TiO₂ doping by hydroxyurea at the nucleation stage: towards a new photocatalyst in the visible spectral range

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We report an original method of preparation of OCN-doped TiO₂ for photocatalysis in the visible spectral range. The preparation is achieved by a sol-gel route using titanium tetraisopropoxide precursor. Special attention was paid to fluid micromixing, which enables homogeneous reaction conditions in the reactor bulk and monodispersity of the produced clusters/nanoparticles. The dopant hydroxyurea (HyU, CH₄N₂O₂) is injected into the reactive fluid at the nucleation stage, which lasts tens of milliseconds. The doping results in a strong yellow coloration of the nanocolloids due to the absorption band in the spectral range 380–550 nm and accelerates the aggregation kinetics of both nuclei at the induction stage and sub-nuclei units (clusters) at the nucleation stage. FTIR, Raman and UV-visible absorption analyses show the formation of a stable HyU–TiO₂ complex. EXAFS spectra indicate no appreciable changes of the first-shell Ti atom environment. The doping agent takes available surface sites of TiO₂ clusters/nanoparticles attaining ~10% molar loading. The reaction kinetics then accelerates due to a longer collisional lifetime between nanoparticles induced by the formation of a weak =O··Ti bond. The OCN-group bonding to titanium atoms produces a weakening of the C=O double bond and a strengthening of the C–N and N–O bonds.

Introduction

Much research has been devoted to nitrogen-doped TiO₂ since the publication by Asahi *et al.*,¹ who first systematically and theoretically overviewed anionic C, N, F, P or S insertion into its solid structure. The main idea behind this is to extend the operating range of this famous photocatalyst into the visible spectral range. Although the exact material composition and the place that nitrogen takes in the TiO₂ lattice (substitutional or interstitial) and its local composition (bonding to additional N, C and O atoms) has been subject to debate until now, we will call this family N–TiO₂ in the following.

Different methods were applied to the N–TiO₂ fabrication: laser pyrolysis,² pulsed-laser deposition,³ electrophoretic deposition,⁴ plasma treatment,⁵ annealing under gas atmosphere,^{6–8} hydrothermal,⁹ solvothermal,¹⁰ mechanochemical,¹¹ spray pyrolysis,¹² wet^{13,14} and sol-gel^{15–18} methods, with addition of nitrogen-containing precursors (*e.g.* urea, ammonia) followed

by calcination. Typically, nitrogen loading achieved in these materials is between 0.1 and 1 at%, although values above 10 at% were also reported.¹⁶

These synthesized materials in the form of bulk powders, mesoporous and thin films generally exhibit photocatalytic activity towards organic pollutants decomposition and even antibacterial activity⁸ under visible light illumination, considerably higher than pristine TiO₂ samples.

The problem of thermal stability of the nitrogen-doped TiO₂ has been raised by Batzill *et al.*¹⁹ As Okato *et al.* have shown,³ photocatalytically active substitutional sites N_O saturate at very low dopant level and suggest low-temperature non-equilibrium growth conditions to overcome this limitation.

An important requirement related to a successful implementation of TiO₂ in photocatalysis is the small size and narrow polydispersity of the particles.²⁰ Moreover, high homogeneity of the dopant repartition over the TiO₂ matrix is of key importance in view of different strategies and mechanisms of the material activity.²¹ In particular, better homogeneity permits finer optimisation of the material composition at the nanoscale and therefore obtaining higher gain in the photocatalytic efficiency.

Because of the extremely high surface to volume ratio, nanosized particles and clusters offer better access to Ti sites. In general, the chemical activity of such units is higher than their bulk counterparts, and a formation of strong bonds to Ti atoms can be expected. These conditions may facilitate impregnation of dopant molecules and atoms, leading to a better catalyst stability and requiring lower temperatures.

A mild-chemistry sol-gel method permits realisation of this approach. It is based on hydrolysis-condensation reactions

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involving metal–alkoxide precursors, which have been extensively studied in the past.^{22,23} Different reactive clusters and nanoparticles appear at the initial stage of growth and serve as building blocks of new advanced solids²⁴ that define their macroscopic properties and open many interesting applications in nano-technologies.

Difficulties of experimental realisation are related to a high chemical reactivity of the titanium alkoxide precursors. As a result of this, reaction products are highly sensitive to the local micro-composition. Its initial heterogeneity results in generally broad particle size distribution and brings importance to the micromixing of the reactive fluids. Recently, we have proposed an improved sol–gel approach to the fabrication of chemically active TiO₂ clusters and nanoparticles based on the turbulent micromixing of reactive fluids containing titanium precursor and water.^{25–27} Using a sol–gel reactor quasi-monodispersed titanium-oxo-alkoxy Ti_xO_y(OⁱPr)_z clusters and nanoparticles can be produced in macroscopic quantities.²⁸ By doping of these units we expect to attain a high homogeneity of the resultant bulk solids down to the scale as small as their size. Recently, we reported preliminary results of the realisation of nano-coatings by this approach, which exhibit an enhanced photocatalytic activity under visible light illumination.²⁷

In the present article, we report on the underlying sol–gel chemistry that is responsible for the clusters and nanoparticles doping. We characterise the obtained material and explain the structural unit involving nitrogen, which enables visible absorption of the material and related photocatalytic activity. The doping is achieved by an injection of the nitrogen-containing compound, hydroxyurea into the turbulent mixing zone of the sol–gel reactor. As a result, this study is carried out at perfect micromixing of the reaction components TTIP/H₂O/CH₄N₂O₂/2-propanol. The growth kinetics of clusters and nanoparticles have been measured *in situ* by light scattering methods.

