Ti\textsuperscript{3+}-containing titania: Synthesis tactics and photocatalytic performance

Wibawa H. Saputra\textsuperscript{a}, Guido Mul\textsuperscript{a}, Mohamed S. Hamdy\textsuperscript{a,b,∗}

\textsuperscript{a} Photocatalytic Synthesis Group, Faculty of Science and Technology, MESA Institute of Nanotechnology, University of Twente, The Netherlands
\textsuperscript{b} Chemistry Department, Faculty of Science, Helwan University, Ain Helwan, 11719 Cairo, Egypt

A R T I C L E   I N F O

Article history:
Received 1 May 2014
Received in revised form 4 July 2014
Accepted 20 July 2014
Available online 29 August 2014

Keywords:
Ti\textsuperscript{3+}
Hydrogenation
TiO\textsubscript{2}
Photocatalysis
Stability
Pt photo-deposition

A B S T R A C T

Three different synthesis techniques were applied to prepare Ti\textsuperscript{3+}-containing TiO\textsubscript{2}. The first is a self-doped technique in which TiO\textsubscript{2} was reduced in situ at 500 °C by NO and CO gases to produce blue powder (blue titania). The second method is a calcination treatment of a physical mixture consisting of commercial TiO\textsubscript{2} Hombikat and Ti\textsubscript{3+}O\textsubscript{2} at 600 °C to produce a yellow powder (composite). The third technique is hydrogenation of different commercially available titania (Rutile, P25, and Hombikat) samples at elevated temperatures to produce yellowish white powders. The prepared samples were characterized by means of X-ray diffraction (XRD), nitrogen physisorption measurements, diffuse reflectance UV-Vis and Raman spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, and scanning electron microscopy (SEM). The photocatalytic activity of the prepared materials was tested in the decolourization reaction of methyl orange (MO) under the illumination of ‘black light’ (λ = 375 nm). The kinetic data of the photocatalytic reactions show that reduced titania samples exhibit higher photocatalytic activity than titania. Furthermore, the highest photocatalytic activity was obtained by hydrogenation of P25 at 500 °C. Moreover, the photo-deposition of platinum nanoparticles on the prepared materials enhanced the photocatalytic performance significantly. Titania samples which were firstly platinnized and then hydrogenated were much more active than samples which were hydrogenated first and then platinnized. The stability of the Ti\textsuperscript{3+} containing titania samples in aqueous conditions was found to be low, and needs to be improved to allow application in practice.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Heterogeneous photocatalysis constitutes one of the most important and promising technologies for removal of organic pollutants from water and air [1]. TiO\textsubscript{2} is by far the most frequently applied photocatalyst [2], and has been used as an active photocatalyst in several applications such as organic syntheses [3], hydrogen production [4], CO\textsubscript{2} reduction [5,6], air cleaning [7] and wastewater treatment in which organic compounds are totally converted into carbon dioxide [8–10]. The main drawback of TiO\textsubscript{2} is the wide band gap (3.2 eV), which limits its light response to the UV region [11]. Several attempts have been reported to shift the light absorption of TiO\textsubscript{2} towards the visible light region, such as doping with metal ions (Cr [12], V [13], Fe [14]), or N [15], or using dye sensitization techniques [16].

Reduced titania (TiO\textsubscript{2−x}, where 0 < x < 1) has attracted a lot of interest because it shows a visible light response [17]. Different methods have been reported to prepare the reduced titania crystals, such as plasma or laser treatment [18,19], thermal treatment under vacuum or helium [20,21], bombardment with high energy particles (e.g., neutrons, or γ-rays) [22], in situ reduction by reducing gases such as CO and/or NO [17], ozone treatment [23], using NaBH\textsubscript{4} as a reducing agent [24], or adding TiF\textsubscript{4} during the formation of TiO\textsubscript{2} nanoparticles [25].

Furthermore, thermal treatment of TiO\textsubscript{2} and Ti\textsubscript{3+}O\textsubscript{2} resulted in a composite showing a photocatalytic response much higher than that of the parent TiO\textsubscript{2} [26,27]. In addition, the hydrogenation of titania at elevated temperatures to create Ti\textsuperscript{3+}-sites was reported by Mao et al. [28]. After the report of Mao and co-workers, the hydrogenation of titania has attracted scientists to use this technique to produce reduced titania and study its performance in various photocatalytic applications [29–31].

