Čari, neznanke in grožnje

Saša Novak[1], Martina Lorenzetti [1], Anja Drame [1,2]

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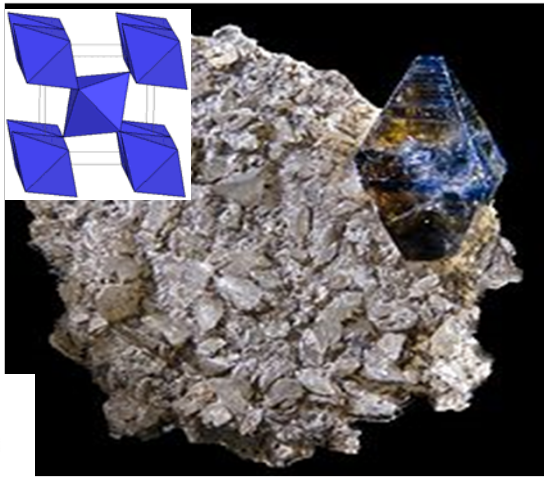
[2] Mednarodna podiplomska šola Jožefa Stefana

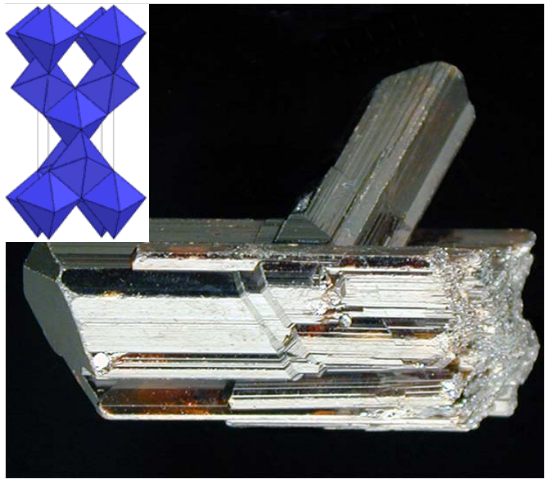
Safety
Quality
Traceability

TiO2

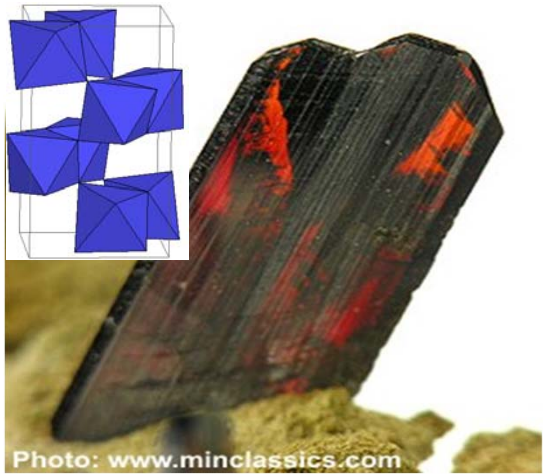