Experimental

The sol particles in the following experiments were generated in isopropanol solutions with titanium tetra-isopropoxide (TTIP) at concentration 0.146 M and hydrolysis ratio $H = C_W/C_{Ti}$ (where C_{Ti} and C_W are respectively TTIP and water molar concentrations) varying between 1.0 and 2.6.

Reproducible reaction kinetics and particle sizes were obtained in the sol–gel reactor^{25–27} with temperature and humidity control. Two thermostatic stock solutions of equal volumes (50 mL) containing TTIP/2-propanol (A) and water/2-propanol (B) are injected into the static T-mixer at velocity varying from 2 to 12 m s^{−1} by applying an external pressure of dry nitrogen gas. This injection is exocentric: two fluids form a vortex before entering the main tube. The diameters (d) of two input (1.0 mm) and the main (2.0 mm) tubes are chosen to conserve the Reynolds number ($Re = 4Q\rho/\pi\eta d$, where Q , ρ , and η are the fluid flow rate, density and dynamic viscosity), which was fixed at $Re = 4400$ for the best reactor performance in terms of the size and polydispersity.²⁷ In these operating conditions the rate of the physical process “mixing” r_{Ph} gets over the rates of the chemical hydrolysis-condensation reactions r_{Ch} leading to nucleation corresponding to small Damköhler numbers $Da = r_{Ch}/r_{Ph} \leq 1$.

The doping was achieved by an addition of hydroxyurea (HyU, CH₄N₂O₂) to the stock solution B with different molar concentrations (C_d), which maximum value of ~ 0.015 M is explained by the HyU solubility limit in 2-propanol. It is then brought into the turbulent mixing zone of the sol–gel reactor and reacts in the perfectly homogeneous environment. It may be then incorporated into the TiO₂ nanoparticles or take surface sites depending on whether nucleation or doping rate, is higher.

The reactor temperature was maintained at 20.0 °C using a thermo-cryostat (Haake, DC10K15). TTIP of 98% purity, 2-propanol (Interchim) and distilled water were used. A monomode optical fiber probe was developed to monitor *in situ* the particle size ($2R$) and the scattered light intensity (I) of He–Ne laser by photon-correlated spectroscopy method, using a 16-bit, 255 channels PC board plugged digital correlator (PhotoCor Instruments) developed by Yudin *et al.*¹³ The observation volume defined by a mutual positioning of two monomode optical fibres is small enough ($\sim 10^{-6}$ cm³) to prohibit multiple scattering events. The measurements (I, R) are carried out in the automatic sampling mode with the data accumulation over 60 s during the period of the solution stability (induction period) or over 24 h if no solid precipitation (turbidity) were observed. This relatively short accumulation time and small observation volume considerably decrease experimental series rejection due to a non-desirable strong light scattering on rare dust particles (because of the $I \sim R^6$ dependence, large μ m-size dust particles prohibit observation of nm-size TiO₂ clusters). In the case of the smallest clusters, which provide the weakest scattering of light, averaging over many short-lasting measurement series (with exclusion of rare noisy series) was employed to increase the signal-to-noise ratio. The solution stability was controlled to avoid a decrease of the temporal resolution of the growth kinetics, and the averaging was only applied on a time-scale of the mean cluster size stability.

The FTIR spectra have been measured by IRPrestige-21 (Shimadzu) operating in the range 400–4000 cm^{−1} with spectral resolution of 4 cm^{−1}.

Raman spectra have been measured using a micro-Raman high-resolution HR800 installation from Jobin Ivon Horiba with the spectral and spatial resolution correspondingly 0.25 cm^{−1} and ~ 5 μ m. The scattered light is collected by Peltier-cooled CCD camera in backscattering configuration. Most of the measurements were conducted at 488 nm using argon ion laser.

UV-visible absorption spectra were measured by an optical fiber probe using D_2 lamp (Oriel). The fiber transmits the signal to a Cromex monochromator (grating 150 l mm^{−1}, $f = 30$ cm, slit 20 μ m) coupled to a CCD detector (Princeton). For each tested colloid, these measurements were completed within first half of the correspondent induction period.

The XPS analyses were performed on Axis Ultra spectrometer (Kratos Analytical, Shimadzu) equipped with a monochromatised aluminium X-ray source (15 kV/10 mA). The pressure in the sample chamber was around 10^{−6} Pa. The hybrid lens magnification mode was used with the slot aperture resulting in an analysed area of 700 μ m $\times$ 300 μ m. The pass energy was set at 40 eV. In these conditions, the

energy resolution gives a full width at half maximum (FWHM) of the Ag 3d_{5/2} peak of about 1.0 eV. The stability of charge compensation and absence of sample degradation was checked during the measurements. The binding energies were calculated with respect to the C 1s component at 284.8 eV. The spectra were interpreted with the CasaXPS program (*Casa Software Ltd*) with a Gaussian/Lorentzian (70/30) profile after the linear baseline subtraction. Molar fractions were calculated using peak areas normalised on the basis of acquisition parameters after a linear background subtraction, experimental sensitivity factors and transmission factors provided by the manufacturer.

The EXAFS spectra have been measured at E4 station of Hasylab of synchrotron DESY operating in the transmission geometry at LN temperature. The monochromator Si(111) offered spectral resolution of 0.55 eV at the Ti *K*-edge 4.966 keV.

Results and discussion

A. Reaction kinetics

Before the sol–gel reaction kinetics in presence of the dopant are discussed, we make a point on that of the pristine TiO₂ particles.