In this study, three different techniques to prepare Ti\textsuperscript{3+}-containing titania samples are compared for effectiveness in creating photocatalytically attractive composites, i.e. hydrogenation of commercial titania (P25, Hombikat and Rutile), self-doping...
of titania, and preparation of a TiO$_2$/Ti$_2$O$_3$ composite. The photocatalytic performance of the prepared samples was compared in the decolorization of methyl orange as a model compound. The effect of Pt addition on the photocatalytic activity was also evaluated.

2. Experimental

2.1. Material synthesis

Three different techniques were applied to prepare Ti$^{3+}$ containing titania. The first technique is the self-doping technique [31], the second technique is calcination of a TiO$_2$/Ti$_2$O$_3$ composite [27], and the third technique the hydrogenation of different commercial titania samples. The synthesis and characterization of the self-doped materials and the composite TiO$_2$/Ti$_2$O$_3$ samples were reported recently [27,31]. In the following sections, the synthesis and characterization of hydrogenated samples will be discussed in detail.

2.1.1. Hydrogenation techniques

Hydrogenation of commercial TiO$_2$ samples was carried out in a tube furnace with H$_2$ flow at different temperatures. In a typical synthesis procedure, 1 g of Rutile TiO$_2$ (99.5%, Sigma-Aldrich), P25 (99.9%, Evonic), or Hombikat UV-100 (99.9%, Sachtleben Chemie) was placed on a small holder and inserted into a 1.2 m quartz tube with 10 cm internal diameter. The tube was placed in the tube furnace (Tamson Heraeus). Nitrogen gas was flowed for 30 min to remove air from the tube with a flow rate of 100 ml/min. Then, hydrogen gas was flowed into the quartz tube with a rate of 20 ml/min, and the oven was heated to different temperatures of 400, 500, 600 and 700 °C at 10 K/min, and maintained at these temperatures for 5 h. The samples obtained this way are labeled HR-x, HP-x and HH-x, where H refers to hydrogenated, and R, P, or H refers to Rutile, P25, or Hombikat, respectively, and x refers to the applied heating temperature (from 400 to 700 °C) during hydrogenation.

2.1.2. Photo-deposition of platinum

2 wt.% of platinum was deposited on the different titania samples by the photo-deposition technique. In a typical procedure, a suspension of 200 mg of titania in 23.7 ml of water was introduced into a top illumination reactor, followed by 26.3 ml of a H$_2$PtCl$_6$ solution (1 g/L), and 12 ml of methanol. The solution was then irradiated with UV light (Carl Zeiss, HBO 50W) for 24 h using an air flow of 20 ml/min. Finally, the residue was centrifuged, washed few times, and dried overnight at 100 °C.

The Hombikat sample was chosen to study whether the order of the reduction and Pt modification process, respectively, has an effect on the resulting photocatalytic performance of Hombikat. Two samples were prepared: in the first sample, Hombikat hydrogenated at 600 °C was platinized as mentioned above (Pt-HH-600), while in the second sample Hombikat was first platinized and then hydrogenated at 600 °C (H-Pt-H-600).

2.2. Characterization

The crystal structure of the samples was determined in air by X-ray diffraction using a Bruker D2 phase instrument. The samples were ground and sieved to obtain a fine powder of particle sizes <50 μm. Data were collected varying the angle of detector between 10° and 90°, with a step size of 0.005°.

Nitrogen physisorption measurements were carried out at 77 K using a Micromeritics Tristar system (ASAP 2400) to determine the textural properties. Prior to the adsorption measurements, the samples were degassed at 573 K and 10$^{-3}$ Pa for 24 h. The specific surface areas were calculated according to the Brunauer–Emmet–Teller (BET) method.

Diffuse reflectance UV–Vis spectra were collected at ambient temperature on an EVOLUTION 600 (ThermoScientific) spectrometer, using BaSO$_4$ as reference. Spectra were recorded in the wavelength range of 200–800 nm.

Raman spectra were recorded using a Bruker Senterra Raman Spectrometer equipped with a N$_2$ cooled CCD detector (213 K). A green 532 nm laser with an intensity of 2 mW was used for excitation. Spectra were acquired at a resolution of 9 cm$^{-1}$, and 10 scans were accumulated to generate each spectrum.

