On the Controlled Loading of Single Platinum Atoms as a Co-Catalyst on TiO$_2$ Anatase for Optimized Photocatalytic H$_2$ Generation

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Single-atom (SA) catalysis is a novel frontline in the catalysis field due to the often drastically enhanced specific activity and selectivity of many catalytic reactions. Here, an atomic-scale defect engineering approach to form and control traps for platinum SA sites as co-catalyst for photocatalytic H$_2$ generation is described. Thin sputtered TiO$_2$ layers are used as a model photocatalyst, and compared to the more frequently used (001) anatase sheets. To form stable SA platinum, the TiO$_2$ layers are reduced in Ar/H$_2$ under different conditions (leading to different but defined Ti$^{3+}$-$O_v$ surface defects), followed by immersion in a dilute hexachloroplatinic acid solution. HAADF-STEM results show that only on the thin-film substrate can the density of SA sites be successfully controlled by the degree of reduction by annealing. An optimized SA-Pt decoration can enhance the normalized photocatalytic activity of a TiO$_2$ sputtered sample by 150 times in comparison to a conventional platinum-nanoparticle-decorated TiO$_2$ surface. HAADF-STEM, XPS, and EPR investigation jointly confirm the atomic nature of the decorated Pt on TiO$_2$. Importantly, the density of the relevant surface exposed defect centers—thus the density of Pt-SA sites, which play the key role in photocatalytic activity—can be precisely optimized.

Single-atom (SA) or single-site catalysis (SACs) has over the past years become an increasingly fascinating topic in the catalysis field. SACs have allowed new approaches in heterogeneous catalysis and enabled an unprecedented control over atomistic effects, resulting in improved active sites, and at the same time enabled the design of metal–support interfaces with a high level of structural and chemical control. A diverse range of supports and features is known to stabilize isolated metal atoms, notably through pinning at electronic and/or structural defects associated with coordinatively unsaturated sites. However, it is still difficult to create a high density of thermally stable support sites and hence the fabrication and control of high SA loading remains a challenge.

Different strategies have been developed to form SA trap sites, mainly by using localized charge cavities (zeolites) or crystal features such as triple points (step edges or single vacancies). For SA-deposition (decorating above reactive sites) methods such as bath deposition, vapor deposition, galvanic replacement, or atomic layer deposition (ALD) have been used. Particularly, lattice-defect formation on an ideal support material is a main approach in which these defects act as a trap for anchoring SAs. This has extensively been studied for noble metal fixation (Au,Pt) on FeO$_x$, key in this system is that non-stoichiometric oxides are widely available and that for example oxygen (or iron) vacancies can easily pin a noble metal atom. Such type of SACs are highly promising in the field of, for example, water gas shift reactions.

Another SA system that is of high interest is provided by noble metals on titanium dioxide (TiO$_2$). In general, in photocatalysis, TiO$_2$ is still the most investigated substrate, especially in its anatase polymorph, due to its high chemical stability and photocorrosion resistance. Also it has a conductive band which allows, in combination with Au SA decoration, a high efficiency for photocatalytic CO$_2$ conversion or in the case of SAC-Pt on anatase for the photocatalytic generation of H$_2$ from aqueous electrolytes (with or without sacrificial agents). In the photocatalytic H$_2$ generation on TiO$_2$, a main disadvantage is the sluggish electron transfer from the TiO$_2$ surface to the aqueous reactant; as a result, the hydrogen production efficiency is low. Exactly this issue is usually addressed by using a proper co-catalyst on the TiO$_2$ surface.

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Extensive work, both theoretical and experimental, show platinum to be most efficient for photocatalytic H₂ generation. However, it is rare and expensive; therefore, wide research tried to enhance the noble metal utilization efficiency. One of the most effective approaches would be an increase of the catalyst active surface area by decreasing the catalyst size.