According to our previous studies,²⁸ there exist two domains of the stability of subnucleus particles (clusters), $H < 1.45$ and $1.45 \leq H \leq 1.75$, which correspond to the size of $2R = 2.0$ nm and 3.2 nm. Moreover, in the domain $1.75 < H \leq 2.0$ the clusters undergo saturated growth: they agglomerate in short chains, where maximum size depends on H . In the domain $H > 2.0$ nuclei of the size 2.6 nm are formed and are subject to the irreversible accelerated growth during the so-called induction period. However, the induction time can be as long as ten hours (when $H \rightarrow 2.0$) while the nuclei possess relative stability. All the observed units are metastable and readily react in presence of traces of water forming powder-like precipitates since the induction kinetics shows a high reaction order relative to the reagents concentrations C_{Ti} and C_w : $k_{ind} \propto C_{Ti}^6(H-1.45)^5$.²⁹ The induction kinetics exhibits weak temperature dependence and influences the morphology of the growing particles.²⁶ In the experimental conditions and temperature of 20 °C, the nuclei aggregate into quasi-linear chains of a low fractal dimension $D_f = 1.4$.

With addition of a dopant the reaction kinetics can change, which can be shown by the light scattering method providing information about temporal evolution of particle radius R and intensity I scattered by the ensemble of nanoparticles. In particular, the last can be represented by the second momentum of the mass distribution function $F(m,t)$:²⁵

$$I(t) \propto \mu_2(t) = \int m^2 F(m,t) dm \quad (1)$$

In order to validate the doping, we used the critical hydrolysis ratio of $H = 2.0$, which is required for nucleation but is not sufficient to aliment the subsequent growth. The dominant oxolation reactions

vanish in these conditions and the induction period, which precedes solid precipitation, tends to infinity (we don't consider

Fig. 1 Scattered light intensity and particle radius evolution during the induction period of the sol–gel process at different HyU concentrations: 4 (a) 4, 5 (b), 7 (c), 8 (d), 9 (e), 10 (f), 12 (g) and 13 mM (h) ($C_{Ti} = 0.146$ M, $H = 2.0$, 20 °C, $Re = 4500$).

here much slower kinetics, *e.g.* due to the alcoxolation reactions).

The curves $I(t)$ and $R(t)$ for different molar concentrations of hydroxyurea are shown in Fig. 1. They are characteristic of the classic sol–gel induction kinetics²⁸ with a slow increase of the signal followed by the explosive growth at precipitation. At the induction time large agglomerates are formed, resulting in a strong scattered light intensity. However, the addition of the dopant shortens the induction time. This shows the condensation reactions between TiO₂ nanoparticles and hydroxyurea molecules. A similar tendency has been observed with addition of water: an increase of the hydrolysis ratio H accelerates the induction kinetics. This is shown in Fig. 2. Moreover, this behaviour is maintained over an extended range of H correspondent to different domains of the nucleation kinetics, according to Azouani *et al.*²⁸

As our early studies have shown, the induction time (t_{ind}) can be a measure of the reaction rate presented by the initial slope of the $I(t)$ curves: $r \propto t_{ind}^{-1}$. We use this relation to account for the reaction rates as a function of H and hydroxyurea concentration presented in the semi-logarithmic frame in Fig. 3. One can see that the induction rate $r(M,H)$ varies almost exponentially with the addition of either HyU (fixed H) or water (fixed HyU). Moreover, the curve slopes $d \log(r)/dC_d = 153 \pm 12 \text{ M}^{-1}$ do not significantly depend on H and are considerably larger than $d \log(r)/dC_w = 21 \pm 1 \text{ M}^{-1}$ (where $C_w = HC_{Ti}$ is the concentration of water). The explanation of this result will be given below in chapter F.

As Soloviev has shown,³⁰ simultaneous SLS/DLS measurements of the scattered light intensity $I(t)$ and mean hydrodynamic

Fig. 2 Scattered light intensity evolution during the induction period of the sol-gel process at different hydrolysis ratios: $H = 1.5$ (a), 1.6 (b), 1.7 (c), 1.8 (d), 1.9 (e), 2.0 (f) and 2.2 (g) ($C_{Ti} = 0.146$ M, $C_{HyU} = 0.013$ M, 20°C , $Re = 4500$).

Fig. 3 Induction rate versus (a) H for $C_{HyU} = 0.013$ M and (b) versus C_{HyU} concentration for $H = 1.7, 2.0$ and 2.5 ($C_{Ti} = 0.146$ M, 20°C , $Re = 4500$).

radius $R(t)$ of nanoparticle at aggregation allow determination of the fractal dimension of the growing structures. This fact is not evident when their size belong to the Rayleigh domain: $R \ll \lambda$. However, the scattered light intensity can be expressed at aggregation (process with mass conservation) as

$$I \propto N \cdot m^2 \propto m \propto R^{D_f} \quad (3)$$

Therefore, the slope of the parametric curves $I(R)$ (t being the parameter) in the logarithmic frame reflects the fractal dimension D_f .

$$D_f = \ln(I)/\ln(R) \quad (4)$$

Fig. 4 Logarithmic plot of the scattered light intensity versus particle radius ($C_{Ti} = 0.146$ M, $C_{HyU} = 13$ mM, $H = 2.0$, 20°C , $Re = 4500$).

The plot for one HyU concentration and $H = 2.0$ (nucleation threshold according to ref. 28) is shown in Fig. 4.

It has been shown earlier experimentally³¹ and theoretically³² that the regime of Diffusion Limited Aggregation (DLA) results in the fractal growth with $D_f = 1.8$ while Reaction Limited Aggregation (RLA) results in a slightly higher value of $D_f = 2.1$.³³ The values obtained in our experiments correspond to the RLA aggregation regime and are markedly different from those characteristic of the induction period of pure TiO_2 (we note that in the latter case low-dimension structures of $D_f \approx 1.4$ are observed in our experimental conditions²⁶). The observed fractal dimension about 2 may also result from a Brownian-walk aggregation process. In any case, this strong modification of the nanostructure morphology on addition of HyU shows an efficient nanoparticle doping.