The presence of Ti$^{3+}$ in various composites was also evaluated using EPR spectroscopy, using a Bruker Elecsys 680 instrument. The EPR measurement was conducted at 9.73 GHz (X-band). The microwave power was set at 2.526 mW, the modulation amplitude at 5 G, and the temperature of measurement at 80 K.

The morphologies of the samples were investigated by scanning electron microscopy (SEM), using a HR-SEM-LEO 1550 equipped with NORAN EDS and WDS capabilities.

2.3. Catalytic activity

The photocatalytic activity of the prepared materials was tested in the decolorization reaction of methyl orange (MO). The applied photo-reactor was described earlier in detail [33]. In a typical reaction, 50 mg of the catalyst was introduced into a beaker containing 50 ml of MO solution (20 mg/L). The suspension was ultra-sonicated for approximately 10 min and then placed into the reactor. The pH of the solution was measured to be 5.4. The solution was stirred for 30 min in the dark at room temperature to allow for complete adsorption. Once this time had elapsed, a sample of the solution was taken, and the remaining reaction solution irradiated with UV light. Additional samples were taken every 20 min, filtered through a 0.2-mm PTFE Millipore membrane filter to remove suspended catalyst agglomerates, and finally analyzed using a UV–Vis spectrometer (EVOLUTION 600, Thermo Scientific) in the range between 250 and 600 nm to determine the concentration of the dye. The reaction rate constant ($k_R$) was then determined assuming quasi first order kinetics using the following equation:

$$\ln \left( \frac{C_0}{C} \right) = k_R t$$

where $C_0$ is the concentration of the dye in solution after adsorption, $C$ is the concentration at time $t$, and $k_R$ is the reaction rate constant. All reactions were repeated at least two times with fresh catalyst. The standard deviation was estimated to be ±5%. Catalyst stability was evaluated as follows: a catalyst composite was filtered after use, washed several times with distilled water, and finally dried at 100 °C for 24 h in static air. Re-suspension in fresh dye solution was followed by the steps indicate above for the fresh catalyst samples. Catalysts were used up to as much as three times.

An additional experiment was carried out to study the complete mineralization of MO, in which, 50 mg of catalyst was added to 50 ml of methyl orange solution of 0.02 g/L. The suspension was sonicated for approximately 20 min. Then, the suspension was injected into a spiral reactor fitted with a UV black light tube (18 W, 365 nm), peristaltic pump and modular controller. The conductivity of CO$_2$ was measured by using a conductivity probe 3540pH, and conductivity meter supplied by JENWAY.

3. Results and discussion

3.1. The morphology of the hydrogenated titania samples

From previous studies, the morphology of the parent titania samples can be summarized as follows: (a) Hombikat is a semi-crystalline mesoporous titania, consists of the anatase phase, and
possesses a high surface area (S_{BET} > 250 m^2/g), (b) Rutile is a highly crystalline pure rutile phase titania with a small surface area (S_{BET} < 5 m^2/g), and (c) P25 is a crystalline titania with mixed phases, almost 70% anatase and 30% rutile, with a surface area of 52 m^2/g.

Upon hydrogenation, the physical and chemical properties of the titania samples had changed. The color of the hydrogenated samples at different temperatures is demonstrated in Fig. 1. The color of hydrogenated Hombikat and Rutile changed from white to pale yellow, dark yellow, yellowish gray and finally gray to gray for the samples hydrogenated at 400, 500, 600, and 700 °C, respectively. The color of the P25 sample was slightly changed to pale yellow for the sample hydrogenated at 400 °C and then off-white for the other hydrogenated samples at elevated temperatures. The change in the color of hydrogenated titania was also observed by other researchers [34,35] and it has been reported that the main reason is the creation of oxygen vacancies in the lattice associated with the presence of Ti^{3+} atoms.