In this context, only recently, Pt atoms trapped at surface defects of anatase have attracted significant attention. These reports on SA catalyst formation are almost exclusively carried out on hydrothermally grown thin anatase sheets with large (001) facets. Wei et al. showed that in fact also the crystallographic orientation of hydrothermally produced sheets plays a considerable role for the achievable density of deposited Pt atoms and the resulting catalytic activity. These sheets have the advantage that they can be produced by a facile hydrothermal approach, which leads to sizes of 50–100 nm edge length and a thickness of a few nanometers—the thinness allows for easy TEM investigations. It has been shown that Pt SAs can be anchored on native lattice defects on these sheets, and such SA-Pt-decorated sheets provided indeed a co-catalytic enhancement in photocatalytic H₂ generation reactions. Nevertheless, these sheets have two main drawbacks: i) they are fluoride-terminated after hydrothermal synthesis, and ii) already a very low sintering temperature leads to their morphological deformation. Both effects, the degree of F-termination and low temperature sintering, prevent a true control of the formation of surface defects by a defined thermal treatment in a reductive atmosphere (H₂, Ar/H₂). To form in these reductive gases structural surface defects (Ti³⁺-Ov) it takes >300 °C (in Ar/H₂ atmosphere). Several works show that annealing TiO₂ in H₂ or Ar/H₂ mainly leads to two types of defect centers that is, Ti³⁺ centers located in regular lattice positions and surface exposed Ti³⁺(Ov). The density of these defects on the TiO₂ surface can be adjusted by the annealing conditions (namely by the annealing atmosphere and the temperature)—this is also illustrated in Figure S1, Supporting Information. The defects can be distinguished and characterized most effectively by EPR spectroscopy where regular lattice positions provide a typical signal with a g value of ≈1.99 and surface exposed Ti³⁺ show a signal with a characteristic g value of ≈1.93. The data in the present work shows that relevant surface exposed Ti³⁺ defects are formed between 300 and 900 °C in Ar/H₂ atmosphere (which is beyond the modification temperatures of the hydrothermal sheets, as we will show below—this prevents the desired control over defect formation on hydrothermal sheets). In order to overcome these problems, we constructed a different anatase platform as outlined in Figure 1a,b. We show below that on these defined thin-film substrates via annealing parameter control (defect control), a high SA density can be established and the resulting co-catalytic effects for photocatalytic H₂ generation can be optimized (a comparison with classic sheets will then be given at the end of the paper).

As mentioned, for the main investigations we started with a substrate as schematically shown in Figure 1a. Amorphous TiO₂ layers were deposited by reactive sputtering (as explained in the experimental section) on a patterned TEM support that contained thin transparent windows of amorphous SiO₂. To convert the as-sputtered amorphous TiO₂ layers to polycrystalline anatase, the samples were then annealed at 450 °C in air. The crystal structure of the sputtered layer was confirmed by the selected-area electron diffraction (SAED) as shown in Figure S2, Supporting Information. The SAED pattern gives marked Miller indices in accordance with anatase TiO₂ (JCPDS card no. 21–1272).

We then exposed this grit structure to thermal treatments in Ar/H₂ up to 700 °C to form various surface defects in the TiO₂ surface. SA-trapping of Pt is obtained by immersion of the substrate in a very dilute Pt containing solution. Due to the instability of hexachloroplatinic acid in non-acidic aqueous solution, the immersion time and the concentration of hexachloroplatinic acid was optimized as illustrated in Figures S3–S5, Supporting Information and according description in the Supporting Information. In order to control the SA-Pt density, the most successful approach is variation of the annealing temperature while keeping time and Pt deposition constant. In order to correlate defects with activity, we used highly pure anatase powder under the same annealing conditions and measured EPR spectra. Overall, in line with above mentioned literature there are two characteristic defects in the EPR spectra. At lower temperature lattice-embedded Ti³⁺ forms and at higher temperature the density of surface exposed Ti³⁺ starts increasing. To obtain layers with different densities of defects, we annealed the layers in the range of 300–700 °C in Ar/H₂ atmosphere. Figure 1g shows HAADF-STEM images of sample reduced at 300, 400, and 500 °C in Ar/H₂. After immersion in 120 µmol hexachloroplatinic solution, these samples show different Pt distributions. In every case HAADF-STEM shows clear proof for SA Pt decoration on TiO₂. Most important is that the defect distribution is strongly affected by the thermal treatment and this leads to correlating amounts of Pt atoms deposited, that is, the Pt loading can be controlled by pre-reduction in Ar/H₂. Figure 1e presents the number of Pt SAs on a surface of 100 nm²—it is noteworthy that the values correlate well with previous published work of Wan et al. A schematic of a Pt-SA-decorated TiO₂ layer is provided in Figure 1f.

