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Photocatalytic properties of aqueous systems containing TiO_2 nanoparticles

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ABSTRACT

This work describes the aging of aqueous colloidal TiO_2 nanoparticles at different temperatures and pH values. Emphasis was particularly given to the behaviour in the alkaline region, since this has not yet been properly reported. Aging of colloidal TiO_2 suspensions has previously been investigated using spectroscopic methods (band gap energy determination) and a dynamic light scattering method (particle size determination). The photocatalytic activity, representing the most important property of TiO_2 nanoparticles, was determined through the quantum yield of 4-chlorophenol degradation. It was found that the size of acidic colloidal TiO_2 particles depends on the storing temperature; lower temperature leads to a small increase in particle size. The process of aging of TiO_2 nanoparticles consists in slow re-crystallization that leads to slightly larger particles, and it seems that this process is faster at higher temperatures. In alkaline environments it was found that the change in particle size depends on the type of alkaline reagent used (KOH and NH_4OH), on its concentration and also on the starting concentration of the TiO_2 suspension. In contrast to the quantum yield of acidic TiO_2, the quantum yield of alkaline suspensions decreased during aging.

1. Introduction

Photocatalytic materials, such as colloidal titanium dioxide nanoparticles, are very promising materials from an environmental perspective. The main problem in the use of colloidal suspensions of photocatalyst is separation from the reaction system. The properties of nanosized titanium dioxide particles are highly size-dependent, especially for particles with diameters smaller than 10 nm [1]. For example, it has been found that anatase is more stable at the nanoscale, below 15 nm in diameter, but for larger bulk particles rutile is more thermodynamically stable [2].

Nanoparticles of TiO_2 may be prepared by hydrolysis of $TiCl_4$ [3–7] leading to highly acidic colloidal suspensions. Therefore it is of interest to study the properties of TiO_2 colloidal suspensions not only in acidic conditions but also in alkaline. It is known that the stability of nanoparticles of TiO_2 and the formation of aggregates are a function of pH. TiO_2 nanoparticles are more stable at pH values that are far from their point of zero charge, pzc (defined as the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface [8]). For nanoscale particles the value of pzc changes with size in the range 4.8–6.2 [9,10]. When the pH approaches these values, repulsive forces between nanoparticles decrease, which leads to aggregation.

Another important parameter affecting the properties of TiO_2 colloidal suspensions of TiO_2 is temperature. The temperature effect during suspension preparation [11] and short time treatment at temperatures higher than room temperature [12] have been reported, but there are few studies of the behaviour of colloidal suspensions during long time aging at constant temperature.

Aging of colloidal suspensions of TiO_2 nanoparticles has been studied at single pH (acidic) and a single temperature (4 °C) [3]. It was found that during aging the size of the particles increased, which also led to changes in other properties such as a decrease in band gap energy and a related increase in photoactivity. At other temperatures and in alkaline pH conditions this phenomenon has not yet been studied. Thus, in the present study we investigated the influence of both significant parameters pH and temperature, not

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only on particle size, but also on band gap energy and photocatalytic activity.

2. Experimental

2.1. Preparation of colloidal suspension of TiO_2 nanoparticles

The TiO_2 nanoparticles were prepared in the form of an aqueous suspension: 3.5 ml of pure $TiCl_4$ (99% Fluka) was added drop-wise under vigorous magnetic stirring to 900 ml of distilled water cooled to 1 °C in ice bath. After 30 min of further slow stirring, the formed colloidal suspension was dialyzed (Spectra/Por 7 Membranes (EW-02902-58, MWCO 1000, flat width 45 mm, diameter 28.6 mm)) against distilled water until the pH of the colloidal suspension reached a value of 2.5 at room temperature. Then the required amount of distilled water was added to top up the total volume of the suspension to 960 ml which corresponded to the final TiO_2 concentration of 33.3 mmol/dm^3.

The titration of the TiO_2 nanoparticles suspension was performed using two different alkaline reagents (KOH (90% Sigma–Aldrich) and NH_3 (99.9% Fluka)). The concentrations of KOH were either 0.2 or 1 mol/dm^3, whereas the concentrations of NH_4OH were 0.5 or 1 mol/dm^3. Various volumes of basic agents were added to the acidic suspension in one fast addition, under ultrasound. Then the suspension was kept under ultrasound for less than 1 min.

2.2. Particle size measurement

Measurement of the particle size was performed on a Zetasizer Nano (Malvern Instruments) working on the principle of dynamic light scattering [13,14]. The particle size of the sample TiO_2 suspensions was measured after different time periods and at different pH values. The standard deviation of the measured particle size was ±0.6 nm.

