Particle Networks from Powder Mixtures: Generation of TiO$_2$–SnO$_2$ Heterojunctions via Surface Charge-Induced Heteroaggregation

Nicolas Siedl, Stefan O. Baumann, Michael J. Elser, and Oliver Diwald*

Institute of Particle Technology, Friedrich-Alexander University Erlangen-Nuremberg, Cauerstraße 4, 91058 Erlangen, Germany

ABSTRACT: We explored the impact of interfacial property changes on aggregation behavior and photoinduced charge separation in mixed metal oxide nanoparticle ensembles. TiO$_2$ and SnO$_2$ nanoparticles were synthesized by metal organic chemical vapor synthesis and subsequently transformed into aqueous colloidal dispersions using formic acid for adjustment of the particles’ surface charge. Surface charge-induced heteroaggregation was found to yield blended nanoparticle systems of exceptionally high mixing quality and, after vacuum annealing, to extremely high concentrations of heterojunctions between TiO$_2$ and SnO$_2$ nanoparticles with dehydroxylated surfaces. For tracking charge transfer processes across heterojunctions, the photogeneration of trapped charge carriers was measured with electron paramagnetic resonance (EPR) spectroscopy. On blended nanoparticles systems with high concentrations of SnO$_2$–TiO$_2$ heterojunctions, we observed an enhanced cross section for interparticular charge separation. This results from an effective interfacial charge transfer across the interfaces and gives rise to substantially increased concentrations of electrons and hole centers. The here presented insights are key to the rational design of particle-based heterojunctions and mesoporous nanoparticle networks and help to engineer composite nanomaterials for photocatalysis and solar energy conversion.

INTRODUCTION

An efficient photocatalyst minimizes recombination of photoexcited electron–hole pairs and maximizes electron and hole transfer to the adsorbate upon consecutive surface reactions. In general, the photocatalytic activity of an given particle system depends on multiple factors. For a reliable photoactivity assessment, relative contributions from the particles’ bulk and interfaces have to be sorted out, and their impact to the overall performance requires a careful evaluation. A major limitation of any photocatalytic process originates from charge carrier recombination. Efforts have been made to identify and eliminate the responsible defects. An important approach to counteract charge carrier recombination in photocatalytic particle systems is based on the coupling of different semiconductor components with desirable matching of their electronic band structures.

In the case of composite nanoparticle systems, synergistic properties and those that are enhanced with respect to the individual components can only emerge if the particles are mixed intimately enough. For that reason, researchers have explored efficient and cost-effective methods for combining different metal oxide nanoparticles. Chemical ways could offer great control in this respect. While a variety of experimental approaches leading to the coupling of two semiconductors have been successfully employed for particles that were grown in colloidal solutions, there are very few reports about the charge separation properties of dry particle systems that feature corresponding types of interfaces. With this study we present a simple as well as versatile approach that involves surface charging of multiple particle systems inside the same aqueous dispersion medium to achieve blended nanoparticle systems of superior mixing quality and, thus, a maximum concentration of functional interfaces between different particle types.

We have shown in previous work that water-mediated aggregation of TiO$_2$ and ZrO$_2$ nanoparticles and subsequent dehydration procedures under high vacuum conditions are effective in the generation of solid–solid interfaces. The mechanistic steps of the underlying material transformation process are as follows (Figure 1): in aqueous dispersion, mutual attraction and agglomeration of metal oxide nanoparticles takes place. Upon vacuum treatment dehydration/dehydroxylation processes (evaporation of liquid phase) in conjunction with particle condensation lead to the formation of chemical interparticle metal oxygen bonds. Annealing-induced aggregation of particles during thermal treatment results in interconnected particles but, according to N$_2$ sorption measurements, does not reduce the specific surface area in comparison to the unprocessed nanoparticle powders.