EDX mapping was performed at various locations of the TEM windows to evaluate the distribution of Pt, Ti, and O. Figure 1d shows the EDX map of Ti, O, and Pt of the sample, which was annealed at 500 °C in Ar/H₂ followed by immersion in 120 µmol platinate solution. Due to the detection limit of EDX, a precise quantitative assessment cannot be achieved, the mapping nevertheless presents an entirely uniform distribution of Pt on the surface, that is, neither intense investigations with SEM nor TEM-EDX mapping show agglomeration or nanoparticle formation of Pt.

In order to characterize the deposited Pt, X-ray photoelectron spectroscopy (XPS) was performed. Please note that trapped SA Pt shows a chemical shift of δ₀ due to the changed co-ordination (e.g., Pt bound to oxygen instead of Pt). This is also evident for the SA samples in comparison to classic Pt nanoparticle samples. Figure 2a shows the XPS survey spectra of the SA Pt deposited layers annealed at different temperatures in Ar/H₂. XPS survey results indicate that the samples mainly contain Pt, Ti, O, and adventitious carbon. No Cl₂p peak can be detected in the samples which proves that the Pt signals originate from the trapped Pt and not, for example, from remnants of the precursor solution. Figure 2b and c show the deconvoluted high resolution XPS spectra of the Pt4f region for the atomic-scale decorated sample and for a sample that was decorated...
with Pt nanoparticles using a sputter deposition–dewetting method\cite{38} (see also Figure S6, Supporting Information and Experimental Section). The Pt4f peak for the SAC-Pt sample can be deconvoluted into four peaks. The peaks at 72.93 and 76.28 eV correspond to the Pt\textsuperscript{δ+}4f\textsuperscript{7/2} and Pt\textsuperscript{δ+}4f\textsuperscript{5/2}, respectively, whereas the peaks at 75.04 and 78.51 eV can be attributed to Pt\textsuperscript{4+}4f\textsuperscript{7/2} and Pt\textsuperscript{4+}4f\textsuperscript{5/2}, correspondingly. In contrast, for the sample with classic Pt nanoparticle decoration, the Pt is in the metallic state with peaks at 71.07 eV and 74.35 eV corresponding to Pt\textsuperscript{0}4f\textsuperscript{7/2} and Pt\textsuperscript{0}4f\textsuperscript{5/2}, respectively. The XPS results therefore further confirm the atomic-scale deposition of Pt on the TiO\textsubscript{2} surface. In line with literature, when Pt is in the SA state, it is coordinated to its trap environment that is mainly oxygen atoms of the oxide surface, thus forming Pt-oxide-similar Pt\textsuperscript{δ+} and Pt\textsuperscript{4+} states.\cite{32,53,56–58} High-valent Pt (Pt\textsuperscript{4+}) is evidence of a strong Pt–TiO\textsubscript{2} interaction which arises from a covalent bonding interaction.\cite{32} Figures S7 and S8, Supporting Information show the comparison of high resolution XPS spectra of Pt4f for the samples annealed in Ar/H\textsubscript{2} at different temperatures and corresponding Pt concentrations detected from the different layers. The XPS results are well