2.3. Solid state particle characterization

To access powder from the suspension of TiO_2, 20 ml were dried at ambient temperature. The powders were then analyzed using an X'Pert Pro Philips diffractometer with diffracted beam graphite monochromator using a Cu Kα radiation source. Diffractograms were recorded in the 2θ range of 15–70° with a step of 0.013° and a counting time per step of 20 s.

Raman spectra were recorded at room temperature in air using a 514 nm laser line of an Ar^+/Kr^+ laser and a JOBIN YVON T64000 triple spectrometer, equipped with an Olympus confocal microscope using 50× magnification and a nitrogen-cooled CCD detector. Low-frequency Raman measurement was performed in backscattering geometry. The wavelength of the excitation source was 514.5 nm. The power of the excitation beam was fixed at 200 mW. Spectra were acquired (2× 600 s) in the frequency range 50–600 cm^{-1} and 200–1800 cm^{-1} using a triple and single detector configuration, respectively. Profile analysis of the Raman bands was performed using a Lorentzian function.

2.4. Measurement of quantum yield

The quantum yield represents the photocatalytic activity of a photocatalyst. This measurement reflects the efficiency of the photochemical process. In terms of photochemistry, it is very important to control the change in quantum yield during aging of the nanoparticles. In our case we measured the quantum yields of photocatalytic degradation of 4-chlorophenol. These measurements were performed in 2 cm (path length) cylindrical quartz cells. The light source was a high-pressure mercury lamp (Osram HBO 1000 W) equipped with monochromator (Jobin Yvon). The monochromatic irradiations were carried out at a wavelength of 365 nm. The intensity of the light source was measured by actinometry (2.18×10^{14} photons/(s cm^2)). Measurement by actinometry is described in [15] and calculation of quantum yield was carried out using formulae described in [16].

The change in concentration of the 4-chlorophenol during the measurement of quantum yield was measured by high-performance liquid chromatography (HPLC), the starting 4-CP concentration being 10^{-4} mol/l. The measurement was performed on an Alliance® HPLC System chromatograph. The flow rate was 1 ml/min and the eluent was a mixture of pure water and methanol (50/50, v/v). The column used was a Lichrosphere (Merck) RP18 (reverse phase) of 125 mm × 4.6 mm with a particle diameter of 5 μm and a pore diameter of 100 Å. Every sample was injected a minimum of two times and the obtained error was less than 10%.

2.5. UV–VIS absorption spectroscopy and band gap energy

The measurement of UV–VIS spectra (in the range 200–800 nm) was performed on a Varian Cary 100 Scanning UV–VIS Spectrophotometer and a Perkin-Elmer Lambda 19.

For the absorption spectra of colloidal suspensions containing very small particles of titanium dioxide, as well as for other semiconductor materials, the exponential growth of absorbance from the specific wavelength is characteristic. For very small particles of semiconductor (nanometer size) this so-called spectral edge, compared with the same material of macroscopic dimensions, is shifted to shorter wavelengths in proportion to the reduction in particle size. The resulting spectral blue shift is one sign of the quantum size effect, which is characteristic for objects on the transition between the isolated molecules and the macroscopic solid phase. In this study, the average band gap energies were determined on the basis of the absorption spectra of very small colloidal suspensions of semiconductor particles using a procedure described in the literature [17].

3. Results and discussion

3.1. Influence of pH

One of the most important properties of the TiO_2 colloidal suspensions is the particle size. Because in the nanometer range dispersed particles display specific physico-chemical properties and lead to transparent suspensions, specific attention must be paid to the change in particle size under various conditions. In our synthetic process, the colloidal TiO_2 suspension obtained had a strongly acidic pH (around 2.5). For environmental applications, the stability of the TiO_2 colloidal suspension under basic conditions is of great interest. Thus, a series of titrations were performed using two types of alkaline reagent KOH and NH_4OH at different concentrations, 0.2 and 1 mol/dm^3 for KOH and 0.5 and 1 mol/dm^3 for NH_4OH. It should be emphasized that the particle size in acidic suspension was 7 nm which compares well with other sources, where sizes of 20 nm [5] and 4 nm [11] were reported. The differences in size are caused by slight differences in the method of preparation (different concentrations and temperatures).

In a preliminary step, the pH was changed to the alkaline region for two different starting concentrations of freshly prepared TiO_2 colloidal suspensions, namely 33.3 and 6.3 mmol/dm^3. Using the most concentrated colloidal TiO_2, the particle size obtained after titration was systematically bigger than that obtained from dilute suspension whatever the titrating agent. Thus in the following, only results obtained from dilute TiO_2 will be presented. Upon titration, it was systematically found that the colloidal suspension coagulates for pH values in the range 4–8 (see Table 1). This phenomenon

Table 1
Dependence of particle size on pH for 6.3 mmol/l TiO$_2$ suspension.