Anataz

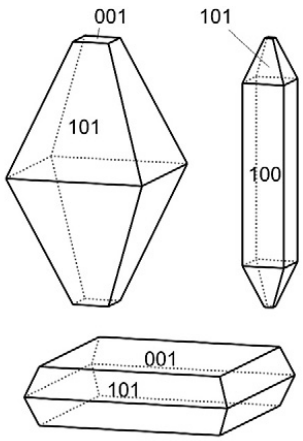


Rutil



Brukit

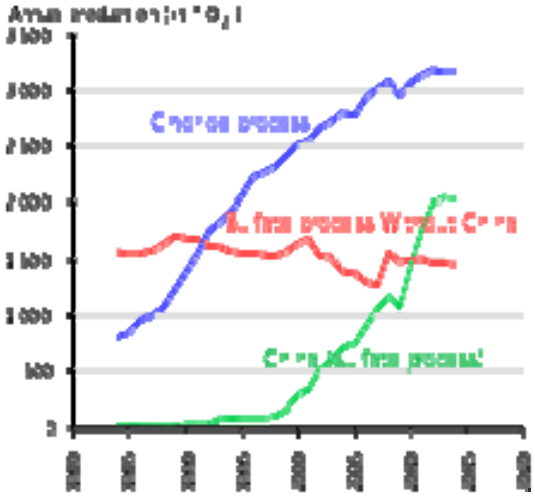


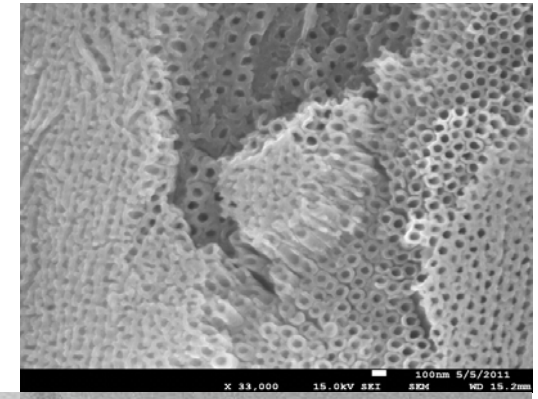


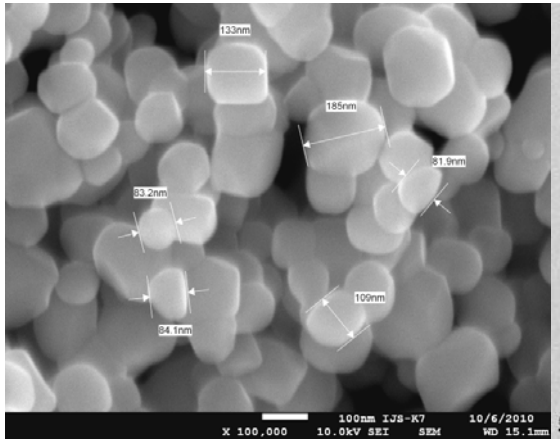
Ti: 0,63 ut. % v zemeljski skorji (ilmenit $FeTiO_3$, ..)

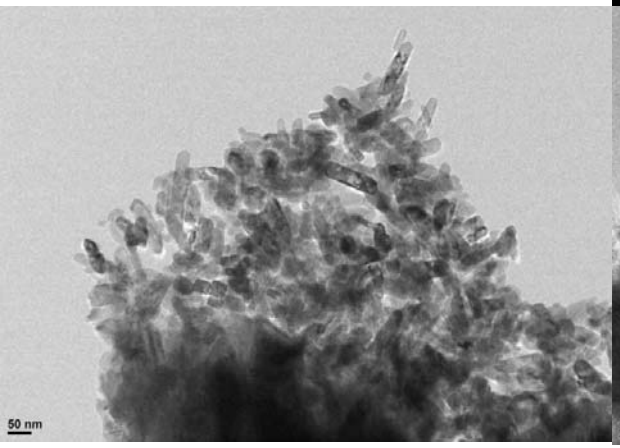
Sinteza iz ilmenita ($FeTiO_3$)