The changes in the degree of crystallization, and phase composition were investigated by XRD. In Fig. 2, the XRD patterns of hydrogenated P25 and Hombikat samples are compared to the patterns of commercial P25 and Hombikat, respectively. The XRD patterns of hydrogenated Rutile samples did not show significant morphology changes. However, hydrogenated P25 samples exhibited a phase transformation at temperatures above 700 °C. The intensity of the peak of the Rutile phase (at 2θ 25°) was developing as a function of increasing thermal treatment temperature. The Rutile peak becomes dominant with finally a total disappearance of the anatase peak (at 2θ 25°) at 700 °C. Hydrogenated Hombikat samples became more crystalline, however, phase transformation from anatase to rutile was not observed for this titania sample. The observed phase transformations of P25 and Hombikat are in a good agreement with the work of Rao [36] and Roy et al. [37]. Hence, the hydrogenation step – most likely – does not influence the phase transformation of TiO_2, and the main parameters of phase transformations are temperature, titania synthesis method, and initial phase composition [38].

The phase transformation of hydrogenated P25 and hydrogenated Hombikat was confirmed by Raman spectroscopy at ambient conditions (Fig. 3). P25 showed the three bands associated with the presence of the anatase phase at 635, 512, and 395 cm\(^{-1}\), and in addition a small band around 439 cm\(^{-1}\) associated with the presence of the rutile phase. Upon heating and hydrogenation, the crystalline phase was stable up to 600 °C. However, at 700 °C, the anatase phase was disappearing and only the bands of the rutile phase (610 and 439 cm\(^{-1}\)) can be observed, consistent with the XRD data. For the hydrogenated Hombikat samples, neither the positions nor the intensities of the bands were changed, indicating that hydrogenated Hombikat samples consist only of the crystalline anatase phase.

The morphological structure of the hydrogenated samples vs. the non-hydrogenated commercial parent titania was investigated by SEM (Fig. 4). Hombikat seems to show a morphology of low crystallinity, which turns after hydrogenation into a dense crystalline phase. However, the P25 sample did not seem to change dramatically after hydrogenation (sample HP-600). Neither the degree of agglomeration nor the crystallization showed significant alteration. Results are consistent with XRD and Raman spectroscopy.

The optical absorption of the hydrogenated samples was investigated by UV–Vis spectroscopy. In Fig. 5, the Kubelka–Munk function of the hydrogenated samples is compared with the parent titania samples. The absorption spectra of hydrogenated P25 (left panel) showed slight enhancement in the visible light region, as compared to the parent P25. Moreover, the HP-700 sample exhibited a significant shift towards the visible light region, probably because of the phase transformation from anatase to rutile. Moreover, in the hydrogenated Hombikat samples, the visible light absorption (λ larger than 400 nm) is enhanced as a function of the treatment temperature. HH-600 exhibited the biggest shift towards the
Fig. 3. Raman spectra of the hydrogenated P25 (left panel) and of hydrogenated Hombikat (right panel).

Fig. 4. SEM micrographs of the Hombikat sample (upper left) compared to hydrogenated Hombikat HH-600 (upper right). The morphology of P25 (bottom left) is compared to the hydrogenated P25 HP-600 sample (bottom right).

Fig. 5. UV–Vis diffuse reflectance spectra of the hydrogenated P25 samples compared to the parent samples (left panel), and hydrogenated Hombikat samples compared to the parent samples (right panel).
visible light region (from λ = 400 nm to 700 nm), in agreement with the increasing Ti$^{3+}$ concentration in the samples. Similar behavior was reported by Xu et al. [39] and Li et al. [40].

EPR spectra were recorded to identify the presence of interstitial Ti$^{3+}$ or formation of oxygen vacancies in the hydrogenated samples, which are difficult to distinguish. The EPR spectrum of calcined P25 at 500 °C without hydrogen treatment (P-500) is compared to two hydrogenated P25 samples at 500 °C and at 700 °C in Fig. 6. The spectrum of P-500 did not show the presence of paramagnetic Ti$^{3+}$ centers at g = 1.974 Gauss [41,42]. The spectra of the hydrogenated samples show the paramagnetic Ti$^{3+}$ centers, which increase in quantity as a function of increasing temperature from 500 to 700 °C.

Based on the above indicated characterization results, it is clear that hydrogenation at high temperature generates oxygen vacancies ($V_0$-Ti$^{3+}$) in the framework of titania, independent of the starting phase, i.e., rutile, anatase or a mixture of them, or its texture properties i.e. surface area and type of porosity. The main properties of the samples used in the current study are summarized in Table 1.