pH	KOH		NH$_4$OH	
	1 mol/l	0.2 mol/l	1 mol/l	0.5 mol/l
	Size (nm)			
2.5	7	7	7	7
3.5	315	303	271	404
6	Precipitated	Precipitated	Precipitated	Precipitated
10	208	255	79	110
11	42	93	25	27

totally hampers any measurement of the particle size. Solutions were highly turbid (at pH either 3.5 or 10) and at pH 6 particles began settling due to precipitation. The point of zero charge (pH$_{zpc}$ = 5.3) of TiO$_2$ being in this range, the surface charge of the particles decreased strongly leading to aggregation, in agreement with other studies [9,18]. However, when the pH reached values higher than 10, the change in particle size was limited. Titration up to pH 11.0 ± 0.2 led to clear basic colloidal suspensions of TiO$_2$. It appears that titration using NH$_4$OH solutions induces a smaller increase in particle size compared to KOH (Fig. 1A). Indeed, a particle size of 25 nm was obtained using 1 M NH$_4$OH, whereas the use of 1 M KOH led to a size of 42 nm. In parallel the use of dilute alkaline solutions led to opposite effects, particles of 27 nm and 93 nm, respectively, were prepared for 0.5 M NH$_4$OH and 0.2 M KOH. These results highlight the strong influence of the nature and concentration of the titrating agents used to modify the surface charge of TiO$_2$ particles. In all these experiments the increase in particle size arises mainly from the Ostwald ripening process [19], coalescence or aggregation.

The preparation of alkaline TiO$_2$ colloidal suspensions was described in [18]. However, the preparation method is too different from ours and the particles produced were less homogeneous in size. Particles prepared at pH 10 had a size of ~50 nm and contained aggregates of ~120 nm; at pH 12 the particle size was ~20 nm and the suspension also contained aggregates of size ~80 nm.

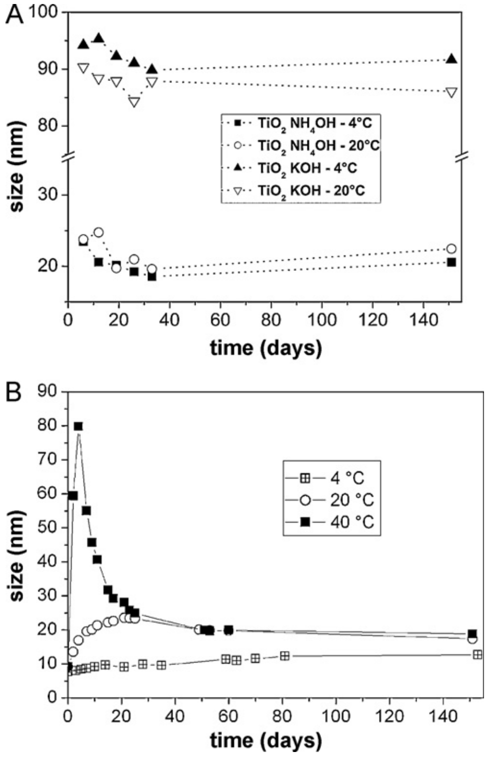

Fig. 1. (A) Dependence of particle size on age of basic colloidal suspension (6.3 mmol/dm^3 TiO$_2$), pH 11.0 ± 0.3 and (B) dependence of the size of TiO$_2$ particles on the age of acidic colloidal suspension (6.3 mmol/dm^3 TiO$_2$), pH 2.5 ± 0.3.