For the exploration of surface charge-induced heteroaggregation, we chose the TiO$_2$–SnO$_2$ system. Both materials are...
central to photocatalysis, solar water splitting, and dye sensitized solar cells. As a result of composite formation upon generation of heterointerfaces, light-induced charge separation and vectorial charge transfer (Figure 2) were found to be facilitated in composites.\textsuperscript{19} The conduction band position of SnO\textsubscript{2} is lower than that of TiO\textsubscript{2} and such that it is incapable of reducing oxygen molecules to form superoxide anions. The band offsets between TiO\textsubscript{2} and SnO\textsubscript{2} will promote charge separation across the interfaces. Using electron paramagnetic resonance (EPR) spectroscopy, we address the vectorial transfer of separated charges to generate paramagnetic \( \text{O}^- \) radicals as well as paramagnetic Ti\textsuperscript{3+} sites. Another reason for selecting this system has been the exclusion of Sn–Ti–O compound formation. For SnO\textsubscript{2}–TiO\textsubscript{2} core–shell nanostructures, it was found that the phase boundary between the two oxides remains abrupt up to \( T = 1200 \text{ K} \) without substantial chemical transformations in this region.\textsuperscript{20} Thus, heteroaggregated SnO\textsubscript{2}–TiO\textsubscript{2} nanoparticle networks represent an ideal model system to explore the potential of surface charge-induced heteroaggregation with regard to the generation of heterojunctions that enhance the separation of photogenerated charges.

**EXPERIMENTAL SECTION**

**Synthesis.** TiO\textsubscript{2} and SnO\textsubscript{2} nanoparticles were prepared by metal organic chemical vapor synthesis (MO-CVS) based on the decomposition of either titanium(IV) isopropanoxide (Aldrich, 99.999\% trace metals basis) or tetra-n-butyltin (Aldrich, technical grade, > 93\%) vapor at \( T = 1073 \text{ K} \) in a flow reactor system. The details of this technique are given elsewhere.\textsuperscript{21} For purification, the obtained powder samples were subjected to thermal treatment under high vacuum conditions. First, the powder sample was heated to \( T = 870 \text{ K} \) using a rate of \( r \leq 5 \text{ K min}^{-1} \). Subsequent oxidation with O\textsubscript{2} at this temperature followed by cooling in O\textsubscript{2} atmosphere was successfully applied to remove organic remnants originating from the precursor material, on the one hand, and to guarantee the stoichiometric composition of the oxide on the other. The average particle size determined by transmission electron microscopy (TEM) and nitrogen sorption was 13 nm for TiO\textsubscript{2} and 10 nm for SnO\textsubscript{2} nanoparticles. For the preparation of mixed ensembles of TiO\textsubscript{2} and SnO\textsubscript{2} nanoparticles, 250 mg of the powder samples were dispersed in 100 mL of \( c = 10^{-6} \text{ mol·L}^{-1} \) formic acid solution for 30 min under ultrasonication (Hielscher Sonifier 200S) and simultaneous agitation by a magnetic stirrer. Cooling with an ice–water mixture was applied to avoid unwanted sample heating. Centrifugation and subsequent drying in vacuum at room temperature resulted in the formation of monolithic pieces, which were transferred to a quartz glass cell and annealed to \( T = 873 \text{ K} \) at \( p < 10^{-5} \text{ mbar} \) prior to spectroscopic...
investigations. Prior to liquid exposure TiO$_2$–SnO$_2$ nanoparticles were mixed in the desired 1:1 particle ratio.

**Characterization.** Zeta potentials and agglomerate size distributions of suspensions of 2.5 g oxide nanoparticles–L$^{-1}$ formic acid solution were derived from dynamic light scattering measurements on a Malvern ZetaSizer Nano ZS. Nitrogen sorption isotherms were obtained at $T = 77$ K using nitrogen adsorption/desorption (Quantachrome NOVA 4000c). Samples were degassed for 2 h in the degas unit of the adsorption apparatus at $T = 473$ K under vacuum prior to analysis. The BET surface area $S_{\text{BET}}$ was evaluated using adsorption data in a relative pressure range $p/p_0$ from 0.05 to 0.2. The pore size distribution was calculated by applying the Barrett–Joyner–Halenda (BJH) model using the desorption branch of the isotherm.