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**Figure 1.** a) Schematic of the sputtered layer. b) top-surface SEM image and (inset) optical image of the TiO\textsubscript{2} layer deposited on SiO\textsubscript{2}-Si TEM grid; c) HAADF-TEM image and d) EDS map of Pt-SA-decorated TiO\textsubscript{2} layer; e) surface density of atomic Pt for different samples; f) schematic of Pt-SA-decorated TiO\textsubscript{2} for H\textsubscript{2} evolution application; g) HAADF-TEM images of samples treated in different annealing condition followed by immersion in the 120 μm hexachloroplatinic acid solution.
in line with the STEM images and confirm that the surface stabilized Pt concentration can be tuned by increasing the annealing temperature. Figure 2d compares the atomic concentration of Pt deposited on the TiO$_2$ layer with different annealing temperatures and a Pt-nanoparticle-decorated sample as a reference. The results show that by using the same Pt solution concentration for Pt deposition, an increasing reduction temperature (from 300 to 500 °C) leads to a higher amount of Pt deposited on the surface. Likewise, fixing the reduction temperature at 500 °C and increasing the Pt concentration in the solution leads to more Pt deposition but in the form of nanoparticles. Thus, for variation of annealing temperature from 300, 400, and 500 °C, followed by immersion in the 120 µm hexachloroplatinic acid solution at a fixed time, XPS results reveal that atomic-scale decoration of Pt on TiO$_2$ layers can be achieved yielding Pt concentrations of 0.14, 0.25, and 0.47 at%, respectively. By increasing the concentration of hexachloroplatinic acid, very fine nanoparticles form and the Pt concentration reaches 0.89 at% while the amount of Pt in the nanoparticle reference decorated sample (prepared by sputter-dewetting) is around 15 at%.
To show the effect of the presence of H$_2$ in the annealing environment, a series of samples was annealed in pure Ar atmosphere at temperatures of 300, 400, and 500 °C, followed by immersion in 120 μm hexachloroplatinic acid solution. XPS results for the Ar treated samples show much lower Pt concentrations (0.06, 0.09, and 0.14 at% of Pt for samples annealed at 300, 400, and 500 °C) in comparison with the Ar/H$_2$ treated samples (see Figure S9, Supporting Information). This difference is mainly due to formation of defects with different nature upon annealing in different environments[49]. Ar atmosphere leads to formation of Ti$_{3+}$ centers that have mainly the nature of regular lattice position defects[49].

Figure 2e,f show the EPR resonance signals recorded at $T = 123$ K on the TiO$_2$ powder samples (Ar/H$_2$-500) taken before (black spectra) and after (blue spectra) Pt decoration. Neither Pt$^{4+}$ (5d$^6$) nor Pt$^{2+}$ (5d$^8$) species are paramagnetic and thus cannot give an EPR resonance signal. The EPR spectra, before and after Pt cations entrapment, show the typical lattice embedded Ti$_{3+}$ resonance signals, with $g$ value of $\approx 1.99$, a broad resonance at $g$ value of $\approx 1.93$–1.95 associated to surface exposed Ti$_{3+}$centers, and signals that are addressable to hole sites (e.g., Ti$^{4+}$-O, Ti$^{4+}$-O-O$^\cdot$), falling in the $g$-value range of 2.030–2.009. Following incubation of Ar/H$_2$-500 with the H$_2$PtCl$_6$ solution, a significant drop in surface exposed signal at $g$ value of $\approx 1.93$–1.95 is observed. Additionally, the signals addressable to the successful entrapment of paramagnetic Pt$^{4+}$/Pt$^{3+}$ cations appear in the spectra (Figure 2f, blue spectra) with dominant resonance value at $g_{\text{avg}} \approx 2.15$ (see Supporting Information, EPR section) for Ar/H$_2$-500 120 μm Pt. No hyperfine components arising from metallic Pt is observed in either case. Similar $g$-values for trapped Pt$^+/Pt^{3+}$ species have been reported by Akdogan and co-authors for platinum cations being entrapped in the pores of NaX, NaY, and NaA zeolites[59]. These EPR findings are well in line with the HAADF-STEM and XPS results, which strongly suggest that the Ti$^{3+}$ surface centers appear to act in a way to generate preferential site-locations for the Pt deposition onto the TiO$_2$ surface. EPR spectra were re-measured at 80 K for the samples annealed at 300–500 °C before and after H$_2$PtCl$_6$ treatment and additional results and discussion are provided in the Supporting Information.

To determine the photocatalytic activity of the decorated samples, photocatalytic open circuit H$_2$ evolution was measured in water–methanol solution using a 325 nm, 50 mW laser. Figure 3a shows the H$_2$ evolution rate of the plain TiO$_2$ sputtered grid layers treated after different reduction treatments in Ar/H$_2$ environment. The results show that by increasing the temperature up to 500 °C, the H$_2$ evolution rate increased and by further increasing the temperature to 600 °C and 700 °C, the activity drops—this is well in line with previous work showing that Ti$^{3+}$ states can act as mediators for photocatalytic H$_2$ generation.[25,46,47] Figure S10, Supporting Information compares the H$_2$ evolution rates from differently Pt deposited layers (using a variation of temperatures of the reduction treatment and different concentrations of Pt). The results show that by increasing the reduction temperature the amount of evolved hydrogen increased, which can be due to a higher loading of