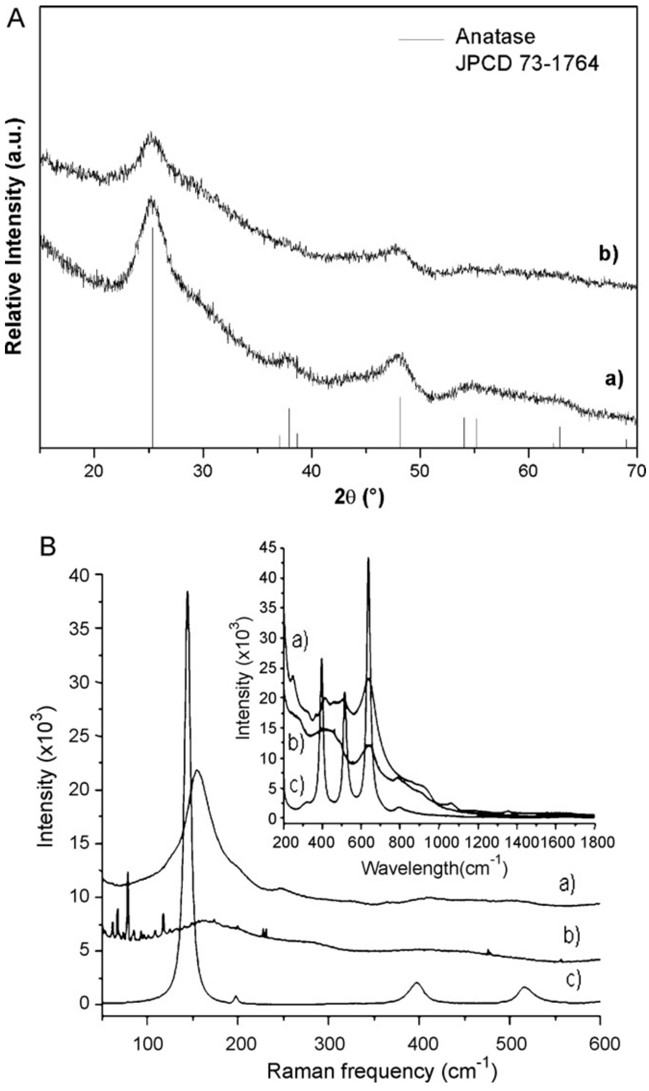

Fig. 2. (A) PXRD and (B) Raman spectra of TiO$_2$ obtained by drying of (a) an acidic colloidal suspension, (b) a basic colloidal suspension (NH$_4$OH, 1 M) and (c) TiO$_2$ anatase.

To obtain better insight into the structure of the TiO$_2$ upon titration, X-ray powder diffraction and Raman spectroscopy experiments were performed on both acidic and basic TiO$_2$ suspensions (Fig. 2). The X-ray patterns show rather large peaks of low intensity which correspond mainly to the diffraction lines of the anatase phase. The titration clearly induces an enlargement of the reflection lines, probably due to partial amorphisation of the particles under basic conditions.

The Raman spectra of the freshly prepared acidic and basic TiO$_2$ nanoparticles were compared with the spectrum of TiO$_2$ from Degussa. This reference material corresponds to the anatase phase (tetragonal, *I*41) whose Raman vibrations appear at 144 cm^{-1}, 197 cm^{-1}, 396 cm^{-1}, 514 cm^{-1} and 640 cm^{-1} corresponding, respectively, to the Eg(1), Eg(2), B1g(1), A1g and Eg(3) active modes [20]. Raman spectra of the acidic TiO$_2$ display large vibration bands (155 cm^{-1}, 413 cm^{-1}, 504 cm^{-1} and 635 cm^{-1}) characteristic of the anatase structure with low crystallinity. A slight shift in the peak positions occurs compared to the Degussa TiO$_2$ compound. However, in the 200–600 cm^{-1} frequency region, additional peaks are observed at 245 cm^{-1}, 323 cm^{-1}, 364 cm^{-1} and 459 cm^{-1}. These peaks may be associated with the presence of Brookite (orthorhombic, *Pbca*), another polymorph of TiO_2, whose Raman modes are reported to appear at 156 cm^{-1} (A1g), 245 cm^{-1} (A1g), 287 cm^{-1} (B3g), 320 cm^{-1} (B1g), 365 cm^{-1} (B2g), 637 cm^{-1} (A1g) [21]. After basic titration, a clear enlargement of the Raman peaks simultaneous with a deep decrease in the band intensities is observed due to a large decrease in the crystallinity. Even though some spectral features of anatase remain, the occurrence of the amorphous TiO_2 phase seems to prevail.

3.2. *Effect of temperature and aging*

Previous studies have demonstrated that aqueous TiO_2 colloidal suspensions undergo structural changes with time due to an increase in the average particle size [3].

In this study, the aging of both acidic and basic colloidal suspensions of TiO_2 was studied at three different temperatures of storage 4 °C, 20 °C, and 40 °C to determine the best way of keeping the particles for long time periods. Fig. 1A and B shows the particle size dependence of TiO_2 colloidal solutions, kept at different temperatures, versus the aging time.

For the acidic suspension pH 2.5 (Fig. 1B) the change in particle size is the slowest at 4 °C. After five months, the size increase does not exceed 5 nm and the suspension retains its transparency. In the first 10 days, there is only a slight increase in particle diameter from 7 to 9 nm. After three months, the average particle size remains stable at 12 nm. At 20 °C, the increase is faster; in the first 20 days the size increases from 9 nm to 24 nm. Then the particle size starts to slowly decrease and appears to be stabilized at 17 nm after five months. Note that the suspension in these conditions was slightly turbid after less than 10 days and this appearance did not disappear after an extended period of storage. The biggest increase in particle size was observed for a temperature of 40 °C. Initially, a rapid increase up to 80 nm is observed and then a continuous decrease to 20 nm occurs. This fast size increase can be explained by the formation of agglomerates as a consequence of the moderate thermal treatment. However, these agglomerates were not stable and broke down with time. In this case the suspension was very turbid after two days of storing at 40 °C. This white turbidity did not decrease, even after more than 50 days, whereas the particle size was almost the same as for temperature maintained at 20 °C, showing that the suspension still contained large agglomerates.

