscript{2} shell decorated with gold clusters at the outer surface and additional gold decorated inside the tube (Fig. 3c,d). The GD process occurs by diffusion of reactants through the permeable TiO\textsubscript{2} layer and oxidation of the Si core to SiO\textsubscript{2} yielding reduced metal clusters inside the core region. The resulting SiO\textsubscript{2} is dissolved by the HF and diffuses via the permeable TiO\textsubscript{2} layer leading to the partially hollow core with the pea-pod like structures. By varying the preparation parameters the distribution of hollow to filled structures can be tuned ranging from predominantly hollow pea-pod like structures with gold clusters in the internal surface to predominantly filled structures with the SiNW core retained and gold deposition at the external surface (Fig. S5). Maximal SSC of H\textsubscript{2}O\textsubscript{2} is obtained for 60 MLD cycles and an anneal temperature of 520 °C. TEM analysis and X-ray photoelectron spectroscopy (XPS) characterization (vide infra) show at optimal catalyst preparation parameters a mixture of full and hollow structures decorated with gold clusters as described above. The permeable TiO\textsubscript{2} layer obtained by annealing the Ti-EG MLD film results in a gold-TiO\textsubscript{2} interface where the deposited gold is directly incorporated into the oxide not only at the nanotube surface as would be in the case of metal evaporation or attachment of preformed nanoparticles. This characteristic assists in enhancing Au-TiO\textsubscript{2} interfacial interactions that are critical for promoting charge separation at the interface.\textsuperscript{30-32}

Catalyst composition was studied by XPS analysis for various MLD film thicknesses at constant anneal temperature of 520 °C and for various anneal temperatures for 60 MLD cycles. As expected, the Ti signal increases with number of MLD cycles (Fig. 4a-i). The Au signal decreases with MLD cycles because of screening of the XPS signal arising from Au clusters deposited inside the tubes with increasing tube wall thickness. Si/Ti and F/Ti atomic ratios decrease with the number of MLD cycles, as shown in Figs. 4a-ii and 4a-iii, respectively.

For the various anneal temperatures, the Ti signal remains quite constant. In contrast, a sharp increase in Au/Ti atomic ratio is measured for 650 °C (Fig. 4b-i). We attribute the sharp increase in the Au/Ti ratio to the increase in photocatalytic activity of the annealed Ti-EG film at this temperature, leading to higher PD of gold, in accordance with previous work.\textsuperscript{14} The XPS analysis demonstrates that the F/Ti ratio varies with temperature. In addition, F1s binding energy (BE) changes from 685.8 eV for thin MLD films up to 30 cycles to 684.3 eV for thicker MLD films (Fig. S6). This result suggests mainly Si-F and Ti-F species for thin and thick MLD layers, respectively. In addition, for optimal catalyst preparation conditions F1s BE corresponds to surface Ti-F species rather than F-doped TiO\textsubscript{2}.\textsuperscript{33-35} Numerous studies have shown that surface fluorination improves TiO\textsubscript{2} photocatalytic performance in general and for H\textsubscript{2}O\textsubscript{2} and water oxidation processes in particular.\textsuperscript{36-39} Thus, the gold deposition in the presence of HF not only results in deposition of gold clusters both inside and outside the TiO\textsubscript{2} shell for improving the charge separation, but also yields a beneficial Ti-F surface modification of the catalyst by the same process.

**Conclusions**

In conclusion, we have demonstrated the direct photocatalytic production of H\textsubscript{2}O\textsubscript{2} from O\textsubscript{2} and H\textsubscript{2}O by a heterogeneous catalyst made from non-toxic materials such as TiO\textsubscript{2}, silicon and gold. Although the materials used are conventional, the photocatalyst exhibits unique architecture that results in the exceptional...
photocatalytic activity. The unique hybrid structure design allows achieving this breakthrough using well studied materials such as TiO$_2$, Au and Si and further emphasizing the novelty of our approach. The unprecedented reactivity of the materials used in the hybrid structure is owing to exquisite control of the structure and interfaces rather than resorting to exotic compositions and materials. Future work will focus in improved visible light activity by utilizing the MLD layer properties for doping and possibly taking advantage of plasmon enhanced photoactivity.

Acknowledgements

We thank Dr. Vitaly Gutkin for XPS analysis. This work was partially funded by a starting grant from the European Community’s Seventh Framework Programme Grant agreement no 259312 and by the Israel Science Foundation (ISF) under Grant (690/09).

Notes and references

† Electronic Supplementary Information (ESI) available: [Synthesis and characterization of the photocatalyst system.]. See DOI: 10.1039/b000000x/

The table of contents entry

Direct photocatalytic production of H$_2$O$_2$ is demonstrated using heterogeneous catalyst made from environmentally compatible materials and light energy without the need for additional chemical energy (sacrificial compounds) or applied electrical potential. Fine-tuning of catalyst architecture and interface design enables the exceptional photocatalytic activity.