B. Absorption spectra

As we have seen in chapter A, the reaction kinetics strongly changes at the contact of HyU with titanium-oxo-alkoxy TiO_2 clusters and nanoparticles. This allows us to suppose the formation of HyU - Ti -oxo-alkoxy complex, which we will call hereafter HyU - TiO_2 . Complementary and direct evidence of the complex formation can be obtained from the UV-visible absorption spectra of the pure and doped colloids, which are shown in Fig. 5.

Fig. 5 Absorption spectra of the colloidal pure (a) and HyU - TiO_2 (b,c) nanoparticles as prepared (b) and diluted in 2-propanol 1:5 (c) ($C_{Ti} = 0.146$ M, $C_{HyU} = 13$ mM, $H = 2.0$, 20°C , $Re = 4500$). The optical cell length is 1 cm.

In fact, pure TiO_2 colloids are non-coloured while the addition of HyU at the nucleation stage results in their yellow coloration. This is explained by the absorption onset shift from UV to the visible spectral range. Fundamental absorption of pure oxo-alkoxy TiO_2 nanoparticles sets up below 360 nm, as earlier reported by Soloviev *et al.*³⁴ As Fig. 5 shows, the absorption is extended up to ~ 550 nm. This strong blue-green absorption band can be assigned to the HyU– TiO_2 complex. Its absorption coefficient was measured $\alpha_0 = 2.1 \pm 0.1 \text{ cm}^{-1}$ at 425 nm and $0.93 \pm 0.05 \text{ cm}^{-1}$ at 450 nm.

The reversibility of the doping reaction can be accessed from experiments with the colloid dilution. We prepared for these experiments colloidal TiO_2 nanoparticles in standard conditions of the reactor with the addition of 13 mM of HyU at the nucleation stage. Thereafter, absorbance of the colloid has been measured as a function of the dilution in 2-propanol.

We suppose that the formation of the HyU– TiO_2 complex is reversible and can be presented by the reaction:

with the equilibrium constant $k_{\text{eq}} = AN/mn$, where A , N , m and n are respectively molar concentrations of alcohol, complex, HyU and available TiO_2 sites for complexation (n_0 is the total number of such sites and m_0 is the total number of HyU molecules initially injected to the unitary volume of the solution) per unit volume of the solution. Keeping in mind that $n_0 = n + N$, $m_0 = m + N$ and $n_0 \gg m_0$ one can write an expression for the complex concentration:

$$N = \frac{m_0}{1 + A(k_{\text{eq}}n_0)^{-1}} \quad (6)$$

By dilution, the concentrations m_0 and n_0 scale according to $d = m_0/m_{0d=1} = n_0/n_{0d=1}$ ($d < 1$). Because the absorption coefficient α is proportional to the complex concentration (eqn 6), it can be finally presented as:

$$\alpha = \alpha_{0d=1} \frac{(k'_{\text{eq}} + 1)d^2}{(k'_{\text{eq}}d + 1)} \quad (7)$$

where $k'_{\text{eq}} = k_{\text{eq}}n_{0d=1}/A$ and $\alpha_{0d=1}$ corresponds to the complex absorption before dilution. A comparison between the expressions for k_{eq} and k'_{eq} shows that reaction (5) can then be effectively reduced to equilibrium between free and surface HyU molecules:

that is explained by $A \gg n_0 \gg m_0$.

The fit of the experimental data according to eqn (7) in axes α/d and $1/d$ is shown in Fig. 6 and results in $k'_{\text{eq}} \approx 12$. This result indicates that in our experimental conditions (i) the equilibrium eqn (8) is strongly shifted to the HyU– TiO_2 complex formation and (ii) TiO_2 surface sites available for complexation are not saturated at the highest HyU concentration employed in this work. Because no signs of the doping saturation were observed, the HyU loading is limited by its solubility in 2-propanol and not by the ability of TiO_2

Fig. 6 TiO_2 colloid absorbance versus dilution ($C_{\text{Ti}} = 0.146 \text{ M}$, $C_{\text{HyU}} = 13 \text{ mM}$, $H = 2.0$, 20°C , $\text{Re} = 4500$).

nanoparticles to receive it. This maximum loading corresponds to the atomic ratio of $\text{N/Ti} \approx 16\%$ (considering two nitrogen atoms per HyU molecule).

The observed coloration is due to formation of N-O-Ti bonds, since it appears at a very early stage of nucleation and it is not intensified during the induction period. On the contrary, the color might be attributed to Ti-O-C (and probably Ti-C) bonds, since particle aggregation produces them.

C. FTIR and Raman spectra

Important information about the chemical reaction and formed bonds between HyU and TiO_2 nanoparticles can be obtained from FTIR and Raman spectra. Below we consider the most relevant frequency range between 1300 and 1700 cm^{-1} , where important phonon bands of the HyU molecule appear. Their assignment was inspired from data of normal vibrations of urea.³⁵ They are listed in Table 1.

The bands ν_1 and ν_2 have a mixed character of both CO stretching and NH_2 bending vibrations. Although a disagreement exists about their contributions, we used the Yamaguchi assignment,³⁵ who supports his IR absorption and Raman measurements by theoretical calculations. The bands ν_3 and ν_4 respectively belong to almost pure NH_2 bending and CN stretching modes.^{35–36} Rosca *et al.*³⁷ have attributed a band at 1196 cm^{-1} to NO in the ionic compound $\text{H}_3\text{N}^+\text{OH}$ in solution. In neutral compound and condensed phase, which is our case, we expect this band at higher frequencies. Our FTIR spectra show only one non-identified band above 1100 cm^{-1} : at 1400 cm^{-1} . According to the structural difference between urea and HyU, we ascribe this “new” band to NO .

For the comparative measurements we used dry microcrystalline HyU and powders prepared by drying of HyU/TTIP/2-propanol solution in ambient air at 25°C and 80°C .