For the basic TiO_2 colloidal suspensions obtained using 0.5 mol/dm^3 NH_4OH and 0.2 mol/dm^3 KOH, only aging at 4 and 20 °C was followed because we found that aging at 40 °C does not allow storage of the colloidal suspensions. Indeed, such a high temperature induced precipitation of the nanoparticles. As shown in Fig. 1A, the particle size was measured just after synthesis and titration and then periodically up to five months. The particle size decreased slightly with time. However, it should be underlined that after titration with NH_4OH and storage at 4 and 20 °C the particle size remained approximately constant and comparable with that of a freshly prepared acidic suspension of TiO_2.

The structural changes of the TiO_2 particles under different conditions of storage were investigated in acidic suspensions. The PXRD patterns clearly show a net increase in the crystallinity of the phases induced by both temperature and time of aging (Fig. 3). The reflection lines are typically those of the anatase phase, regardless of the conditions used for storing. However, simultaneously with the increase in the crystalline anatase phase, the formation of Brookite is observed. From the PXRD diagrams, the size of the coherent domains have been estimated in applying the Scherrer formula to the 1 0 1 line width at half maximum and these results are displayed in Table 2. The values

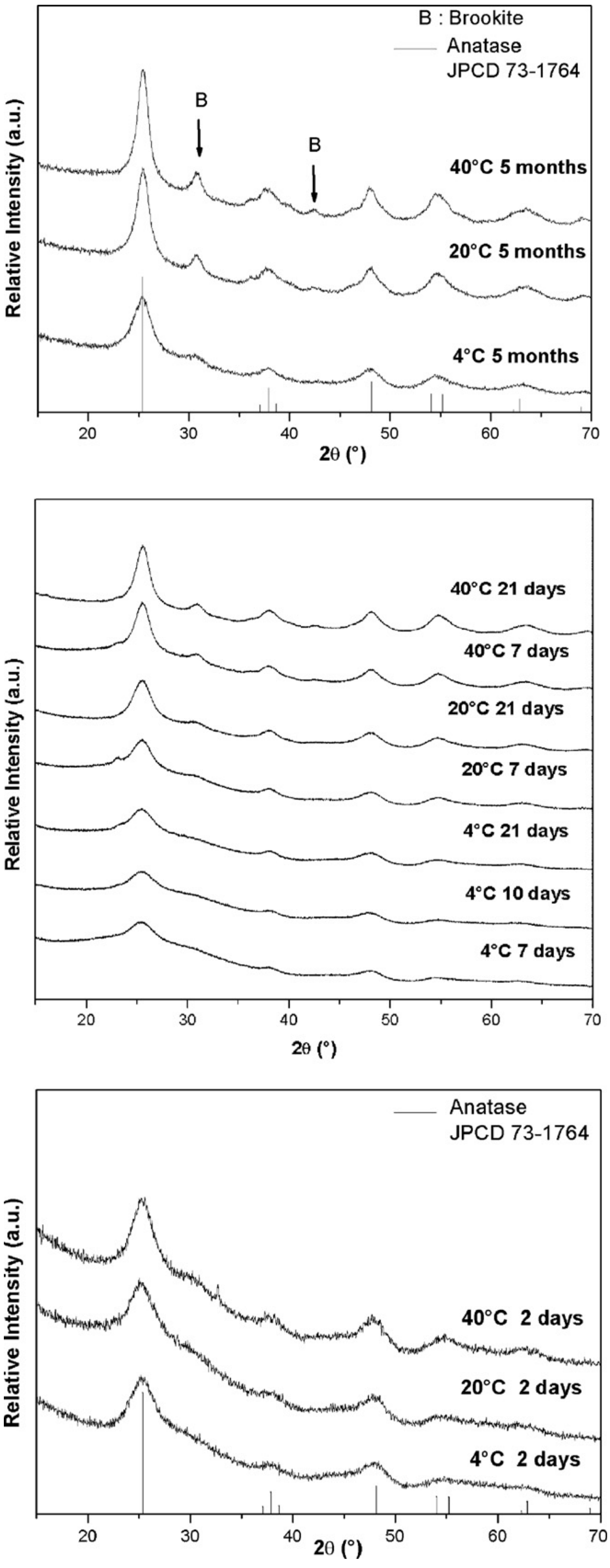

Fig. 3. PXRD of TiO_2 from acidic suspension after different times of storage at 4 °C, 20 °C and 40 °C.

Table 2
Size of the coherent domains determined from the 1 0 1 diffraction line width and position of the Eg band from Raman spectra.