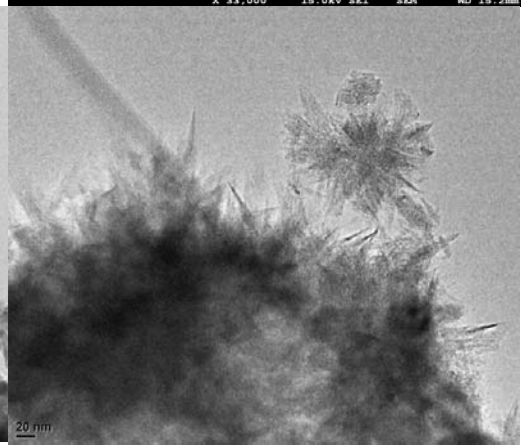
Proizvodnja TiO_2 nano-prahu: > 2 Mt/l



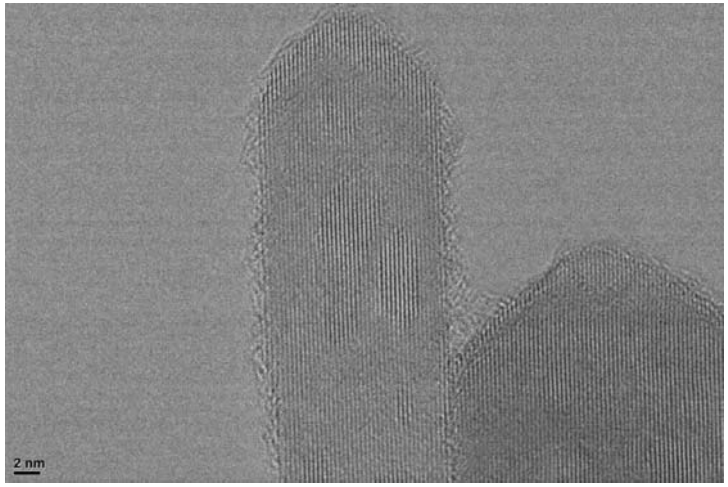


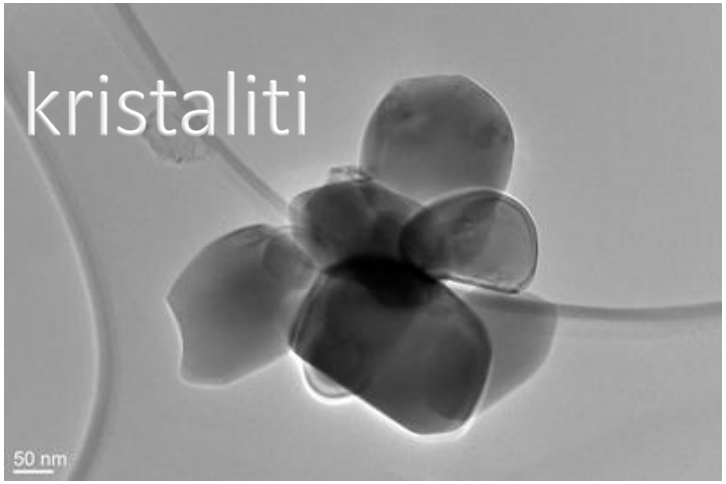




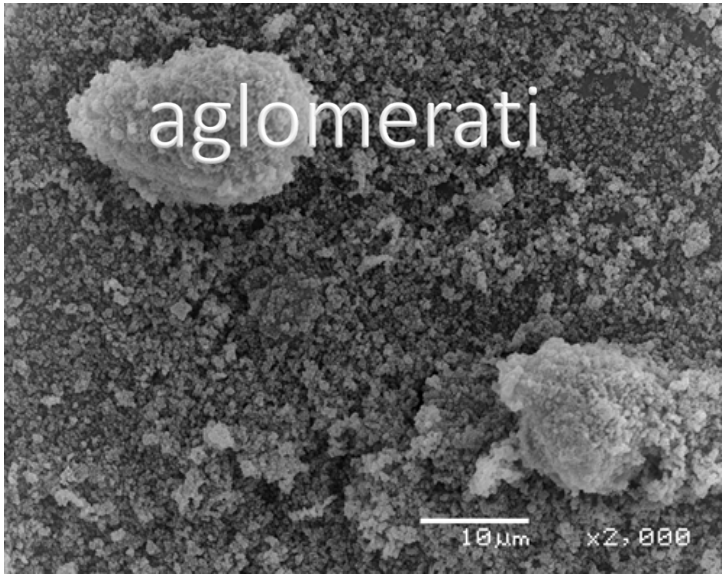


„DELCI“


2 nm

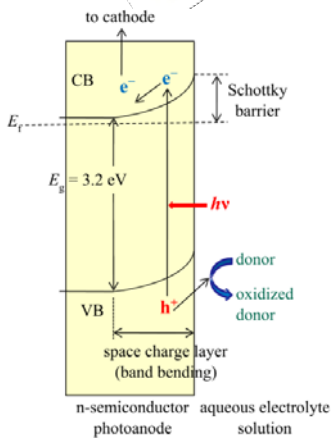

kristaliti
50 nm


agregati
1µm Anatas 8/5/2010
X 25,000 15.0kV SEI SEM WD 7.8mm


aglomerati
10µm x2,000

Tehnološko zanimiv

nima biološke funkcije v telesu



- **Visok lomni količnik n = 2.5 (visoka stopnja sipanja svetlobe)**

  (briljantno bel že v majhnih količinah)

- **Dobra absorpcija UV** (v Vis: zmanjšanje vrzeli z dopanti)

- **Polprevodnik**: prepovedan pas 3.0 (rutil) - 3.2 eV (anataz)

- **Fotokatalitski učinek (anataz >> rutil)**

  ➔ tvori elektronske vrzeli ➔ radikale

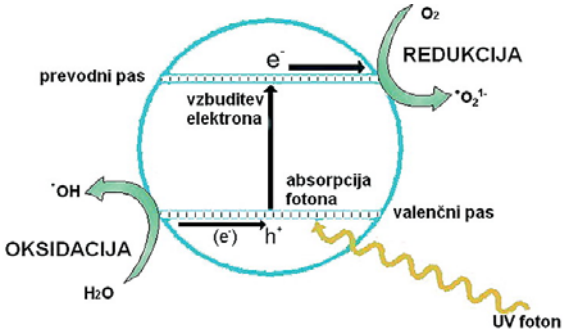
  cepi vodo (sončne celice)

  razgradi organske molekule

  antibakterijski in baktericiden učinek

- **„NETOPEN“**

- **“NI TOKSIČEN“** ?