Scanning electron microscopy (SEM) measurements were performed on a Zeiss Gemini Ultra SS microscope operating at 20 kV equipped with an energy dispersive X-ray emission (EDX) detector. To characterize the mixing quality inside the nanoparticle networks we used EDX to track compositional homogeneity changes in the range of a few hundreds of nanometers. The local resolution of chemical information for EDX analysis is limited to the penetration depth and scattering of the primary electrons and therefore to the volume where characteristic X-rays are emitted of the sample. With acceleration voltages of 20 kV, the sampled volume in EDX studies is on the order of a few cubic micrometers for bulk TiO$_2$ or SnO$_2$ samples. Consequently, the determination of absolute Ti and Sn concentrations via EDX at the nanometer scale is not feasible. Nevertheless, by scanning the aggregate with a linescan, the change in the ratio between Ti and Sn can be tracked with a very high spatial resolution of approximately 100 nm.

For EPR measurements, the powder sample was contained within a Suprasil quartz glass tube connected to an appropriate high vacuum pumping system with a base pressure $p = 10^{-6}$ mbar. This allows for thermal sample activation and UV irradiation in situ. A 300 W Xe lamp (Oriel) was used as UV source. The light beam was passed through a water filter to exclude IR contributions from the excitation spectrum. Light power was measured with a bolometer (International Light). It was held constant at $P_{\text{in}} = 0.9$ mW·cm$^{-2}$ for the energy range $3.2$ eV $< E < 6.2$ eV throughout all experiments. During UV exposure, the samples were held at a temperature between $T = 90$ K and $T = 140$ K in order to keep UV-induced heating effects constant. X-band EPR measurements were performed on a Bruker EMX Micro spectrometer using a Bruker ER 4119 HS resonator. For measurements in the temperature range between $T = 90$ K and $T = 140$ K, an ER 4131 VT variable-temperature accessory was used. EPR computer simulations were done using the SIM 14S program. The $g$ values were determined on the basis of a DPPH standard.

**RESULTS AND DISCUSSION**

The procedure of particle aggregation as outlined by Figure 1 aims at the conversion of aerosol metal oxide nanoparticle powders, of high purity and well characterized particle surface properties, into binary metal oxide nanoparticle networks of high mixing quality and therefore with high concentrations of solid–solid heterointerfaces (Figure 1b). Prior to the process, aggregation between particles must be avoided in the starting mixture in order to achieve nanoparticle networks of different and perfectly intermixed metal oxides. Dynamic light scattering experiments on dispersions of vapor phase-grown TiO$_2$ nanoparticles with an average particle size of 13 nm as determined by TEM clearly demonstrate that metal oxide nanoparticles that were grown by MO-CVS can be efficiently deagglomerated by ultrasonic treatment in aqueous dispersion (Figure 3). As a consequence of ultrasonification, the agglomerate size distribution maximum shifts from 100 nm (Figure 3a) to 20 nm (Figure 3b). After discontinuation of ultrasonic treatment, particles reagglomerate, and the agglomerate size distribution maximum shifts to approximately 40 nm (c).

Zeta potential measurements reveal that both oxides carry a negative surface charge in neutral aqueous dispersion (Figure 4). As a result of particle aggregation, TiO$_2$ and SnO$_2$ form a nonuniform network which has a significant fraction of TiO$_2$–SnO$_2$ and SnO$_2$–SnO$_2$ interfaces. Self-assembly of oppositely charged particles in colloidal dispersion and, in consequence, the generation of desired TiO$_2$–SnO$_2$ heterointerfaces is achievable via control of the surface
charge. In comparison to inorganic acids, which potentially contaminate the particle surface with ions such as Cl\textsuperscript{{-}}, carboxylic acids are eligible candidates for surface charge adjustment since they can be efficiently eliminated from the particle network via oxidation at elevated temperatures. The zeta potential dependence of TiO\textsubscript{2} and SnO\textsubscript{2} nanoparticles on the formic acid concentration (Figure 4) prompted us to choose a formic acid concentration of \(\varepsilon = 10^{-6}\) mol-L\textsuperscript{{-1}} (indicated by gray arrow) where the zeta potential of TiO\textsubscript{2} and SnO\textsubscript{2} particles is +24 mV and −9 mV, respectively.

