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Synthesis and characterization of (photo)catalysts for water/wastewater treatment applications

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Water pollution

Water pollution by organic pollutants is an ever increasing problem for the global concerns. Pollutants such as industrial waste, sewage, wastes from agricultural production, but also the surrounding areas overcrowding contribute to infest the environment more than tolerable.



COMMERCIAL TECNOLOGIES FOR WASTEWATER TREATMENT

- Biological oxidation: not able to remove bio-recalcitrant compounds
- Chemical oxidation: extended treatment times and unpleasant taste
- Physical filtration: costly pumping, need to replace filters
- Ultraviolet disinfection: expensive parts

WHY PHOTOCATALYSIS ?

- The oxidant is atmospheric oxygen
- No consumption of expensive oxidizing chemicals
- No production of sludge
- The photocatalytic reaction may be driven by sunlight
- Able to the mineralization of the majority of organic pollutants
- Able to remove emerging contaminants and bacteria

Heterogeneous Photocatalysis



 A^{-} and D^{+} are highly reactive species which oxidize or reduce the compounds adsorbed on the catalyst surface

Semiconductors

Band gap of some semiconductors



The most used photocatalyst is TiO₂

Active under UV irradiation

TiO₂ preparation methods

- Sol-gel processes
- Thermal plasma synthesis
- Flame aerosol synthesis
- Spray Pyrolysis
- Hydrothermal synthesis

Sol-gel



E.I. Ko, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 1, Wiley/VCH, New York/Weinheim, 1997, p. 86.

Sol-gel

The sol - gel method is based on inorganic polymerization reactions, involving four basic steps:

- Hydrolysis
- Polycondensation
- Drying
- Thermal decomposition of precursors.

The precursors, usually, inorganic metal salts or metal organic compounds such as metal alkoxides.

When specifically preparing TiO_2 -based materials by sol-gel method, titanium alkoxide (*e.g.* titanium tetraisopropoxide) is often used as a precursor.

The main reactions at work can be divided into two steps:

1. first step: hydroxylation upon the hydrolysis of alkoxy groups M-OR + $H_2O \rightarrow M-OH + R-OH$

2. second step: polycondensation and/or alcohol condensation M-OH + HO-M \rightarrow M-O-M + H₂O M-OH + RO-M \rightarrow M-O-M + ROH

Thermal plasma and flame aerosol synthesis

Thermal plasma synthesis

Vapor-phase precursors with plasma \rightarrow rapid quenching \rightarrow homogeneous nucleation

High-purity particles

Flame aerosol synthesis

Oxidation of vapor in atmospheric pressure reactor (\rightarrow metal oxides, e.g. TiO₂)



Spray Pyrolysis

- Controlled composition and morphology
- Good crystallinity
- Uniform size distribution
- One-step method

Technique: Precursor solution is atomized and droplets poured into glass filter. Aerosol is heated and solvent evaporates in the reactor.

 \Rightarrow Anatase-titania particles with nominal size of about 10 nm



Maria Oksa, KE-31.5530 Nanoparticles, Ceramic nanoparticles for thermal spraying

Hydrothermal synthesis

A synthesis methodology where the hydrolysis of a titanium alkoxide in water forms titanium dioxide and the corresponding alcohol, as described in the following reaction

CH CH ---- Ti(OH)4 + 4 CH3-CH-OH (Hydrolysis step) $Ti(CH_3-CH-O)_4 + 4H_2O$ OH OH Ti(OH): HO-Ti-O-Ti-OH + H₂O (Condensation step) $Ti(OH)_4 +$ OH OH OH OH HO-Ti-O-Ti-OH 2 TiO₂ (Further condensation) 3 H₂O OH OH CH₃ CH₁ TiO₂ + 4 CH₃-CH-OH (Overall Reaction) $Ti(CH_3-CH-O)_4 + 2H_2O$

- It is carried out in a closed system (T: 110-200°C) and the content is covered after cooling down at room temperature.
- By controlling the temperature and the duration time of the treatment, various structure and morphology can be obtained

Catalysts characterization

- X-ray diffraction
 - Phase structure
- Raman analysis
 - Bulk and surface characterization
- Electron microscopes SEM, TEM
 - Microstructure, size and shape
- Specific surface area
- UV-Vis diffuse reflectance spectra (DRS)
 - Light absorption properties (Band-gap energy)

X-ray diffraction

X-ray powder diffraction (XRD) is a non-destructive analytical technique widely applied for the characterization of crystalline materials



When a monochromatic X-ray beam passes through a crystalline sample, it interacts with the electrons in the atoms, resulting in scattering of the radiation. If the matter is crystalline, *i.e.* the atoms are organized in planes and the distances between the atoms are of the same magnitude as the X-rays wavelength, constructive and destructive interference will occur.