5- 500 nm

belo

čisto

ekonomično

praktično

TiO_2 „prigrizek“: E171

Stabilizator (izdelki z manj maščobe)
barvilo (bele in svetle glazure)
antibakterijski dodatek, ..

FDA: <1 %

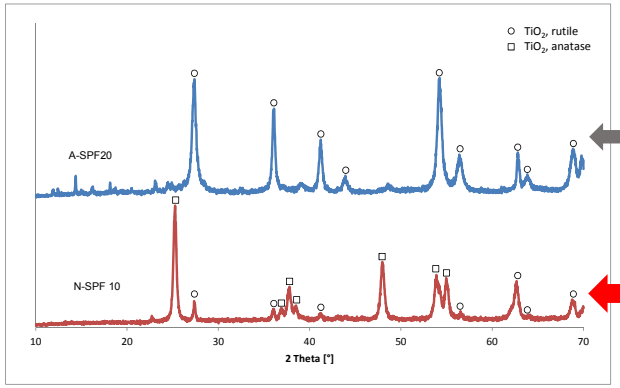
Dodana količina ?
Velikosti delcev ?

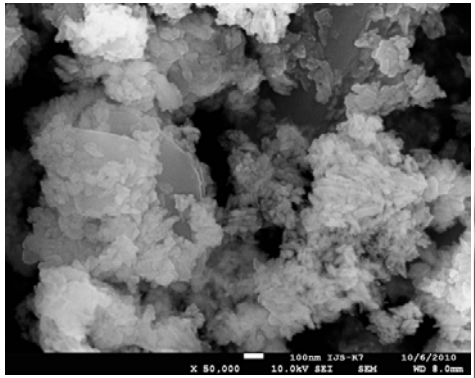
Topnost v prebavnem traktu ?

Belo?

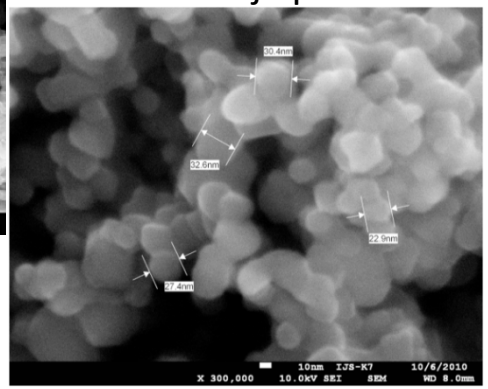
„Večina zaščitnih krem vsebuje (manj fotokatalitičen) **rutil“** (BEL)

nano ➔ anataz

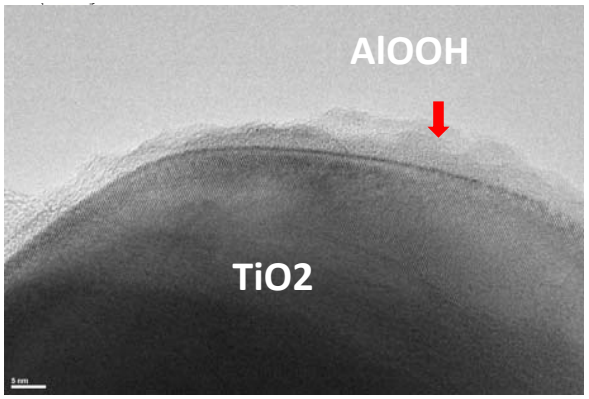




Večja povečava!



nano-TiO_2 pri obsevanju z UV razgrajuje organske molekule



Prevleke za zmanjšanje fotokatalitske aktivnosti:

AlOOH, $Mg(OH)_2$, ZrO_2, SiO_2

Stabilnost in vpliv prevlek ?

Trajanje fotokatalitičnega učinka ?

2005: svetovna proizvodnja n-TiO_2 2 Mt/leto
65 % za kozmetično industrijo

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Product Groups

- Food Grade Titanium Dioxide (1)
- Rutile Titanium Dioxide (4)
- Anatase Titanium Dioxide (4)
- Others (33)

Index

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Velikost delcev?