TiO_2 sample	XRD D_{101} (nm ± 0.5)	Raman Band position
4 °C – 7 days	2.3	–
4 °C – 10 days	3.0	–
4 °C – 21 days	3.2	–
4 °C – 5 months	4.7	154.8
20 °C – 7 days	4.6	–
20 °C – 21days	5.0	–
20 °C – 5 months	6.7	153.2
40 °C – 7 days	6.0	–
40 °C – 21 days	6.2	–
40 °C – 5 months	8.2	151.8

clearly indicate an increase in the coherent domain size when the temperature of storage is higher. Systematically values calculated from XRD give smaller particle sizes than those measured by dynamic light scattering, suggesting either the formation of polycrystalline particles or the presence of an amorphous phase [22].

After 2 days of aging of acidic suspensions, the Raman peaks are large (Fig. 4). The low temperature treatment shows mainly the anatase Raman feature, with broad lines pointed at 417 cm^{-1} (B1g(1)), 514 cm^{-1} (A1g) and 637 cm^{-1} (Eg(3)). However the bands of Brookite also contribute to the general spectrum and appear more clearly when the storing temperature is raised at 40 °C. The effect of longer aging time clearly affects the structure as shown on the Raman spectra (Fig. 4B). The band widths decrease, the relative intensities change and the number of peaks increases as observed for colloidal TiO_2 aged for 5 months at 40 °C (Fig. 4B(d)) compared to colloidal TiO_2 aged for 2 days at 40 °C (Fig. 4A(d)). Both anatase and Brookite are present, the former being the major phase (Table 3). According to thermodynamic considerations the phase stability for the three polymorphs of TiO_2 decreases in the sequence: rutile > brookite > anatase [23]. Then the phase transition from anatase to Brookite may occur [24]. Anatase–Brookite phase transition is dependent on the nanoparticle size. Anatase has been reported to be more stable than Brookite with nanocrystals of size smaller than 11 nm [25] due to the favorable surface energy. However, with changes in grain size, anatase may be transformed to the Brookite polymorph by nanoparticle aggregation.

Colloidal solutions display Raman peaks shifted and broadened in comparison with Raman spectra of crystallized Degussa TiO_2. This is clear for the most intense Eg peak (140–150 cm^{-1}). This phenomenon is due to the nanosize properties of the colloidal TiO_2 which induces breakdown of the $k = 0$ Raman selection rule and the subsequent Raman activation of phonons far from the center of the Brillouin zone [26]. The ratio of the full width at half maximum (FWHM) of the Eg band (144 cm^{-1}) of TiO_2 nanoparticles over TiO_2 anatase (Degussa) was plotted versus the corresponding Raman frequency shift (%) (Fig. 5). Values of FWHM were determined by profile analysis using a Lorentzian function. The change follows the same tendency as that reported by Kelly et al. [27] showing the dependency of the FWHM-frequency on the particle grain size.

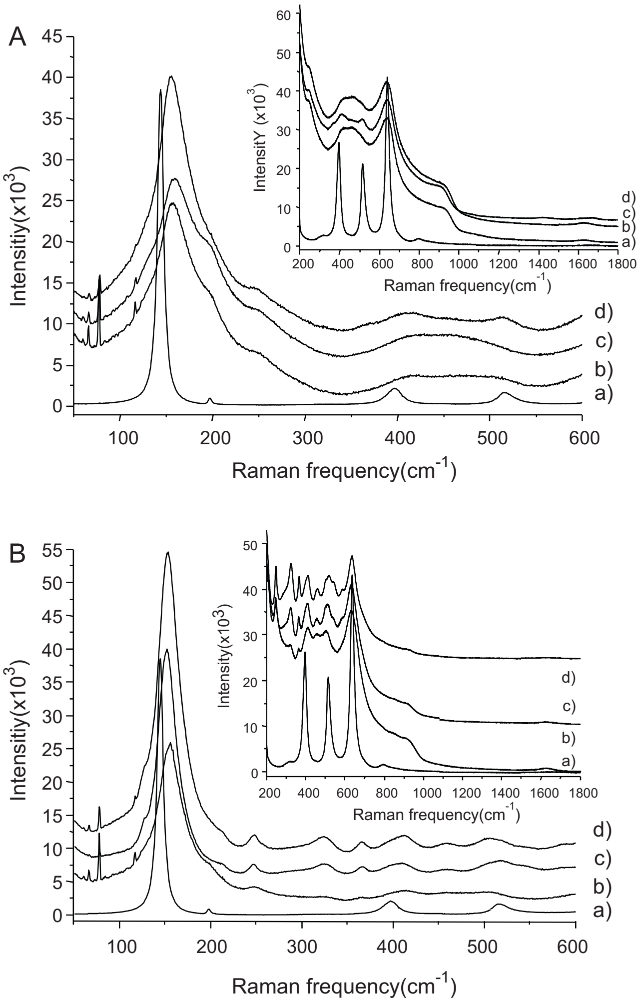

Fig. 4. Raman spectra of TiO_2 anatase (a) and (A) acidic colloidal TiO_2 aged 2 days and (B) acidic colloidal TiO_2 aged 5 months at 4 °C (b), 20 °C (c) and 40 °C (d).