"Bragg's Law":

 $n\lambda = 2d \sin\theta$

- where n is an integer
- λ is the wavelength of the X-rays
- *d* is the interplanar spacing generating the diffraction and
- θ is the diffraction angle
- λ and *d* are measured in the same units, usually angstroms.

X-ray diffraction instrumentation



X-ray diffraction

Scherrer's Formula for Estimation of Crystallite Size

• the crystallite size D can be estimated from the peak width with the Scherrer's formula:

 $D = k\lambda/B\cos\theta_{\rm B}$

Where λ is the X-ray wavelength, B is the full width of height maximum of a diffraction peak, θ_B is the diffraction angle, and k is the Scherrer's constant of the order unity for usual crystal.

Raman spectroscopy

- 1923 Inelastic light scattering is predicted by A. Smekel
- 1928 Landsberg and Mandelstam see unexpected frequency shifts in scattering from quartz
- 1928 C.V. Raman and K.S. Krishnan see "feeble fluorescence" from neat solvents
- 1930 C.V. Raman wins Nobel Prize in Physics
- 1961 Invention of laser makes Raman experiments reasonable





http://www.springerlink.com/content/u4d7aexmjm8pa1fv/fulltext.pdf

Raman spectroscopy

Raman spectroscopy is a technique for the identification and quantification of the chemical components of a sample.

When light is scattered by any form of matter, the energies of the majority of the photons are unchanged by the process, which is elastic or Rayleigh scattering.

However, about one in one million photons or less, lose or gain energy that corresponds to the vibrational frequencies of the scattering molecules. This can be observed as additional peaks in the scattered light spectrum. The process is known as Raman scattering and the spectral peaks with lower and higher energy than the incident light are known as Stokes and anti-Stokes peaks respectively.



http://www.springerlink.com/content/u4d7aexmjm8pa1fv/fulltext.pdf

Micro-Raman spectroscopy: Paman Instrumentation



SEM, TEM microscopy



R. Vijayalakshmi and V. Rajendran "Synthesis and characterization of nano-TiO2 via different methods" Arch. Appl. Sci. Res., 2012, 4 (2):1183-1190

Specific surface area

Surface area is described as the external surface area of a solid object including surface attributable to pores.

The value of specific surface area can be obtained through N_2 adsorption at -196 °C (physical adsorption)

Brunauer, Emmett and Teller (BET), most common method used to describe specific surface area:

The BET equation –

$$\frac{1}{W\left(\left(P_{0}/P\right)-1\right)} = \underbrace{\left(\frac{1}{W_{m}C}\right)}_{W_{m}C} \underbrace{\left(\frac{P}{P_{0}}\right)}_{W_{m}C} W_{m} = \frac{1}{s+i}$$
W= weight of gas adsorbed
P/P_{0}=relative pressure
Intercept (i) Slope (s)
W_{m} = weight of adsorbate as monolayer
C = BET constant

Neal Leddy, CMA Postgraduate Analytical Workshop 2010, Material Characterisation for Surface Area and Porosity utilising Gas Sorption

Specific surface area

• Total Surface area (S_t) can then be derived

$$S_t = \frac{W_m \ N \ A_{cs}}{M}$$

N = Avagadro's number (6.023×10^{23})

M = Molecular weight of Adsorbate

 A_{cs} = Adsorbate cross sectional area (16.2Å² for Nitrogen)

 Specific Surface Area (S) is then determined by total Surface area by sample weight

$$S = S_t / w$$

Neal Leddy, CMA Postgraduate Analytical Workshop 2010, Material Characterisation for Surface Area and Porosity utilising Gas Sorption

Specific surface area: instrumentation



EUROPEAN PHARMACOPOEIA 5.1 2.9.26. Specific surface area by gas adsorption

UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS): Solid samples



An **integrating sphere** (also known as an Ulbricht sphere) is an optical component consisting of a hollow spherical cavity with its interior covered with a <u>diffuse</u> white reflective coating, with small holes for entrance and exit ports.