Home ? Product List ? Food Grade Titanium Dioxide ? Anatase Titanium Dioxide--Food Grade

Product Details

Anatase Titanium Dioxide--Food Grade

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Anatase Titanium Dioxide--Food Grade

Product Description

Product: Titanium Dioxide
Specification Food Grade High Dispersivity
Index TiO2 Min 98.5 %
Heavy Metal contents Plumbum (as Pb) Max 20 mg/kg
Arsenic (as As) Max 8 mg/kg
Barium (as Ba) Max 5 mg/kg
Mercury (as Hg) Max 1 mg/kg
Antimony (as Sb) Max 50mg/kg
Moisture Max 0.5 %
Water soluble substances Max 0.5 %
Acid soluble substances Max 0.5 %
PH 6.5-7.5
Dispersivity 98 %

Usage Food additives titanium dioxide (white pigment) Instructions for use: Nonpoisonous, tasteless, white powder, brightening food and shielding ultraviolet ray. Mainly used in brightening sweetcoating, sugarcoating of pill, candied fruit, non-carbonic acid beverage, chewing gum, solid beverage, concentrated beverage, capsule, aquatic product, etc. Storage method: In cool and dry place, avoiding sunshine.

Package In paper bags within plastic film linings. 25kgs(n. W.) each bag.

Biološki učinki nano TiO_2

sodelovanje z NIB (M. Filipič, J. Petković)

Študij citotoksičnosti in genotoksičnosti TiO_2 prahu z dobro definiranimi lastnostmi

- Kristalna struktura: anataz / rutil
- Velikost delcev: µm – nm
- **Fotoaktivacija**

cito- in genotoksičnost <µm in nm prahu narasteta po obsevanju z UV

Nanotoxicology, September 2011; 5(3): 341–353

informa healthcare

DNA damage and alterations in expression of DNA damage responsive genes induced by TiO_2 nanoparticles in human hepatoma HepG2 cells

JANA PETKOVIĆ[1], BOJANA ŽEGURA[1], MAGDALENA STEVANOVIĆ[2], NATAŠA DRNOVŠEK[3], DRAGAN USKOKOVIĆ[2], SAŠA NOVAK[3], & METKA FILIPIČ[1]

[1]*Department of Genetic Toxicology and Cancer Biology, National Institute of Biology, Ljubljana, Slovenia,* [2]*Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Belgrade, Serbia, and* [3]*Department for Nanostructured Materials, Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia*

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journal homepage: www.elsevier.com/locate/jhazmat

Pre-irradiation of anatase TiO_2 particles with UV enhances their cytotoxic and genotoxic potential in human hepatoma HepG2 cells

Jana Petković[a], Tadeja Küzma[b], Katja Rade[c], Saša Novak[c], Metka Filipič[a,*]

[a] *Department of Genetic Toxicology and Cancer Biology, National Institute of Biology, SI-1000 Ljubljana, Slovenia*
[b] *Faculty of Chemistry and Chemical Technology, University of Ljubljana, SI-1000 Ljubljana, Slovenia*
[c] *Department for Nanostructured Materials, Jožef Stefan Institute, Jamova c. 39, SI-1000 Ljubljana, Slovenia*

DE GRUYTER OPEN

Radiology and Oncology

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review

Titanium dioxide in our everyday life; is it safe?

Matej Skocaj[1], Metka Filipic[2], Jana Petkovic[2], Sasa Novak[1]

[1] Jožef Stefan Institute, Department for Nanostructured Materials, Ljubljana, Slovenia

[2] National Institute of Biology, Department for Genetic Toxicology and Cancer Biology, Ljubljana, Slovenia

Received 7 October 2011
Accepted 27 October 2011

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Phone: +386 1 4773 271; Fax: +386 1 4773 221; E-mail: sasa.novak@ijs.si

Disclosure: No potential conflicts were disclosed.