Surface charge adjustment for dispersed particles in combination with control over the pH in solution shows a complex functional dependence on the formic acid concentration. This is due to the formate adsorption equilibria at the metal oxide particle surfaces which, in turn, are subject to particle concentration in the dispersion and on the concentration of the acid and, concomitantly, on the pH.\textsuperscript{32,33} (For further details please see Supporting Information, Figure S1.)

Dehydration and dehydroxylation as well as oxygen treatment of the obtained particle networks at elevated temperatures were applied in order to eliminate organic surface groups that previously lead to surface charging and heteroaggregation.\textsuperscript{24,29} X-ray diffraction, TEM, and N\textsubscript{2} sorption measurements were carried out to identity potential process-induced structural changes that may result from hydration- and annealing procedures. All methods unambiguously reveal that primary particle properties size, structure, and morphology have been retained (Supporting Information, Figure S2).

Changes in the adsorption desorption hysteresis of nitrogen sorption experiments (left panel of Figure 5) clearly demonstrate that loose nanoparticles transform into a mesoporous network,\textsuperscript{17} which are made up from interconnected particles and show a distinct pore size distribution (right panel of Figure 5b).

We employed SEM to characterize the composition and mixing quality inside the nanoparticle networks and used EDX to track compositional homogeneity changes in the range of few hundreds of nanometers.\textsuperscript{28} A typical EDX line scan on nanoparticle networks obtained from surface charge-induced heteroaggregation in aqueous formic acid solution (\(\varepsilon = 10^{-6}\) mol-L\textsuperscript{{-1}}) is shown in Figure 6a and reveals that the ratio of the two elements should remain constant across the scanned distance (gray line). The mixing quality and thus the concentration of SnO\textsubscript{2}−TiO\textsubscript{2} heterojunctions is expected to be significantly higher than in the water processed networks.

The here presented procedure provides a very good measure of the local mixing quality within the nanoparticle networks. To obtain statistical meaningful information throughout different nanoparticle network samples, we evaluated the deviation of the desired ratio of Ti/Sn for approximately 600 sample spots (Figure 7). Deviations of 0% indicate that the chosen value of one TiO\textsubscript{2} particle per SnO\textsubscript{2} particle has been achieved. It can be shown that the nanoparticle network that originates from processing in pure water displays a very broad distribution of Ti/Sn deviation, while the network which was prepared in aqueous formic acid exhibits excellent mixing quality, i.e., relatively small deviations from desired Ti/Sn ratio.

A good mixing quality of SnO\textsubscript{2} and TiO\textsubscript{2} nanoparticle mixtures represents a necessary requirement for a high concentration of heterojunctions inside the result particle network. To verify that these solid–solid interfaces are truly suitable for interfacial charge transfer, we spectroscopically probed the photoelectronic materials’ properties. For this purpose we utilized EPR to track the photogeneration of surface trapped hole centers O\textsuperscript{{h-}}\textsuperscript{+}, unpaired electrons in shallow trap states Ti\textsuperscript{{3+}} and adsorbed O\textsuperscript{{2-}} ions (Supporting Information).\textsuperscript{27} As demonstrated by previous studies this technique provides site specific information about charge trapping sites.\textsuperscript{35–38} Band gap and conduction band edge energies determine the pathway of electrons or holes from one oxide to the other (Figure 2). The relative positions of the conduction band minima favor electron transfer from TiO\textsubscript{2} to SnO\textsubscript{2}. On the other hand, the valence band positions of the two oxides are such that photogenerated hole centers become accumulated on TiO\textsubscript{2} nanoparticles.