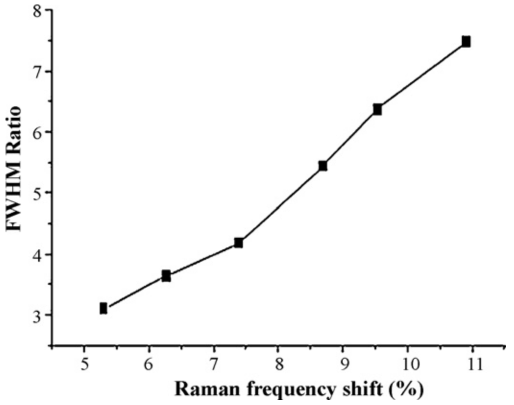

Fig. 5. FWMH ratio versus Raman frequency shift for the Eg(1) mode. Reference material is TiO_2 Degussa.

Table 3
Identification of Raman vibrations for colloidal TiO_2 aged 5 months at 40 °C.

	Bands															
	Eg	A1g	Eg	A1g	B3g		B1g	B2g	B1g	A1g						A1g
Colloid. TiO_2 5 months 40 °C		152	211	247	287		324	367		411	460	502	519	541	587	635
TiO_2 anatase	144		197			318			396				514			640
TiO_2 Brookite		156		245	287		320	365								637

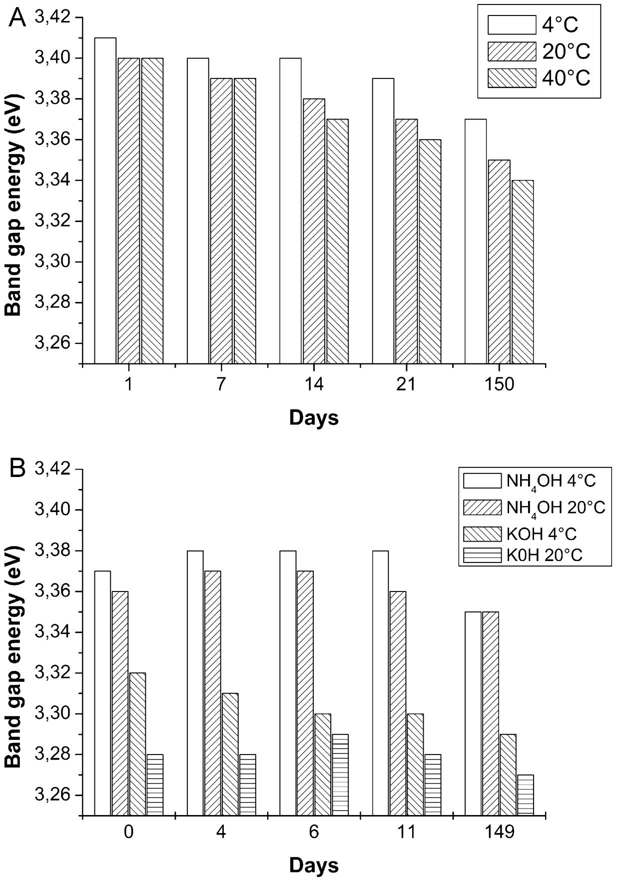

Fig. 6. Band gap energy values after different periods of storage (A) at different temperatures and (B) after titration with 0.2 M KOH or 1 M NH_4OH.

3.3. Evolution of the band gap energy and photocatalytic activity

3.3.1. Band gap energy measurement

Another important property of TiO_2 nanoparticles is their band gap energy. The change in band gap energy (E_g) with time of aging was determined from the absorption spectra. E_g for freshly prepared suspensions was about 3.4 eV. The increase in value of the band gap comparing to 3.2 eV reported for anatase solid phase is due to the so called quantum sized effect causing a blue shift in the UV–VIS spectra. For all acidic colloidal suspensions, the band gap energy decreased with time, the fastest decrease being observed for the suspension kept at 40 °C, and the slowest for that kept at 4 °C. All the values for the band gap energy are summarized in Fig. 6A.

In contrast to acidic suspensions of TiO_2, almost no change in band gap energy was observed under alkaline conditions (Fig. 6B) with time. This is in agreement with the finding that the size of particles in alkaline suspensions decreased very slowly with time. However, it is noteworthy that titration from freshly prepared acidic suspensions caused an immediate decrease of band gap energy on all occasions. In the case of KOH this decrease was higher (from 3.40 to 3.30 eV) than for NH_4OH (from 3.40 to 3.37 eV).