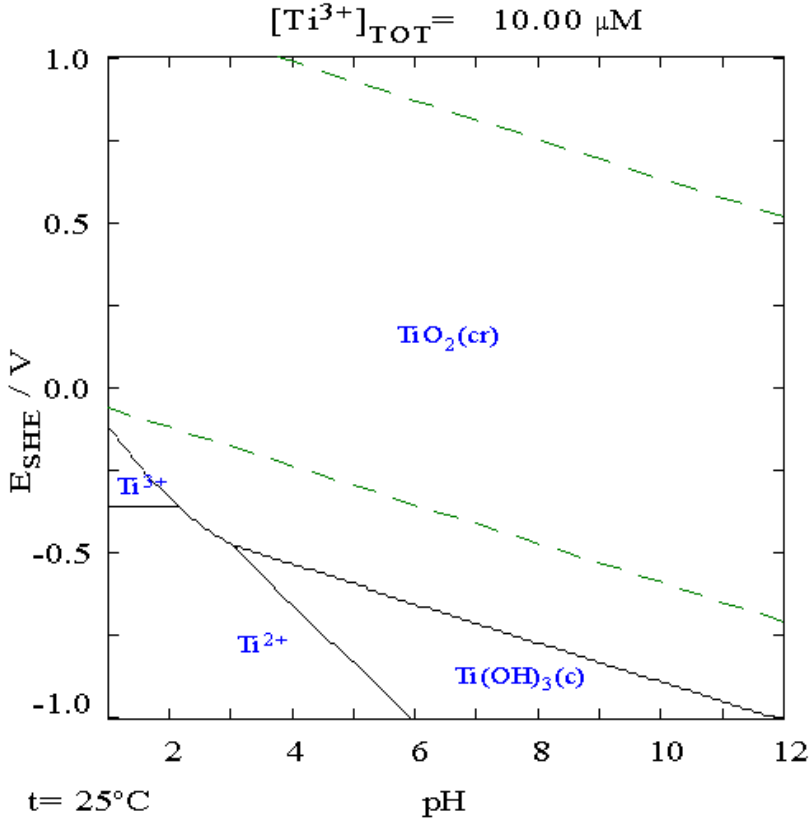
https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3423755/

Glavni parametri, ki vplivajo na biološke odzive na TiO_2

- Kristalna struktura TiO_2 (anataz / rutil /(amorfen)
- Velikost delcev (<50 nm / < 70 nm / > 100 nm)
- Specifična površina
- Naravni pH v suspenziji
- Zeta-potencial v vodi in fizioloških pogojih
- Topnost pri fizioloških pogojih → Biodostopnost
- Fotokataliza inducirana z UV-svetlobo
- ....
- Relevantne koncentracije TiO_2

Topnost ➔ biodostopnost

- Večja pri nizkem pH (želodčna kislina, encimi, ..?)
- Narašča z manjšanjem delcev (velika površinska energija nanodelcev)
- Nečistoče so pogosto bolj topne (še posebno tiste na površini)



Ugotovitve

- **Prisotnost** majhnih TiO_2 delcev narašča, njihova velikost se manjša =>
- Ni enotnega sklepa glede bioloških učinkov (Raziskave bioloških učinkov vključujejo prahove z različnimi lastnostmi!)
- Topnost TiO_2 ni zanemarljiva, raste z manjšanjem delcev
- Površinski naboj vpliva na disperznost in s tem na biodostopnost
- Sprememba lastnosti po **obsevanju z UV** (kozmetika, vdihavanje, …)

J Nanopart Res (2016)18:130
DOI 10.1007/s11051-016-3437-7

RESEARCH PAPER

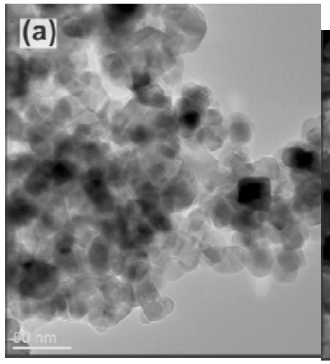
Diversity of TiO_2 nanopowders' characteristics relevant to toxicity testing

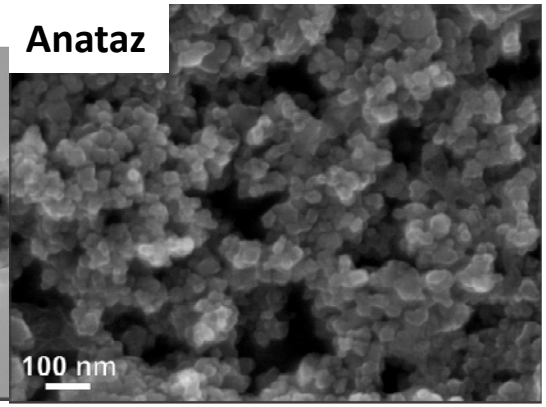
Saša Novak · Martina Lorenzetti · Anja Drame · Janja Vidmar · Janez Ščančar · Metka Filipič