Table 1 Phonon frequencies (in cm^{-1}) of urea/ NO , HyU, and HyU– TiO_2

Vibrations	$\text{NH}_2\text{CONH}_2^{a,b}$	NH_2CONHOH	TTIP + HyU
$\nu_1 \text{ C=O}$	1688	1595	1550
$\nu_2 \text{ NH}_2$	1603	1642	1640
$\nu_3 \text{ NH}_2$	1629		
$\nu_4 \text{ C-N}$	1464	1484	≥ 1530
$\nu_5 \text{ N-O}$	—	1408	≥ 1460

^a Ref. 35. ^b Ref. 36.

We remark that the solution becomes reddish when the initially transparent products are mixed, which signifies the complex formation. This choice of the samples is explained by the fact that the formation of a HyU–TiO₂ complex progresses at higher temperatures and longer times. At the same time, TiO₂ conserves its amorphous nature inherent to the oxo-alkoxy phase of the colloidal nanoparticles.

The measured FTIR spectra are shown in Fig. 7. A comparison of the observed spectra shows changes of the principal phonon modes. The frequencies of the C=O, NO and CN bands shift: however, while ν_1 decreases, ν_4 and ν_5 increases. On the other hand, the ν_2 and ν_3 of NH₂ are not significantly affected by the reactions:

$$\nu_2 \text{ and } \nu_3 (\text{NH}_2) \approx \text{constant}$$

$$\nu_1 (\text{C} = \text{O}) \searrow$$

$$\nu_4 (\text{C}-\text{N}) \text{ and } \nu_5 (\text{N}-\text{O}) \nearrow$$

A confirmation of this hypothesis can be found in Raman spectra presented in Fig. 8. The red shift of the C=O band and the blue shift of the NO band were observed.

These results allow proposing a structure of the HyU–TiO₂ complex. The group NH₂ of HyU (see inset in Fig. 7) is isolated and it is not apparently involved in a new bond formation. In contrast, the strength redistribution in the chain

Fig. 7 FTIR spectra of pure HyU (a) and HyU–TiO₂ dried at 25 °C for 10 h (b) and at 80 °C during 0.5 h (c) and 4 h (d).

Fig. 8 Raman spectra of pure HyU (a) and HyU–TiO₂ dried at 25 °C for 10 h (b) and 80 °C for 4 h (c).

O=C–N–O–(stronger ν_1 bond softens and weaker ν_4 and ν_5 bonds strengthen) suggests its structural integration into the new complex. The hydroxyl group of HyU may be subjected to a condensation reaction with surface hydroxyls of TiO₂, forming a strong covalent bond. The double-bond oxygen of HyU may then form a weak hydrogen-type bond with hydroxyl or titanium atom of another cluster. This is schematically shown below:

While observation of the HyU–Ti complex is new, metal–urea complexes are already known from literature. In particular, Pd²⁺ and Pt²⁺ are formed by metal binding to nitrogen atom, while Cr³⁺, Fe³⁺, Cu²⁺, Zn²⁺ and Ti³⁺ are bound to oxygen.^{38,39} In the first case, the nitrogen binding to a metal brings about increased C=O double bond character.³⁸ In contrast, in the second case the coordination increases the single bond character of the C=O group, moving the correspondent band to low energies; consequently, the C–N band moves to higher frequencies. A comparison with the measured spectra supports our hypothesis of the HyU–Ti complex structure.

D. XPS spectra

The XPS method is sensitive to the surface layer of 2–10 nm. However, in our case it can be accepted for the bulk solid characterisation. Indeed, our solids are powder-like consisting of homogeneously doped aggregated nanoparticles of ~5 nm size. Therefore, information received from first 10 nm can be considered as representative of the total sample.

The position of characteristic bands and atomic ratios of the prepared powder-like pure TiO₂ and HyU–TiO₂ samples are presented in Table 2.

For Ti, all the samples show the same peak shapes and positions with binding energy of Ti 2p_{3/2} peak at 459 eV, indicating the presence of Ti⁴⁺ species (TiO₂). The presence of Ti³⁺ nitride expected for Ti 2p_{3/2} at 455.5 eV is excluded but not that of Ti⁴⁺ species bonded to N in the case when few O are replaced by N inside the TiO₂ lattice: the correspondent BE shift is too small (458.5 eV) to be distinguish from the major peak.⁴⁰

The C 1s peaks can be divided into 3 components. The C–(C,H) contribution at 284.8 eV is a classical aliphatic carbon used to calibrate all our measurements. It is generally present as a contaminant at the surface of all kind of samples. At 1.5 eV higher (286.3 eV) we can find C involved in a simple binding with O or N. At a higher energy about 289 eV we can find many different kinds of C involved in a double binding or two simple bindings with O and/or N. The interstitial carbon atoms⁴¹ were not found in our samples.

The O 1s peaks can be separated into 3 components. The major one (530 eV) corresponds to O bonded to Ti in TiO₂. The two others (531 eV and 532 eV) are more difficult to assign because they can come from different surface species. As an example, the peak at 531.5 eV is consistent with the nitridation process resulting in the Ti–O–N bond.⁴² The O/Ti ratio is close to the expected TiO₂ stoichiometry. It is however higher in the non-calcinated samples, which may be due to the presence of