3.3.2. ***Photocatalytic activity***

The photocatalytic activity was measured using 4-chlorophenol as a model pollutant. In Fig. 7, the quantum yields of the photocatalytic degradation of 4-chlorophenol are shown. The quantum yields were calculated by the equation:

$$\Phi = \frac{(\Delta C/\Delta t)\cdot 6.023\cdot 10^{20}\cdot l_{\mathrm{irr}}\cdot A}{I_0\cdot(1-10^{-\mathrm{OD}_{\lambda_{\mathrm{irr}}}})},$$

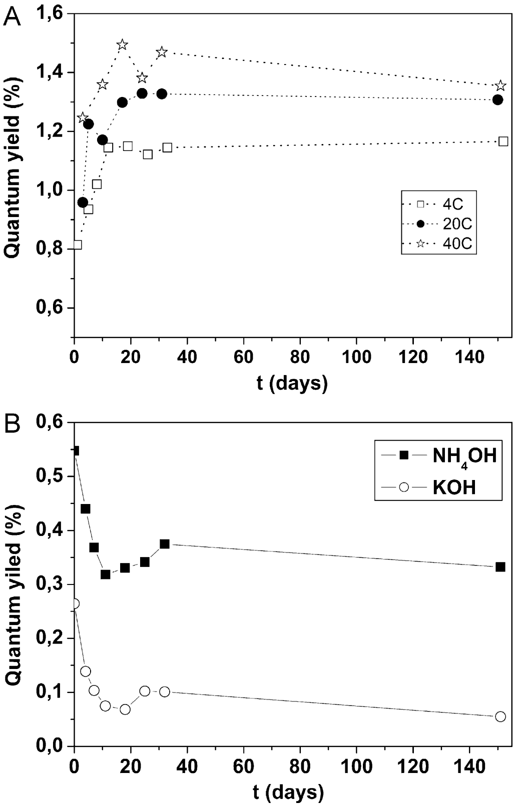

Fig. 7. Dependence of quantum yield of photocatalytic degradation of 4-chlorophenol on age of colloidal suspension (A) for storage at various temperatures and (B) after titration with 0.2 M KOH or 1 M NH_4OH and storage at 4 °C.

where $(1-10^{-\mathrm{OD}_{\lambda_{\mathrm{irr}}}})$ represents the percentage of light absorbed by the solution when $t=0$, I_0 is the number of photons entering the reaction cell per second (determined by actinometry), λ_{irr} is the irradiation wavelength, ΔC is the change in concentration with time in mol/dm^3, and l_{irr} is the length of the irradiation cell in cm.

For the freshly prepared suspension the starting value of the quantum yield of 4-chlorophenol degradation was 0.8%. When the suspension was kept at 4 °C, after 15 days the value increased to 1.1% and it remained almost unchanged for longer aging. For the suspensions stored at 20 °C and 40 °C, the quantum yield increased up to 1.3% and 1.4%, respectively, and then kept constant. The quantum yield for 4-CP photocatalytic degradation increased in the coarse of aging to reach a limiting value after about 30 days at all investigated temperatures. An analogous increase was observed in the mean particle size.

The quantum yields of the degradation of organic compounds obtained with a basic suspension of TiO_2 were always lower than those obtained with acidic TiO_2 suspensions. In contrast to the quantum yield obtained with acidic TiO_2 suspension, that obtained with basic suspensions decreased with time. The titration of colloidal suspensions from acidic to alkaline is connected with partial aggregation. This phenomenon is more pronounce with KOH, the starting average size being between 90 and 95 nm, while with NH_4OH it was only about 25 nm. The average size decreased slightly with time, probably due to partial deaggregation. Parallel to the deaggregation the quantum yield decreased slightly. This partial deaggregation is connected with synchronous amorphisation of the phase and decrease in the quantum yield.

4. Conclusions

With change of TiO_2 colloidal suspensions from acidic to alkaline environments, it was found that the change in particle size depended on the type of basic agent used (KOH and NH_4OH), on its concentration and on the starting concentration of TiO_2. The smallest change of particle size was observed after titration with NH_4OH and during aging of suspensions prepared from 6.3 mmol/dm^3 TiO_2 and 1 mol/dm^3 NH_4OH kept at 20 °C.

It was also found that the acidic suspension kept at 4 °C had the slowest change in particle size during aging. This suspension also had the slowest decrease in band gap energy and the quantum yield of photocatalytic degradation of 4-chlorophenol remained unchanged (∼1%). The suspension, after more than five months, was clear and without turbidity. Other acidic suspensions kept at higher temperatures were turbid after long time periods.

From the perspective of minimal particle size change, storing in acidic suspension at low temperature (e.g. 4 °C) is optimal, the particles remaining transparent. From best photoactivity, storing in acidic suspension at room temperature (e.g. 20 °C) is optimal. The quantum yield of 4-CP degradation for suspensions kept at 20 °C and 40 °C are similar (especially for long aging times); thus storing at room temperature avoids the additional cost of energy for heating.

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