3.2. Photocatalytic performance in methyl orange (MO) decomposition

3.2.1. The performance of hydrogenated samples

The photocatalytic performance of commercial titania samples, i.e. P25, Hombikat and Rutile was in agreement with previously reported data [43,44]. P25 outperformed the other commercially available titania catalysts, and exhibited the highest decolourization rate under 375 nm illumination. The explanation of the higher performance of P25 was reported earlier by Gray et al. [45], in which the co-existence of the two phases, Rutile and Anatase, plays an important role (antenna theory). Hydrogenating the commercial titania samples was found to dramatically enhance their photocatalytic performance. The performance of hydrogenated Rutile was 5–7 times higher than that of the parent Rutile. Furthermore, there is no apparent optimum temperature for the hydrogenation process, i.e. the sample hydrogenated at 400 °C exhibited almost the same performance as the sample hydrogenated at 600 °C. On the contrary, the performance of hydrogenated Hombikat was increasing as a function of the hydrogenation temperature: HH-600 exhibited 3 times higher activity than Hombikat. The performance of P25 was also greatly influenced by hydrogenation process. The performance of hydrogenated P25 was increasing gradually to reach a maximum for the sample hydrogenated at 500 °C, i.e. HP-500, and then the activity decreased again. The photocatalytic performance of the HP-500 sample was 5 times higher than that of the parent P25, and shows the highest activity of all the samples applied in the study. The activity decrease for the samples hydrogenated at T> 500 °C is most likely caused by the extensive phase transformation from Anatase to Rutile. The 1st order rate constants of the hydrogenated samples are presented in Fig. 7.

The hydrogenation of titania at elevated temperatures was reported to improve the photocatalytic performance of titania through creation of new energy levels (Ti$^{3+}$) in the band gap of titania, associated with oxygen vacancies [28]. It is important to note that the catalysts in the present study were photo-excited by 375 nm radiation, and that these vacancies are likely not necessary to create the photo-excited state. On the contrary, usually bulk defects (oxygen vacancies) act as recombination centers of electrons and holes, reducing photocatalytic activity. However, we have previously discussed that reduction might predominantly result in catalytically active surface vacancies, which are responsible for a high oxygen reduction activity. In other words, the catalytic properties of the surface defects are more relevant than the modified optical properties of the obtained TiO$_2$. The major role of the surface is also in agreement with the rapid deactivation of the catalysts, to be further discussed in Section 3.2.5, likely caused by oxidation of the defects during the photocatalytic process. Oxidation of bulk vacancies under the mild conditions of photocatalysis appears much more difficult and less likely.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis method</th>
<th>Phase</th>
<th>Morphology</th>
<th>Surface area S BET (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue TiO$_2$</td>
<td>In situ hydrothermal reduction by NO and CO</td>
<td>Anatase + Rutile</td>
<td>Amorphous mesoporous</td>
<td>96</td>
</tr>
<tr>
<td>M-600</td>
<td>Hydrothermal treatment of TiO$_2$/Ti$_2$O$_3$ mixture</td>
<td>Anatase + Rutile</td>
<td>Crystalline microporous</td>
<td>54</td>
</tr>
<tr>
<td>HH-400–HH-600</td>
<td>Hydrogenation of commercial Hombikat at T=400–600 °C</td>
<td>Anatase</td>
<td>Crystalline microporous</td>
<td>156–45</td>
</tr>
<tr>
<td>HP-400–HP-600</td>
<td>Hydrogenation of commercial P25 at T=400–600 °C</td>
<td>Anatase + Rutile</td>
<td>Crystalline microporous</td>
<td>52–22</td>
</tr>
<tr>
<td>HR-400–HR-600</td>
<td>Hydrogenation of commercial Rutile at T=400–600 °C</td>
<td>Rutile</td>
<td>Crystalline microporous</td>
<td>n.a.</td>
</tr>
</tbody>
</table>
3.2.2. Comparison between the different synthesis techniques

In order to confirm that the higher activity obtained for the hydrogenated samples is due to the presence of surface oxygen vacancies, the synthesis process reported in the experimental section was repeated with the same three commercial samples in the absence of H₂ gas. The comparison of oxidized and reduced samples presented in Fig. 8 shows that hydrogenated Hombikat and hydrogenated P25 are more active than the oxidized samples, and moreover more active than the Ti³⁺-containing titania samples prepared by other techniques, i.e. the blue titania and the composite (M-600).