In Figure 8a, a simulated EPR spectrum of O\textsuperscript{{h-}}\textsuperscript{+} and Ti\textsuperscript{{3+}} centers is shown in comparison to an experimental spectrum (b), which was acquired on dehydroxylated TiO\textsubscript{2} nanoparticles after 30 min of UV/Vis exposure under high vacuum conditions. The separation of photoexcited states (eq 1) is followed by persistent trapping of electrons and holes upon formation of Ti\textsuperscript{{3+}} and O\textsuperscript{{2-}} centers, respectively (eqs 2 and 3).

\[
\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow e^-_{\text{CB}} + h^+_{\text{VB}} \\
\text{e}^-_{\text{CB}} + \text{Ti}^{3+} & \rightarrow \text{Ti}^{4+} \text{trapped electron} \\
\text{h}^+_{\text{VB}} + \text{O}^{2-} & \rightarrow \text{O}^{-} \text{trapped hole}
\end{align*}
\]

The corresponding EPR spectrum of SnO\textsubscript{2} nanoparticles shows no significant signals after irradiation and is therefore not presented here.

After irradiation of a nanoparticle network of low mixing quality, the corresponding EPR spectrum reveals the presence of O\textsuperscript{{2-}} and Ti\textsuperscript{{3+}} stabilized on TiO\textsubscript{2} nanoparticles (Figure 8c). However, the network prepared from surface charge induced heteroaggregation in aqueous formic acid solution shows a strong signal for O\textsuperscript{{2-}} stabilized on TiO\textsubscript{2} nanoparticles but no Ti\textsuperscript{{3+}} centers (Figure 8d). Their absence points to an efficient interfacial electron transfer from TiO\textsubscript{2} particles to SnO\textsubscript{2} particles (Figure 2) upon formation of EPR silent states. For corroboration of this assumption, we exposed the samples after UV exposure to molecular oxygen (\(p = 10\) mbar). In the case of
TiO₂ nanoparticles, photogenerated electrons transfer to O₂ and form paramagnetic superoxide anions (O₂⁻) (eqs 4 and 5), which remain stabilized on the particle surface and give rise to characteristic EPR signal signatures (Table 1, Figure 9a). The redox potential of O₂/O₂⁻ (Figure 2 gray dotted line, \( E = -4.22 \) eV) is slightly above the conduction band minimum of SnO₂ (\( E_{\text{CB}} = -4.5 \) eV), which inhibits the transfer of SnO₂-related conduction band electrons to molecular oxygen and, thus, the formation of surface adsorbed O₂⁻ ions. For particle systems that were only in contact with pure water and dehydrated thereafter, there are no corresponding interfacial charge transfer effects. Obviously, related networks contain too many regions where TiO₂ or SnO₂ particles are aggregated in such a way that interfaces between identical metal oxide nanoparticles, photogenerated electrons to O₂, and form paramagnetic superoxide anions (O₂⁻) (eqs 4 and 5), which remain stabilized on the particle surface and give rise to characteristic EPR signal signatures (Table 1, Figure 9a).27

\[
\begin{align*}
\text{Ti}^{3+} + O_2(g) & \rightarrow \text{Ti}^{4+} + O_2^- \\
e^-_{\text{CB}} + O_2(g) & \rightarrow O_2^-
\end{align*}
\]

The redox potential of O₂/O₂⁻ (Figure 2 gray dotted line, \( E = -4.22 \) eV) is slightly above the conduction band minimum of SnO₂ (\( E_{\text{CB}} = -4.5 \) eV), which inhibits the transfer of SnO₂-related conduction band electrons to molecular oxygen and, thus, the formation of surface adsorbed O₂⁻ ions.40 Figure 9 shows EPR spectra of the preirradiated metal oxide samples after 15 min oxygen exposure at \( T = 90 \) K and subsequent pumping to \( p < 10^{-6} \) mbar. In the case of TiO₂ nanoparticles (a), a superimposition of O⁻ and O₂⁻ signal components is observed. The EPR parameters are given in Table 1.