Its relevant property is a uniform <u>scattering</u> or diffusing effect.

UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS): Solid samples Signal from UV-Vis DRS analysis

Absorbance (A)

Reflectance (R)

Kubelka – Munk function $F(R_{\infty})$ as a function of wavelength

$$\mathsf{F}(\mathsf{R}_{\infty}) = \frac{(1-\mathsf{R}_{\infty})^2}{2\mathsf{R}_{\infty}} = \frac{\mathsf{K}(\lambda)}{\mathsf{S}(\lambda)}$$

Where:

 \mathbf{R}_{∞} = reflectance of a layer so thick to completely hide the substrate e, i.e. the limiting reflectance that is not modified by any additional thickness of the same material

- $K(\lambda)$ = absorption coefficient
- S(λ) = scattering coefficient

UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS)



J. Aguado, R. van Grieken, M. J. Lopez-Munoz, J. Marugan; 2006

UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS): Band-gap evaluation

The Band-Gap is evaluated by plotting the function

□ $(F(R_{\infty})^* hc/\lambda)^2 vs h^*v$ and calculating the x intercept of a line passing through $0.5 < F(R_{\infty}) < 0.8$



C. Anderson, A.J. Bard, J. Phys. Chem. B 101 (1997) 2611.

Example 1: Sol-gel synthesis of N-doped TiO₂ photocatalysts

1. Sacco, O., Stoller, M., Vaiano, V., Ciambelli, P., Chianese, A., and Sannino, D. (2012). "Photocatalytic degradation of organic dyes under visible light on N-doped TiO2 photocatalysts." International Journal of Photoenergy, Volume 2012, Article ID 626759, 8 pages, doi:10.1155/2012/626759.

2. Rizzo, L., Sannino, D., Vaiano, V., Sacco, O., Scarpa, A., and Pietrogiacomi, D. (2014). "Effect of solar simulated N-doped TiO2 photocatalysis on the inactivation and antibiotic resistance of an E. coli strain in biologically treated urban wastewater." Applied Catalysis B: Environmental, 144, 369-378.

3. Vaiano V., Sacco O., Sannino D., Ciambelli P., (2015) "Photocatalytic removal of spiramycin from wastewater under visible light with N-doped TiO2 photocatalysts", Chemical Engineering Journal, Pages 3-8

Photocatalysts active under visible light

One of the major challenges for the scientific community involved in photocatalytic research is to increase the spectral sensitivity of photocatalysts to visible light, which composes the largest part of solar radiation.



Synthesis of N-doped TiO₂: sol-gel method



Catalysts characterization

- X-ray diffraction (XRD)
- Specific surface area (SSA)
- Raman spectroscopy
- UV-vis DRS
- TEM analysis

XRD Results

Catalysts	Crystallites size nm
Undoped TiO ₂	7
N1_1	16
N1_2	15
N1_3	16
N1_4	15
Scherrer eq. $< J$	$L >= \frac{k\lambda}{\beta\cos\theta}$

where D is the grain size; k is a constant (shape factor, about 0.9); λ is the X-ray wavelength;

 β is the full width at half maximum of the diffraction line and $% \beta$ is the diffraction angle corresponding to (1 0 1)

Only diffraction peaks related to TiO₂ in anatase phase

No presence of rutile phase

(101)



Raman and UV-vis spectra



Counts [a.u.]

Optimization of calcination time at 450°C



The band-gap energy for N_4 decreased as calcination time was increased up to 30 min .

For a calcination time higher than 30 min, the value of band-gap energy increased.

The amount of energy absorbed in the visible region reached the highest value for a calcination time of 30 min.



TEM analysis of N_4 sample



A JEM-2010F (JEOL) transmission electron microscope with field emission gun at 200 kV was used to obtain information on particle size and particle structure.