3.2.3. Effect of Pt addition

In our previous study [27], when Pt nanoparticles were photodeposited on the TiO₂/TiO₂O composite, a significant enhancement in the photocatalytic activity was observed. The activity of reduced and oxidized Hombikat in the absence and presence of Pt nanoparticles is presented in Fig. 9.

The kinetic data show a great activity difference resulting from the order in which Pt was added to reduced Hombikat. The H-Pt-H-600 sample (reduction after Pt deposition) was 3–4 times more active than the HH-600-Pt sample (reduction prior to Pt deposition). To explain this difference, we assume that the oxygen vacancies introduced by the hydrogen treatment are restored upon the Pt photodeposition treatment in aqueous conditions. Contrary, in the sample H-Pt-H-600, in which hydrogenation is applied after Pt deposition, the amount of Ti³⁺ present after catalyst synthesis is higher, consistent with the higher photocatalytic activity. In addition, Pt is known to be a good hydrogen activation catalyst, which might further contribute to the large concentration of oxygen vacancies obtained after the reduction at elevated temperatures. The recovery of oxygen vacancies upon illumination in aqueous conditions was proposed first by Anpo et al. [46,47], and confirmed later by studies in our group [32].

3.2.4. Complete mineralization vs. decolorization

To ensure that the catalytic behavior of the hydrogenated samples follows the same activity trend in the total mineralization as well as in the decolorization of MO, the CO₂ concentration was measured by the conductivity method [48,49]. Three catalysts were chosen for this experiment: H-Com, HH-600, and H-Pt-H-600. The amount of CO₂ produced and the rate of mineralization are presented in Fig. 10. It is clear that the photocatalytic activity of commercial Hombikat (H-com) is improved by hydrogenation (HH-600), and improved further by Pt addition (H-Pt-H-600), which confirms the photocatalytic trend as derived from the decolorization experiments.

3.2.5. Stability of the Ti³⁺-containing samples

Obviously, the stability of Ti³⁺-containing titania is a matter of concern. The photocatalytic activity of the samples was decreasing sharply after the first run (Fig. 11), with the exception of the Pt-M-600 sample, where deactivation was less pronounced. In general, the oxidation of surface oxygen vacancies is the main reason of Ti³⁺-containing titania samples to deactivate [46,47]. It should be mentioned that since we operate in batch conditions, the deactivation might (negatively) affect the calculated rate constants, and contributes to the apparent first order behavior. More detailed studies in a continuous reactor are needed to quantify the rate of
deactivation and evaluate the effect on the rate constants, as well as allowing evaluation of methods to stabilize surface Ti$^{3+}$-sites. Table 2 summarizes the performance of the Ti$^{3+}$-containing titania samples investigated in the present study.

As a final remark, after investigating the photocatalytic performance of several Ti$^{3+}$-containing titania samples in different applications such as selective oxidation of methylcyclohexane [32], and decolorization of MO [27], and CO$_2$ reduction (in progress), we noticed that the photocatalytic performance increases dramatically if oxygen vacancies are associated with TiO$_2$ consisting of two phases; rutile and anatase, independent of the synthesis technique. However, further research is necessary to explain this observation.

### 4. Conclusions

The hydrogenation of commercial titania (P25, Hombikat and Rutile) under different temperatures (400–700 °C) in a stream of H$_2$ gas was carried out successfully in a tube furnace. The hydrogenated samples exhibit higher photocatalytic activity in the MO decolorization reaction under black light illumination than the parent samples. The hydrogenated P25 at 500 °C exhibited the highest photocatalytic performance of the Ti$^{3+}$-containing titania samples. The photo-deposition of Pt nanoparticles improved the photocatalytic performance of hydrogenated Hombikat. The stability of Ti$^{3+}$-containing titania was low, likely because of the restoration of oxygen vacancies in the titania lattice.

### Acknowledgements

W.H. Saputra thanks the University of Twente Scholarship (UTS) program and the Indonesian Ministry of National Education for his personal fellowship. The authors thank Prof. Dr. E.J. Groenen and Mrs. F. Nami (Leiden University, The Netherlands) for performing EPR measurements.

### References