Additional EPR resonances are observed on the network of low mixing quality (b) and attributed to O₂⁻ radicals, which are stabilized on SnO₂ surfaces (Table 1).40,41 For the network of high mixing quality, no O₂⁻ stabilized on TiO₂ are observed in the EPR spectrum (c). From the absence of O₂⁻ ions we infer that all photogenerated electrons are drained into SnO₂ (Figure 2). This is different from TiO₂, where photogenerated electrons, irrespective of whether they localize in shallow trap states (Ti³⁺) or whether they remain in the conduction band,42 readily transfer to molecular oxygen.

Figure 6. Characteristic EDX linescans of TiO₂–SnO₂ networks obtained by heteroaggregation in (a) aqueous formic acid solution (\( c = 10^{-6} \) mol·L⁻¹) and (b) water. Scanned paths are shown in the SEM insets. The black and red lines show the distribution of Ti and Sn within the scanned distance. The gray line indicates the deviation of the desired Ti/Sn ratio.

Figure 7. Statistical analysis of the mixing quality throughout the powder samples. Deviations of the desired Ti/Sn ratios within line scans of several micrometers across the particle networks are plotted in the diagram. The samples were prepared in \( c = 10^{-6} \) mol·L⁻¹ aqueous formic acid solution (HCOOH/High mixing quality) and water (H₂O/Low mixing quality).

Figure 8. EPR spectra of metal oxide samples after 30 min UV/Vis light exposure (\( P_{\text{irr}} = 0.9 \) mW·cm⁻² for the energy range \( 3.2 \) eV < \( E < 6.2 \) eV). (a) Simulated EPR spectrum of O⁻ and Ti³⁺ centers on TiO₂ nanoparticles. (b) Experimental EPR spectrum of O⁻ and Ti³⁺ centers on TiO₂ nanoparticles. (c) EPR spectrum of the sample with low mixing quality. (d) EPR spectrum of the sample with high mixing quality. All spectra were acquired at \( T = 90 \) K and \( p < 10^{-6} \) mbar using a microwave power of \( P_{\text{MW}} = 6.32 \) mW.

Table 1. EPR Parameters of Radicals Observed on TiO₂ and SnO₂ Nanoparticle Surfaces as a Result of Charge Trapping

|                  | Ti³⁺ [I] | Ti³⁺ [II] | O⁻ (SnO₂) | O₂⁻ (TiO₂) | O₂⁻ (SnO₂) |
|------------------|----------|-----------|------------|------------|------------|
| \( g_1 \)        | 1.9660   | 1.9904    | 2.0126     | 2.0183     | 2.0235     |
| \( g_2 \)        | 1.9510   | 1.9600    | 2.0045     | 2.0094     | 2.0088     |
| \( g_3 \)        |          |           | 2.0033     |            | 2.0029     |
oxide particles types prevail. Corresponding solid—solid interfaces were found to actually enhance the recombination of photogenerated charge carriers.\textsuperscript{28} The quantitative analysis of persistently trapped photogenerated charges on the three different powder samples shows no concentration increase of stabilized hole centers (\(O^−\) radicals) for the water prepared network with low mixing quality in comparison to the pure MO-CVS TiO\(_2\) nanoparticles (Figure 10). However, a strong enhancement of the concentration of \(O^−\) radicals was observed for the sample of high mixing quality.

The quantitative analysis of the yield of photogenerated charges clearly shows that the adjustment of surface charge during particle network formation allows for the achievement of high mixing qualities and enables the realization of a high concentration of heterojunctions that are vital for the separation of photogenerated electrons and holes. The here presented results clearly underline the necessity to characterize and annihilate charge recombination on photoactive materials.