![Figure 3](image_url)

Figure 3. a) H$_2$ evolution of the TiO$_2$ layers treated in different temperatures, b) normalized H$_2$ evolution of Pt-SA-decorated samples, c) reusability test of H$_2$ evolution of TiO$_2$ layers, annealed at 500 °C in Ar/H$_2$ followed by immersion in 120 μm hexachloroplatinic acid solution for 30 s.
atomic Pt on the surface. Additionally, comparing the results of samples with different Pt concentrations, namely 500–120 µm and 500–1200 µm shows that the sample with atomic-scale decoration (500–120 µm solution) has higher H₂ evolution rate in comparison to the sample which has a higher amount of Pt on the surface (including some particles). To evaluate the effectiveness of the atomic-scale Pt decoration, we normalized the hydrogen evolution rate to the amount of Pt loading (Figure 3b). The normalized data indicates that as soon as SA status is reached, the samples with lower Pt loading present a drastically higher H₂ evolution rate, and a comparison with a reference sample decorated with conventional nanoparticles (Figure S6, Supporting Information) clearly shows the superior effectiveness of atomic-scale decoration on the photocatalytic activity. A comparison of the SAC samples in Figure S10, Supporting Information shows that TiO₂ layers annealed at 500 °C in Ar/H₂ and then immersed in a 120 µm hexachloroplatinic acid solution for 30 s immersion has an almost three times higher activity than the classic nanoparticle samples. To determine long-term behavior of the SA-decorated samples, we used a sample annealed at 500 °C in Ar/H₂ and then immersed it in the 120 µm hexachloroplatinic acid solution followed by a reusability test as shown in Figure 3c. The results indicate an 80% retention of the stability of the H₂ evolution rate over the entire test period of 144 h, which demonstrates an impressive stability of SA Pt sites on the TiO₂ surface. Additionally, to consider the cost of the experiments, the reusability of the H₂PtCl₆ solution was evaluated (see Figure S11, Supporting Information). The results show that the Pt precursor can be reused for several times.

Photocatalytic H₂ evolution was also measured for the samples treated in pure Ar, and the results are presented in Figure S9, Supporting Information. As it was expected from the XPS results, Ar annealed samples show a much lower H₂ generation rate in comparison with Ar/H₂ treated layers due to the lower Pt loading on the Ar treated samples.

In order to compare our substrate to previous work on TiO₂ (001), nanosheets prepared by hydrothermal synthesis as described in the SI were treated in an analogous experimental sequence. That is, after hydrothermal synthesis we annealed the samples at 200–500 °C in Ar/H₂ and decorated Pt atoms with the same immersion approach used for the thin sputtered layers—then we measured the photocatalytic H₂ reduction rate. Up to annealing at 200 °C in Ar/H₂, the sheets remain morphologically intact, as presented in SEM and TEM (see Figure 4a–d,f,g). However, by increasing the temperature to 350 °C, necking of the sheets starts, and at 500 °C the sheets are totally sintered which is in line with previous published work.[60] From the optical images shown in Figure 4e it is evident that although by increasing the temperature up to 500 °C, gray titania with high density of defects is formed, the overall H₂ evolution rate drops significantly. It is worth noting that TEM images show a higher density of SAs on the surface of the sample treated at 350 °C (see Figure 4f,g). Despite the higher density of SAs on the 350 °C treated sample, the H₂ evolution rate starts to decrease compared with RT and 200 °C treated sheets. Therefore, it is plausible that the deformation (necking and sintering) at higher temperatures is a most detrimental factor for H₂ evolution reaction of the SA-decorated nanosheets.

To investigate the possibility of applying this concept to commercially available TiO₂ powder, we followed the above heat treatments on anatase powder (Sigma Aldrich, particle size: 25–35 nm). Interestingly, a trend similar to the sputtered sheets is observed for the H₂ evolution from the commercial powder (see Figure S12, Supporting Information). This confirms that the studied concept on TiO₂ thin films can be applied to commercially available nanopowders and results in a highly efficient use of Pt.