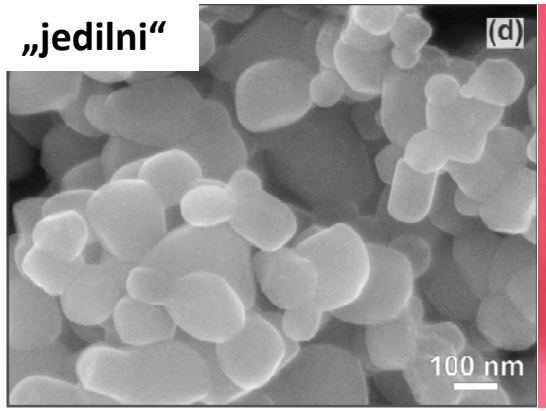
FG = food grade
CG = cosmetic grade

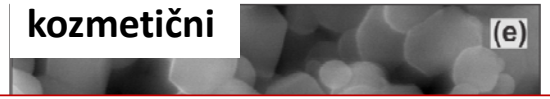
Table 1 Characteristics of the examined TiO_2 powders as specified by the suppliers

Sample ID	An	Ru	P25	FG	CG-DA	CG-NB
Supplier, producer	Sigma-Aldrich	Sigma-Aldrich	Sigma-Aldrich	Cake Stuff	Dr. Adorable	Naturally Balmy
CAS no.	1317-70-0	1317-80-2	13463-67-7	NA	NA	NA
Product no.	637254	637262	718467	NA	712392053501	NB-2257-1
Lot no.	MKBS9143 V	MKBD6250 V	MKBJ8962 V	NA	NA	3732–10
Composition	anatase	Rutile, up to 5 wt. % silicon dioxide	Anatase/rutile	Titanium dioxide (E171)	Titanium dioxide white pigment	Microfine titanium dioxide, alumina, simethicone
Purity	99.7 % trace metals basis	99.5 % trace metals basis	99.5 % trace metals basis	NA	NA	NA
Particle size	<25 nm	<100 nm	~21 nm	NA	NA	NA
Specific surface area	45–55 m^2/g	50 m^2/g	35–65 m^2/g	NA	NA	NA
Notes	–	Contains small amount of anatase	–	100 % edible. No added chemicals or anti-caking agents	For soap; oil dispersible. Approved for use in cosmetics, including eyes	Sunscreens, moisturises, powdered make-up, lip & baby products, almost any skin treatment product

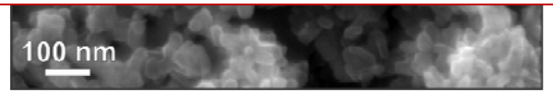


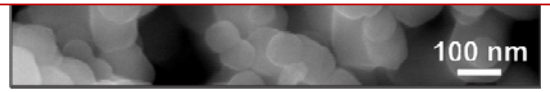


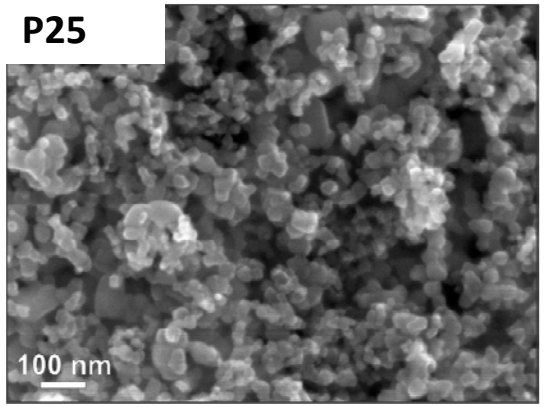


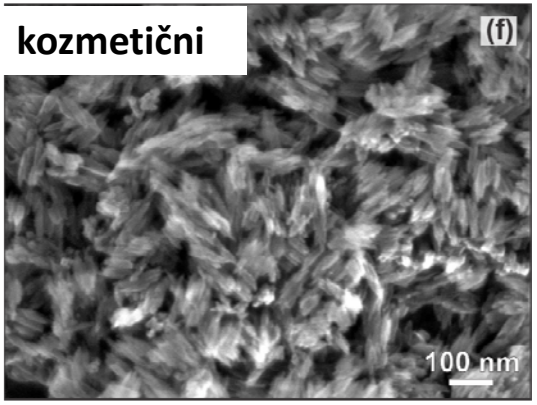


Sample ID	An	Ru	P25	FG	CG–DA	CG–NB
Crystallite size (by Scherrer formula), nm	32 ± 3	38 ± 4	A: 34 ± 3 R: 48 ± 4	116 ± 25	121 ± 22	39 ± 3