It is interesting to observe that N_4 sample has pseudo spherical crystallites.

Summary of characterization results (N-doped TiO₂)

Catalysts	TTIP volume [ml]	NH ₃ solution volume [ml]	N/Ti molar ratio	Crystallites size ² [nm]	SSA ³ [m²/g]	Band gap energy ⁴ [eV]
TiO ₂ ¹	25	0	-	7	171	3.3
N_1	25	25	4.6	16	75	2.6
N_2	25	50	9.3	15	80	2.6
N_3	25	75	13.9	16	75	2.5
N_4	25	100	18.6	15	80	2.5

¹TiO₂ by sol-gel method.
² from XRD analysis
³ from N₂ adsorption at -196 °C (BET method)
⁴ from UV-Vis spectra

Slurry batch Photoreactor



Methylene blue as model pollutant

The removal efficiency was measured by spectrophotometric and TOC analyses. CO, CO₂ and SO₂ evolved were monitored by specific continuous analyzers.

Photocatalytic activity results (MB degradation)



Photocatalytic activity results (MB degradation)





LMB:colourless

Photocatalytic activity results Antibiotics (spyramicin) removal



Photocatalytic activity results E.coli inactivation under solar simulated



Rizzo, L., Sannino, D., Vaiano, V., Sacco, O., Scarpa, A., Pietrogiacomi, D. *Effect of solar simulated N-doped TiO*₂ photocatalysis on the inactivation and antibiotic resistance of an E. coli strain in biologically treated urban wastewater Applied Catalysis B: Environmental Volume 144, January 2014, Pages 369-378

Example 2: Immobilization of N-doped TiO₂ on glass spheres via sol-gel route

- 1. Vaiano V., Sacco O., Sannino D., Ciambelli P., (2015) "Nanostructured N-doped TiO2 coated on glass spheres for the photocatalytic removal of organic dyes under UV or visible light irradiation", Applied Catalysis B: Environmental, Volume 170-171, Pages 153-161
- 1. Vaiano V., Sacco O., Pisano D., Sannino D., Ciambelli P., (2015) "From the design to the development of a continuous fixed bed photoreactor for photocatalytic degradation of organic pollutants in wastewater", Chemical Engineering Science, article in press.

Slurry reactor configuration: problems

Disadvantages of catalysts in aqueous suspension are (slurry reactor):

- •the damages of recirculation pumps
- separation of catalyst from reaction solution is needed

A valid solution is the use of immobilized and structured catalyst

One of the possible solution to solve this technical problem would be to realize heterogeneous fixed bed reactors, in which the photocatalyst is supported on transparent materials.

Immobilization of N-doped TiO₂

There is an important variety of materials that can be used for supporting TiO₂. The most studied are that ones based on glass, owing to their low cost and easy availability

Only few papers regard N-doped TiO₂ /immobilized systems mainly carried out through :

- 1. sputtering technique ¹
- 2. chemical vapor deposition¹.

No study developed a simple sol-gel method that uses ammonia solution as the only doping source. *1. D. Avisar, I. Horovitz, L. Lozzi, F. Ruggieri, M. Baker, M.L. Abel, H. Mamane, Journal of Hazardous Materials.* 244-245 (2013) 463-471.

Effect of sol-gel synthesis temperature on N-doped TiO₂



Triton X-100 in the sol–gel synthesis may provide a convenient way to prepare small sized particles:

- It was easily adsorbed on the surface of the crystal nucleus and hence probably hindered the further growth of these crystals;
- the adsorption of the surface-active agent may also stabilize the nanoparticles.

The use of a low pH limits condensation reactions, imposes a repulsive charge and limits the size of precipitates The obtained gel was calcined at 450°C for 30 minutes

Effect of sol-gel synthesis temperature on N-doped TiO₂

Catalyst	Syntesis reaction Temperature (°C)	Amount Triton X-100 (g)	TiO ₂ average crystallites size (1 0 1) (nm)	S.S.A (m²/g)
N-doped TiO ₂	0	0	17	30
0 NdT	0	5	9	98
-5 NdT	-5	5	8	108
-15 NdT	-15	5	7	128
-20 NdT	-20	5	6	147

The presence of Triton X-100 can effectively prompt the crystallization and inhibit the grain growth allowing to obtain smaller TiO₂ crystallites.