Surface charge-directed aggregation of different types of particles and the subsequent introduction of functional interfaces is a cheap and versatile particle engineering approach to generate high concentrations of heterojunctions inside particle-based devices for photochemical application and energy production.

\section*{CONCLUSIONS}
We intentionally introduced functional particle interfaces between two types of metal oxide nanoparticles and quantitatively determined the yield of photogenerated and trapped charges.\textsuperscript{28} To yield blended nanoparticle systems hosting high concentrations of heterointerfaces, it is vital to prepare nanoparticles that subsequently can be easily deagglomerated in colloidal dispersion and to control the process of interface formation via surface charge induced heteroaggregation. As shown in this study, MO-CVS-grown particles can be simply dispersed by use of ultrasonic treatment to the single particle level. Controlled interface formation was achieved via heteroaggregation, i.e., via the self-assembly of oppositely charged particles in colloidal dispersion using formic acid for the adjustment of surface charge. In comparison to mixed particle systems prepared in pure water via surface charge-directed aggregation-prepared mixed particle systems show a substantially increased yield for photogenerated hole centers. The extremely high concentration of SnO\(_2\)−TiO\(_2\) heterojunctions actually gives rise to an enhanced cross section for the separation of photogenerated charges, which results from an effective interfacial charge transfer across the particle–particle interfaces.

\section*{ASSOCIATED CONTENT}
\subsection*{Supporting Information}
Further information concerning the crystallographic structure, the adsorption of formic acid, and the quantitative EPR measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

\section*{AUTHOR INFORMATION}

\textbf{Corresponding Author}
E-mail: o.dwald@lfg.uni-erlangen.de.

\textbf{Notes}
The authors declare no competing financial interest.

\section*{ACKNOWLEDGMENTS}
The authors thank Deutsche Forschungsgemeinschaft (DFG) for funding this project within the Research Training Group 1161 “Disperse Systems for Electronic Applications”. S.B. and O.D. acknowledge support from the Austrian Fonds zur Förderung der Wissenschaftlichen Forschung FWF-P1312 (ERA Chemistry). This work also made use of the facilities of the Cluster of Excellence “Engineering of Advanced Materials” at the University of Erlangen–Nuremberg.