In summary, we report on a tunable SA decoration strategy by combining surface defect engineering and decoration of Pt atoms. Key trap for the Pt is surface Ti³⁺–O₂⁻ with a characteristic g value of ≈1.93. These surface exposed Ti³⁺ defects can be formed in a highly controlled manner by reducing thin TiO₂ layers in an Ar/H₂ environment at different temperatures. Subsequently these atomic-scale defective sites were used to pin single Pt atoms from a dilute aqueous based Pt solution. HAADF-STEM results confirm the SA decoration of the TiO₂ surface with Pt. Considering the temperature of the heat treatment in Ar/H₂, the amount of Pt deposition can be varied from 0.03 to 0.47 at%. The XPS and EPR results confirm contribution of Ti³⁺ states in the deposition of Pt atoms. Remarkably, the specific H₂ evolution rate achieved for the SA-decorated sample is 150 times higher than the H₂ generation rate of TiO₂ layer decorated by classic Pt nanoparticles. We believe that the concept of controlled defect engineering on a functional oxide layer can be applied for a wide range of semiconductors and thus in the fabrication of defined SACs, which at a same time allow a defined observation with TEM tools.

**Experimental Section**

TiO₂ layers were prepared by using a SP-P-US-6M-32 Createch magnetron-sputtering device. A 5 inch magnetron equipped with titanium target was used. The films were deposited by a reactive sputtering procedure in a mixture 1:5 Ar to O₂ flow rate ratio on silicon dioxide support films; the samples were rotated at 20 rpm. To form layers the deposition power was set at 150 W and at the pressure of 0.5 mbar for 10 min to reach a thickness of 7 nm. To convert amorphous sputtered TiO₂ layers to anatase, all the as-sputtered layers were annealed at 450 °C in air. A 8 mm commercially available palco amorphous silicon dioxide support film from Ted Pella, Inc., USA was used as substrate.

Anatase nanosheets were synthesized by a hydrothermal method using commercially available reagents, tetrabutyl titanate (Ti(OBu)₄) and concentrated hydrofluoric acid (HF, 48%) from Sigma-Aldrich Merck. Both reagents were used as received without further purification. 1.2 mL HF was added dropwise to 10 mL Ti(OBu)₄ placed in a 250 mL Teflon liner, under stirring at RT. The stirring was continued for the next 40 min before the Teflon liner containing the mixture was sealed in an autoclave which was eventually transferred to a preheated oven at 200 °C. The reaction was completed after 24 h and the autoclave was allowed to cool in the oven. After HT reaction, the precipitates were collected and washed with distilled water and ethanol several times and finally dried in oven at 75 °C overnight.

SA decoration was carried out by annealing in Ar/H₂ 10% at different temperatures and the samples were then immediately immersed for different times in the deposition solution. The deposition bath was prepared with a concentration of H₂PtCl₆ in volume of 200 mL of 1:4 solution of DI water and 0.1 M NH₄NO₃. After reduction, the samples were directly, without any further treatments, immered in the platinate solution.
The reference nanoparticle-decorated sample was prepared by magnetron sputtering of Pt on the air annealed (at 450 °C) 7 nm TiO₂ surface according to previous published work. To keep a similar heat treatment condition the sample followed a 500 °C annealing in Ar/H₂ environment (See Figure S6, Supporting Information).

Vesta software was used to draw the Pt SA on TiO₂ surface scheme represented in Figure 1f. The layers were investigated using a field-emission scanning electron microscope (FE-SEM) Hitachi FE-SEM 4800. The chemical composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI).

Figure 4. a–d) SEM images and e) optical images of TiO₂ anatase nanosheets treated in different temperatures in Ar/H₂ environment; f,g) HAADF-STEM images of Pt-SA-decorated nanosheets treated at 250 °C (f) and 350 °C (g); h) H₂ evolution rate of Pt-SA-decorated nanosheets.
For the photocatalytic H₂ generation experiments the samples were immersed in a quartz tube containing 50 vol% methanol–water solution at 1000 rpm. A chromatograph (GCMS-QO2010SE, SHIMADZU) with a TCD detector was used to measure the amount of generated H₂. The normalized H₂ evolution was calculated by dividing H₂ evolution rate corresponding to atomic concentration of Pt on the TiO₂ surface.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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