Effect of sol-gel synthesis temperature on N-doped TiO₂



N replaces O in the TiO₂ structure due to differences in binding properties meaning that the crystalline structure of anatase has been doped with nitrogen.

Preparation of structured catalyst



Preparation of structured catalyst

Catalyst

Glass

spheres

3 NdTgc

4 NdTgc

6 NdTgc



Preparation of structured catalyst





N-doped TiO₂ is more uniformly distributed on the surface of 4 Ndtcg and 6 Ndtcg as compared to 3 Ndtcg.

Photocatalytic tests in a batch photoreactor to optimize the amount of N-doped TiO₂ on glass support



Photocatalytic tests in a batch photoreactor to optimize the amount of N-doped TiO₂ on glass support



Up to four dip coating steps (4 NdTgc), photocatalytic activity markedly increased indicating that the overall of N-TiO₂ nanoparticles dispersed on the surface of glass spheres are effectively irradiated

Tests about the reuse of the optimized structured catalyst



The photocatalytic activity of 4 NdTgc was nearly the same indicating that there is no leaching of NdTgc from coated glass spheres.

These results also confirm the stability of NdTgc coated on glass spheres.

Photocatalytic tests in presence of visible and UV light on the optimized structured catalyst





It is possible to observe a progressive decrease of colour and TOC of aqueous sample as a function of irradiation time indicating that 4NdTgc sample is able to decolorize and mineralize MB and EBT both under UV and visible light irradiation.

1. Sacco O., Vaiano V., Han C., Sannino D., Dionysiou D., Ciambelli P., (2015) " Long Afterglow Green Phosphors Functionalized with Fen Doped Tio2 for the Photocatalytic Removal of Emerging Contaminants", Chemical Engineering Transactions, Vol. 43, 2107-2112.

SrAl₂O₄:Eu^{2+,}Dy³⁺ long persistent *phosphors (green)*

Under irradiation, some electrons and/or holes generated by the excitation are trapped in such localized levels. Due to a spatial separation between these defects and the luminescent centers (or more precisely, due to the lack of their orbital overlap), the probability of direct recombination is very low. Excited state $B A C_{d} C_{d} C_{d} C_{d}$

5_um

PHOSPHORS SPECTRUM EMISSION under UV irradiation (365 nm)





SEM-EDAX





Huihui Li,*,†,‡ Shu Yin,*,† Yuhua Wang,‡ and Tsugio Sato† Persistent Fluorescence-Assisted TiO2-xNy-Based Photocatalyst for Gaseous Acetaldehyde Degradation dx.doi.org/10.1021/es300987s | Environ. Sci. Technol. 2012, 46, 7741–7745



... how to use the photoluminescence of long persistent phosphors as light carriers in the photocatalytic process?

N-TiO₂ is an effective photocatalyst when exposed to visible light at wavelength lower than $490 \text{ nm} \longrightarrow \text{LIMITATION}$

In this case, for using the light emitted by green phosphors, it is necessary to formulate a photocatalyst able to work at wavelength lower than 600 nm

...development of different photocatalysts...

Some of the various approaches for making TiO_2 effective in visible light are doping TiO_2 especially with a metal substance such as Fe

\longrightarrow Fe-N-doped TiO₂

Fe-N-doped TiO₂ (FeNT) synthesis and characterization



Fe-N -doped TiO₂ vs N- doped TiO₂ : UV-vis



Structured Fe-N-doped TiO₂ on green phosphors (PEG 400° r PEG 200)





Washing with water and centrifugation

5. Calcination at 450°C for 30 minutes



Structured Fe-N-doped TiO₂ on green phosphors (PEG 400° r PEG 200)



SEM-EDAX









Long Afterglow Green Phosphors Functionalized with Fe-N Doped TiO₂ for the Photocatalytic Removal of Emerging Contaminants

Photoreactor configuration



Light source	Nominal Power	System efficacy	Life span
	[W]	[lux/W]	[hours]
lamp	15	3.0	16000-24000

Activity test with uv-visible light:Oxytetracycline



Thanks for your attention