\section*{REFERENCES}

\begin{itemize}
\item[(1)] Zhang, H.; Chen, G.; Bahnemann, D. W. J. Mater. Chem. 2009, 19 (29), 5089.
\item[(2)] Kudo, A.; Miseki, Y. Chem. Soc. Rev. 2008, 38 (1), 253.
\item[(3)] Henderson, M. A. Surf. Sci. Rep. 2011, 66 (6–7), 185–297.
\item[(4)] Fujishima, A.; Zhang, X.; Tryk, D. A. Surf. Sci. Rep. 2008, 63 (12), 515–582.
\item[(5)] Maeda, K.; Domen, K. J. Phys. Chem. Lett. 2010, 1 (18), 2655–2661.
\item[(6)] Kamat, P. V. J. Phys. Chem. Lett. 2012, 3 (5), 663–672.
\item[(7)] Kamat, P. J. Phys. Chem. C 2007, 111 (7), 2834–2860.
\end{itemize}
information about local distribution of elements within a de
integral value of the composition of the sample but do not carry any
(inductively coupled plasma optical emission spectrometry) provide an
micrometers for bulk TiO$_2$ or SnO$_2$ samples. Consequently the
sampled volume in EDX studies are on the order of a few cubic
volume. The local resolution of chemical information for EDX analysis
point to a nonuniform distribution of the two elements and therefore
distance (Figure 6a, gray line). Deviations of the desired Ti to Sn ratio
ratio of two di
erent elements should stay constant across the scanned
X-ray diffraction as well as quantitative analysis like ICP-OES
acceleration voltages of 20 kV, the
nanometer scale is not feasible. Nevertheless, by scanning the
ratio after oxygen exposure of MO CVS SnO$_2$
emitted of the sample. With acceleration voltages of 20 kV, the
FEI Europa 2250 SEM operated at 15 kV at a working distance of 30
nanometer scale is not feasible. Nevertheless, by scanning the
the EDX spectrum for TiO$_2$ nanoparticles. O$_{2}$ is the predominant
is not feasible. Nevertheless, by scanning the
aggregated with a linescan, the change in the ratio between Ti and
Sn can be tracked with a very high spatial resolution of approximately
100 nm. In the case of binary mixtures with a high mixing quality, the
ratio of two different elements should stay constant across the scanned
distance (Figure 6a, gray line). Deviations of the desired Ti to Sn ratio
point to a nonuniform distribution of the two elements and therefore
to low mixture quality of the network (Figure 6b, gray line).
EPR spectrum simulation, 1996.
Siedl, N.; Elser, M. J.; Halwax, E.; Bernardi, J.; Diwald, O. J.
Phys. Chem. C 2009, 113 (21), 9175–9181.
Berger, T.; Sterrer, M.; Diwald, O.; Knözinger, E. ChemPhysChem 2005, 6 (10), 2104–2112.
Siedl, N.; Elser, M. J.; Bernardi, J.; Diwald, O. J. Phys. Chem. C 2009, 113 (36), 15792–15795.
López-López, J. M.; Schmitt, A.; Moncho-Jordá, A.; Hidalgo-Alvarez, R. Soft Matter 2006, 2 (12), 1025.
Piekewa, M. A.; Videcoq, A.; Ferrando, R.; Bochichio, D.; Pagnoux, C.; Rossignol, F. Phys. Chem. Chem. Phys. 2012, 14 (4), 1431.
Piekewa, M. A.; Videcoq, A.; Rossignol, F.; Pagnoux, C.; Carrion, C.; Cerbelaud, M.; Ferrando, R. Langmuir 2010, 26 (15), 12540–12547.
Pmandou, A.; Siffert, B. J. Colloid Interface Sci. 1984, 102 (1), 138–145.
Zhao, J.; Hidaka, H.; Takamura, A.; Pelizzetti, E.; Serpone, N. Langmuir 1993, 9 (7), 1646–1650.
Cerbelaud, M.; Videcoq, A.; Abelard, P.; Pagnoux, C.; Rossignol, F.; Ferrando, R. Soft Matter 2010, 6 (2), 370–382.

(35) Fujishima, A.; Rao, T. N.; Tryk, D. A. J. Photochem. Photobiol. C 2000, 1 (1), 1–21.
(36) D’Arienzo, M.; Carbajo, J.; Bahamonde, A.; Crippa, M.; Polizzi, S.; Scotti, R.; Wahba, L.; Morazzoni, F. J. Am. Chem. Soc. 2011, 133 (44), 17652–17661.
(37) Macdonald, I. R.; Howe, R. F.; Zhang, X.; Zhou, W. J. Photochem. Photobiol. A 2010, 216 (2–3), 238–243.
(38) Dimitrijevic, N. M.; Rozhkov, E.; Rjab, T. J. Am. Chem. Soc. 2009, 131 (8), 2893–2899.
(39) Yong, X.; Schoonen, M. A. A. Am. Mineral. 2000, 85 (3–4), 543–556.
(40) In fact, we evidence O$^-$ signals that results from UV exposure as well as an O$_2^-$ signal after oxygen exposure of MO CVS SnO$_2$ nanoparticles. Both types of signals are by a factor of ~100 lower in intensity and therefore negligible with respect to signals of the other samples discussed in this study.
(41) Meriaudeau, P.; Naccache, C.; Tench, A. J. J. Catal. 1971, 21 (2), 208–211.
(42) Berger, T.; Sterrer, M.; Diwald, O.; Knözinger, E.; Panayotov, D.; Thompson, T. L.; Yates, J. T., Jr. J. Phys. Chem. B 2005, 109 (13), 6061–6068.