Table 2 Atomic ratios of the prepared powder-like pure TiO₂ and HyU–TiO₂ samples

Atoms	BE (eV)	TiO ₂ ^a	HyU–TiO ₂ ^a C _{HyU} = 4 mM	HyU–TiO ₂ ^a C _{HyU} = 8 mM	HyU–TiO ₂ ^a C _{HyU} = 11 mM	HyU–TiO ₂ ^a C _{HyU} = 13 mM	TiO ₂ /T ^b	HyU–TiO ₂ /T ^b C _{HyU} = 13 mM	TiO ₂ ^{a,c}	TiO ₂ ^{a,d}
O/Ti	—	2.58	2.45	2.53	2.43	2.37	2.12	2.16	2.51	2.47
O1/Ti	~530	1.96	1.83	1.90	1.86	1.82	1.84	1.77	1.76	1.75
O2/Ti	~531	0.44	0.40	0.41	0.37	0.36	0.16	0.25	0.56	0.51
O3/Ti	~532	0.18	0.22	0.22	0.21	0.19	0.12	0.13	0.20	0.21
N/Ti	—	0.072	0.105	0.094	0.120	0.149	0.015	0.014	0.054	0.060
N1/Ti	~398	—	—	—	—	0.006	—	—	—	—
N2/Ti	~400	0.051	0.078	0.068	0.090	0.119	0.015	0.014	0.049	0.054
N3/Ti	~401.5	0.022	0.027	0.025	0.030	0.024	—	—	0.005	0.007
C/Ti	—	2.01	2.09	2.12	2.01	1.71	0.77	0.73	4.01	3.56
C1/Ti	284.8	1.44	1.42	1.46	1.42	1.18	0.58	0.54	3.24	2.80
C2/Ti	286.3	0.43	0.51	0.47	0.44	0.38	0.11	0.11	0.72	0.58
C3/Ti	~289	0.15	0.16	0.19	0.15	0.15	0.08	0.08	0.15	0.18

^a Only drying at 80 °C is applied. ^b Samples thermally treated at $T = 450$ °C for 4 h. ^c N₂ replaced by He. ^d Standard sol–gel preparation.

adsorbed 2-propanol molecules. The evolvement of 2-propanol would require higher temperatures of about 150 °C,⁴³ as compared to what was presently used for the drying.

As reviewed by Emeline *et al.*,⁴⁴ the attribution of the N 1s binding energies is still discussed and remains controversial. In our case, the N 1s peaks, depending on sample, can be split into several components: very weak 398 eV (N1), major 400 eV (N2) and weaker 401.5 eV (N3) peaks (see Fig. 9a). Earlier, these components were attributed to atomic (N1) and molecular (N2, N3) species.⁴⁵ More precisely, as N₂ is known to not chemisorb at ambient temperature on metal oxides such as TiO₂,⁴² those impurities could be attributed to NO species as a result of atmospheric degradation.⁴⁶ Again N–Ti bonds are excluded because of the absence of N 1s at 396 eV.

Trying to progress in the understanding of the XPS results, we have also analyzed three TiO₂ reference samples (Table 2): TiO₂ prepared inside the sol–gel reactor under dry nitrogen gas, or under helium, and TiO₂ prepared inside a classical open reactor. The presence of N2 and N3 indicates first that we can probably attribute those two components to surface impurities coming from the nitrogen gas used for the sol–gel reactor and/or from contact with ambient air. Furthermore, after thermal treatment (TiO₂/T), N3 and a significant part of N2 disappear, confirming that those species were only weakly adsorbed onto the extended interface of nano-TiO₂ ($S_{\text{BET}} \sim 450 \text{ m}^2 \text{ g}^{-1}$).

Fig. 9 N 1s XPS spectra of the dried HyU–TiO₂ (a), dried pure TiO₂ (b) calcined HyU–TiO₂ (c) and calcined pure TiO₂ (d).

One could envisage the same attribution for the HyU–TiO₂ samples. N3 shows the same behavior but N2 is clearly sensitive to the dopant addition; moreover, this sensitivity shows up at relatively high HyU concentrations $C_{\text{HyU}} \geq 8 \text{ mM}$. We conclude that its origin is not only due to external impurities. However, our UV-visible absorption measurements showed an efficient production of the HyU–TiO₂ surface complex at all used HyU concentrations (see Fig. 6). This speaks strongly in favour of a partial substitution of the weakly bound surface nitrogenous impurities by HyU. Moreover, while the binding energy of N 1s for the –NH₂ group of HyU is usually measured at ~400 eV, it should be expected at higher BE in the case of the hydroxylamine group (–NHOH) as it is coordinated with a metal, as shown with such of organic compound by Kalinowski *et al.*⁴⁷ This strengthens the idea that a part of N2 and N3 is well related to the HyU adsorption.

At first glance, thermally treated HyU–TiO₂ samples show the same “N2 only” composition as for TiO₂/T (see Fig. 9c and d). According to Asahi *et al.*,⁴⁸ N2 may also belong to interstitial NO_i sites. In addition, Yates and coworkers⁴⁹ list several other potential attributions: molecularly chemisorbed N₂ but unexpected on TiO₂ as explained above, NH_x species located at interstitial sites, NO_x or even oxynitride (closer to 399 eV). At present, it is difficult to draw conclusions about attribution of the N2 peak, but the coloration of the doped samples indicates that the nitrogen species interaction with the support is, in this case, different than just adsorption of nitrogenous impurities. Following the same authors, N1 that is only present for the highest HyU concentration can be attributed to substitutional NO_o sites. Theoretical analysis by Di Valentin *et al.*⁵⁰ supports dominant interstitial nitrogen species in our preparation conditions.

The calcination at $T \geq 450$ °C (measured BET area $\sim 100 \text{ m}^2 \text{ g}^{-1}$) strongly weakens the N 1s signal in the HyU–TiO₂ samples (see Fig. 9 and Table 2). This indicates a critical influence of temperature on the nitrogen species retention in nanostructured samples with the extremely large specific surface. This issue will be a subject of our future studies.

Finally, the nitrogen loading at doping can be accessed from the atomic composition in Table 2. It reaches 15% in the non-calcined HyU–TiO₂ samples. This value is in a very good

agreement with the N-loading obtained from the UV-visible absorption measurements, 16% (Chapter B).