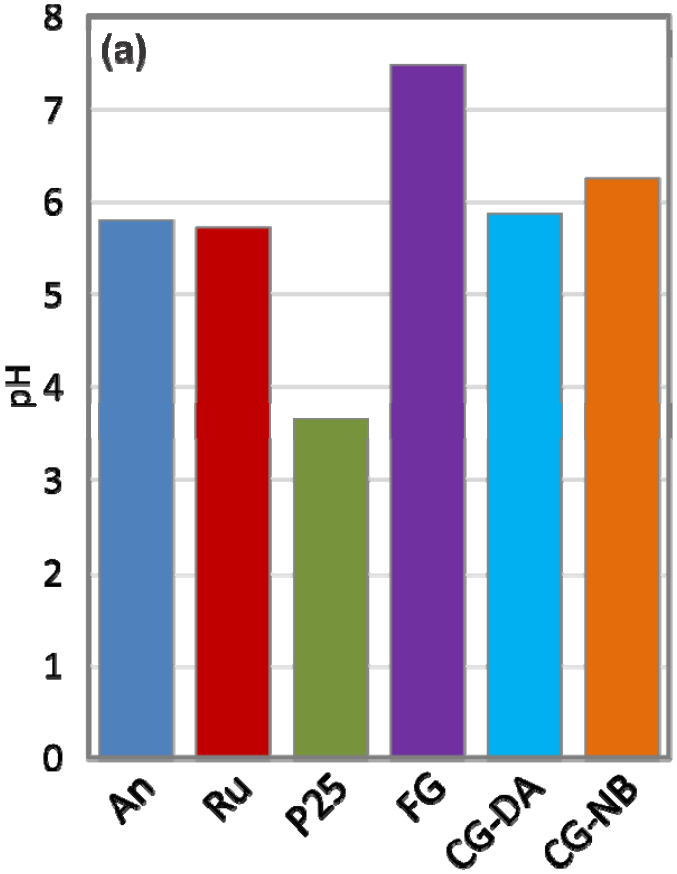


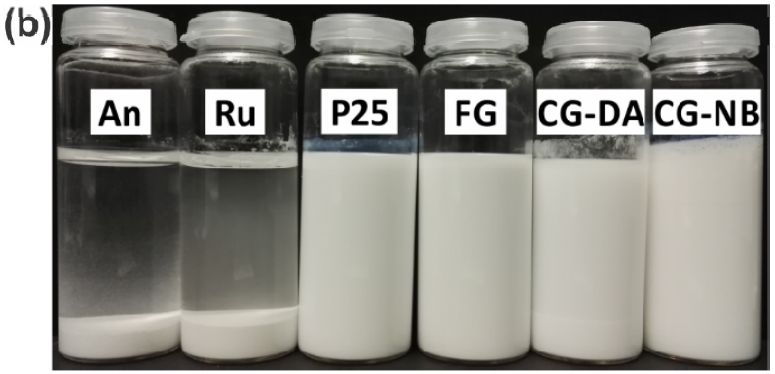




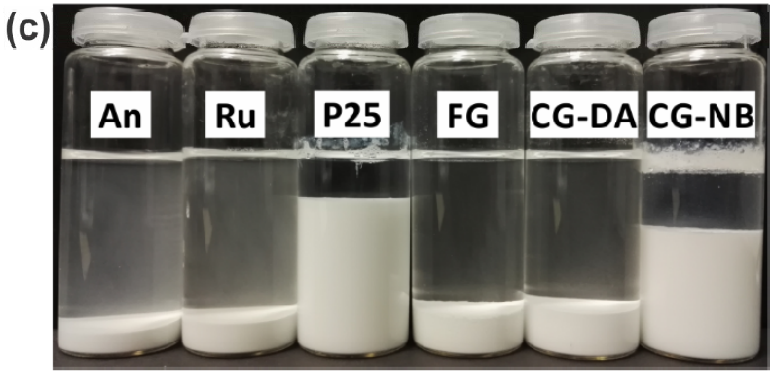


Suspenzija 3 ut. % TiO2





Voda (2h)



0,1 M PBS (2h)