E. EXAFS spectra

An inspection of the local Ti atom environment was carried out by EXAFS spectroscopy. Fig. 10 shows EXAFS spectra of two TiO₂ and HyU–TiO₂ powder-like samples in the Fourier-transform *r*-space. Both samples are amorphous as they were dried at 80 °C with no subsequent calcinations.

The spectra look quite similar. The only significant difference between the two spectra may be explained by a sharp feature in the *k*-range of 11.5–12 Å^{−1}. Its origin may not be a usual EXAFS oscillation but more likely another absorption edge. This feature position would be around 5482 eV. Although the source of this contamination is not clear, several impurities may be considered as *e.g.* V K-edge (5465 eV, though the relative shift seems too big even for strongly oxidized vanadium) and La L3-edge (5483 eV). If we exclude this *k*-region, the difference between two spectra decreases. The picture in the *r*-space related to the reduced *k*-range of 3–11 Å^{−1} shown in Fig. 10. They look rather similar, with the exception of the amplitudes in the range of 2.6–3.0 Å, which correspond to the higher-shell (*n* > 1) atoms.

The measured spectra of our amorphous samples exhibit reduced amplitudes as compared to the pure rutile and anatase polymorphs. This is characteristic of a disordered material. Previous experimental⁵¹ and theoretical⁵² studies of amorphous TiO₂ suggested two different distances for the nearest oxygen atoms at 1.94 Å and 1.79 Å. We have attempted two models, which include respectively one and two types of oxygen atoms in the 1st coordination shell, to fit the measured spectra. They result in:

$$\text{1 model: } R_1 = 1.91 \pm 0.01 \text{ \AA}, \text{CN}_1 = 5.3 \pm 0.5, \\ \sigma^2 = 0.014 \pm 0.003 \text{ \AA}^2$$

$$\text{2 model: } R_1 = 1.94 \pm 0.07 \text{ \AA}, \text{CN}_1 = 4.0 \pm 1.7, \\ \sigma^2 = 0.01 \pm 0.015 \text{ \AA}^2$$

$$R_2 = 1.79 \pm 0.09 \text{ \AA}, \text{CN}_2 = 1.2 \pm 1.3, \sigma^2 = 0.007 \pm \infty \text{ \AA}^2$$

A large error in the second model is due to strong mutual correlations. The fits according to the 1-subshell and

Fig. 10 EXAFS analysis of the amorphous samples TiO₂ and HyU–TiO₂ (*C*_{Ti} = 0.146 M, *C*_{HyU} = 13 mM, *H* = 2.0, 20 °C, *Re* = 4500) in the Fourier-transform *r*-space ($3 \leq k \leq 11$).

2-subshell models are found of a similar quality. Considered purely statistically *via* F-test, the probability that the two-types model is valid is ~20%.

These findings evidence no perturbation of the first shell by the doping. This means that Ti–N bonds are not formed, in support of the XPS measurements. On the other hand, perturbations of the second shell atoms may exist due to a formation of Ti–O–N–(C=O) bonds.

The XANES spectra were measured as well. They are all identical within statistical significance. This indicates that the local environment of most Ti (type and number of the nearest neighbours and the symmetry) is preserved.

F. Reaction kinetics involving HyU

As Rivallin *et al.* have shown,²⁵ the induction kinetics (*R*_{ind}) can be expressed as the first derivative of the second momentum of the particle mass (*m*) distribution *F*(*m*,*t*):

$$\mu_2(t) = \int_{m^*}^{\infty} m^2 F(m, t) dm \quad (9)$$

which is equivalent to its general representation by means of the reverse induction time:

$$R_{\text{ind}} = \tau_{\text{ind}}^{-1} \propto \dot{\mu}_2 \Big|_{t=0} \quad (10)$$

This process of low probability belongs to the RLA class reactions³⁰ with a rate expressed as:²⁹

$$R_{\text{ind}} = C_{\text{Ti}}^6 (H - h^*)^5 \quad (11)$$

where the initial hydrolysis ratio in the reactive solution *H* = *C*_{H₂O}/*C*_{Ti} has to be above the critical one of *h** = 1.45. An explanation of (11) was proposed by Rivallin *et al.*,²⁶ who has shown that the condensation reaction

between several (*k* ≥ 2) surface hydroxyls assures the irreversible sticking of two TiO₂ nanoparticles in contact, while only one O-bridging of surface Ti atoms remains reversible: the activation energy of the aggregation process *E*_a = 0.33 eV has been reported.

The basic idea of this previous consideration is that the induction rate (10) defined from the induction time measurements also defines the initial aggregation kinetics, which can be expressed as

$$d\mu_2/dt \propto dI/dt \quad (13)$$

where *I* is the light intensity scattered by the colloids.

As our results show (see Fig. 11), the aggregation kinetics of the TiO₂ nanoparticles in presence of HyU reflects similar tendency and the induction rate was found to be proportional to the initial slope of the curves *I*(*t*). We therefore suppose that the basic mechanism of the particles agglomeration proposed by Rivallin *et al.*^{25,26} is conserved. Below we consider the expression for the induction rate in order to explain the process acceleration in presence of the dopant.

The rate of the RLA process can be expressed in terms of the particles collisional frequency *ν*_{coll}, their lifetime in a

Fig. 11 Correlation between the induction rate and the initial slope of the $I(t)$ curves in Fig. 1.

collision τ_{coll} and reaction constant k (oxolation reaction involving surface Ti atoms of two particles in collision):

$$R_{\text{ind}} = \nu_{\text{coll}} \cdot \tau_{\text{coll}} \cdot k \quad (14)$$

In 2-propanol solutions ν_{coll} is only a function of temperature and initial TTIP concentration, which were kept constant in the current experiments. According to Azouani *et al.*,²⁸ the monodispersed nuclei are formed at $H \geq 2.0$ in our experimental conditions, which implies $k = \text{const}$. As a result the expression (14) can be reduced to

$$R_{\text{ind}} = K \cdot \tau_{\text{coll}} \quad (15)$$

where K is a constant.

We suppose that HyU grafted to the surface of one nanoparticle can attract another TiO_2 particle by forming a weak binding with surface Ti atom.

This bounding increases τ_{coll} . Indeed, if the bonding energy of (16) is δE , its dissociation rate can be expressed as

$$r_{\text{diss}} = \tau_0^{-1} \cdot \exp(-\delta E/kT) \quad (17)$$

and the corresponding collisional lifetime becomes

$$\tau_{\text{coll}} = \tau_0 \cdot \exp(\delta E/kT) \quad (18)$$

where τ_0 stands for the time of a collision between two particles when no binding is formed.

In a similar way, the collisional lifetime increases further when several (n) HyU molecules are grafted on the TiO_2 particle surface.

$$\tau_{\text{coll}} = \tau_0 \cdot \exp(n \cdot \delta E/kT) \quad (19)$$

We now relate the n value to the HyU and TTIP concentrations (respectively C_{HyU} and C_{Ti}). We suggest that only a part of HyU molecules grafted on TiO_2 nanoparticle can contribute to the bonding formation. This fraction $\gamma = l_{\text{OCNO}}/2R_{\text{particle}} \approx 0.076$ can be estimated from the contact surface between two nanoparticles of radius 2.5 nm and the OCNO group length $l_{\text{OCNO}} \approx 3.8 \text{ \AA}$. Because HyU molecules take only the surface sites, their surface density is proportional to the nanoparticles concentration in the colloid. The number of Ti per nanoparticle (n_{Ti}) can be estimated from the known particle radius

$r_p = 2.5 \text{ nm}$, length of the surface alkoxy group $l_a = 0.4 \text{ nm}$, and interatomic Ti–Ti distance $l_{\text{Ti}} = 0.30 \text{ nm}$:

$$n_{\text{Ti}} = ((r_p - l_a)/l_{\text{Ti}})^3 \approx 350 \quad (20)$$

Then we can obtain

$$n = \gamma C_{\text{HyU}} n_{\text{Ti}} / 2C_{\text{Ti}} = 180 C_{\text{HyU}} \quad (21)$$

where $C_{\text{Ti}} = 0.146 \text{ M}$ is used in the present experiments. Finally, summarizing eqn (15), (19) and (21) we obtain the expression for the reaction rate

$$R_{\text{ind}} = \tau_0^{-1} \cdot \exp(180 C_{\text{HyU}} \delta E/kT) \quad (22)$$

The fit by eqn (22) of the experimental kinetics data presented in Fig. 3b in semi-logarithmic frame results in the exponential factor of

$$180 \delta E/kT = 350 \pm 30 \quad (23)$$

in M^{-1} . This provides an estimation for the weak binding energy of the complex (16): $\delta E = 50 \pm 5 \text{ meV}$.

This last value is characteristic of weak hydrogen bonds. Such bond may be formed between the oxygen atom of a HyU molecule, which double-bond is weakened at grafting onto a TiO_2 nanoparticle (Np1), and the hydrogen atom of a surface hydroxyl of another nanoparticle (Np2):

This may be also a bond between the double-bond oxygen of HyU (Np1) and four-coordinated surface Ti atom (Np2):

Another interesting experimental observation concerns exponential dependence of the induction kinetics on the hydrolysis ratio H (Fig. 3a). This fact can be rationalized in the framework of the proposed mechanism (24a) and not (24b). According to the slopes difference between the $r(C_a, H)$ curves in Fig. 3(a,b), the induction kinetics assisted by the addition of HyU is almost 7 times faster than that by water. However, the same mechanism (24a) is responsible for both observations. This can be explained by the reversibility of the hydrolysis reaction

Indeed, because of (25) the number density of surface hydroxyls onto the TiO_2 nanoparticles is lower than that of the added water molecules to the sol–gel solution. Taking into account the experimental observations, about 12% of added water form surface hydroxyls. This sets the equilibrium of eqn (25) strongly shifted to the left.

Our finding confirms the “catalytic” action of water molecules in the sol–gel process. In fact, water maintains surface hydroxyls through reversible hydrolysis reactions (25), which retain two nanoparticles in collision for a time necessary for production of a critical number k of the condensed bonds Ti-O-Ti ($k = 2$ according to Rivallin *et al.*^{25,26}). In view of its low equilibrium constant, a contribution of the hydrolysis reaction (25) in the activation energy of the induction kinetics $E_a = 0.33 \text{ eV}$ reported in ref. 26 can not be excluded.

Conclusion

The OCN-doped TiO₂ nanoparticles were prepared by sol-gel route starting with titanium tetraisopropoxide precursor. The N-containing dopant (hydroxyurea) is injected to the solution at the nucleation stage. Turbulent mixing of reactive fluids, injected at high Reynold's numbers above 4500, enables homogeneous reaction conditions in the reactor bulk and monodispersity of the produced doped clusters/nanoparticles.

The doping results in a strong yellow coloration of the nanocolloids due to the absorption band in the spectral range 380–550 nm and accelerates the aggregation kinetics of both nuclei and sub-nuclei units (clusters). FTIR and Raman analyses evidence the formation of the HyU–TiO₂ complex. The reaction kinetics then accelerates due to a longer collisional lifetime of two nanoparticles induced by the formation of a weak =O...Ti bond. The OCN group bonding to titanium atoms produce a weakening of its C=O double bond and a hardening of CN and NO bonds. The complex loading attains ~10 mol% with no signs of the doping saturation.

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