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Colloidal behavior of TiO_2 nanoparticles in amino acid solutions

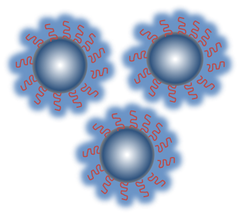
Anna Stanco[1], Iuliia Papina[2]
[1]Tomsk Polytechnic University, Russia, stanco@tpu.ru
[2]SHL-medica, Taiwan, papinayuliya@gmail.com

INTRODUCTION & AIM

Biomedical and environmental applications of TiO_2 NPs

- Cancer therapy [Jukapli N., J. Photochem. Photobiol. B: Biology (2016) 163]
- Anti-microbial agents [Li Q., J. Water Res. (2008) 42]
- UF filters [Popov A., J. Phys. D: Appl. Phys. (2005) 38]
- Water purification [Vatanpour V., Chem. Eng. Process.: Process Intensification (2017) 116]

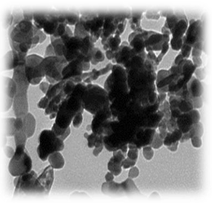
Studying the influence of amino acids (AAs) on the colloidal behavior of NPs may provide valuable insights into the formation of the protein corona and better understanding bio-matrix/nanoparticle (NPs) surface interactions.



- No AAs adsorption on rutile NPs [Ojamäe L., J. Coll. Interface. Science (2006) 296].
- High AAs adsorption on anatase NPs [Ustunoll B., J. Coll. Interface Science (2019) 554].
- Size- and pH- depended aggregation of TiO_2 NPs [Turley R. Microchemical J. (2018) 139].

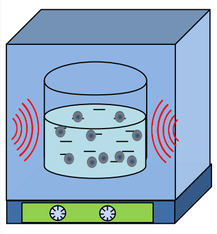
Aim of the paper: to show the influence of surface chemistry and AAs nature on the colloidal behavior of TiO_2 NPs in the wide range of pH.

EXPERIMENT



Characterization of NPs

- TEM (JEM-2100F, Jeol, Japan, copper grid)
- BET (Sorbi M, META PLC, Russia, N_2 adsorption)
- XRD (XRD-7000, Shimadzu, Japan, CuKα)

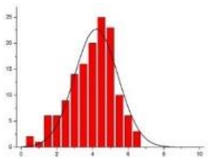


Exposure of NPs in AAs solutions

- AAs: Glu Cys Gly Lys Arg
- NPs: 100 mg/L, 1 M AAs solution, dry mixing NPs:AAs with glass balls before adding water
- Sonication: 15 min, US bath SMC, Russia, 200 W
- Exposure: 24 hours, 3 5 7 9 11

Colloidal properties study

- Zetasizer Nano, Malvern, USA, 633 nm, U-shaped polystyrene capillary cells
- *Dynamic light scattering*
- *Laser doppler electrophoresis*
- RI=0.8872, DC (water)= 1.33, DC (AAs)= 78.5
- RI (anatase)=1.0, RI(rutile)= 2.614
- **Particle size distribution (q_i,d_i)**
- **Average size (d_{av}):** **Zeta-potential (ξ):**

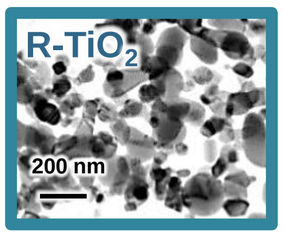


$$d_{av} = \sum d_i \frac{q_i, \%}{100, \%}$$

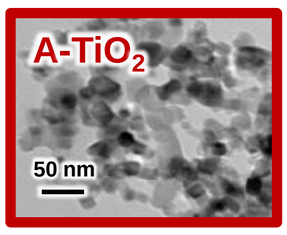
$$\xi = \frac{4 \cdot \pi \cdot \eta \cdot \vartheta}{\varepsilon \cdot H}$$

RESULTS & DISCUSSION

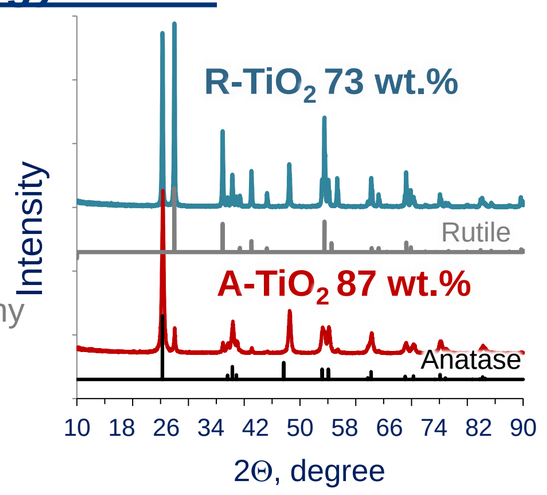
Composition and morphology of NPs



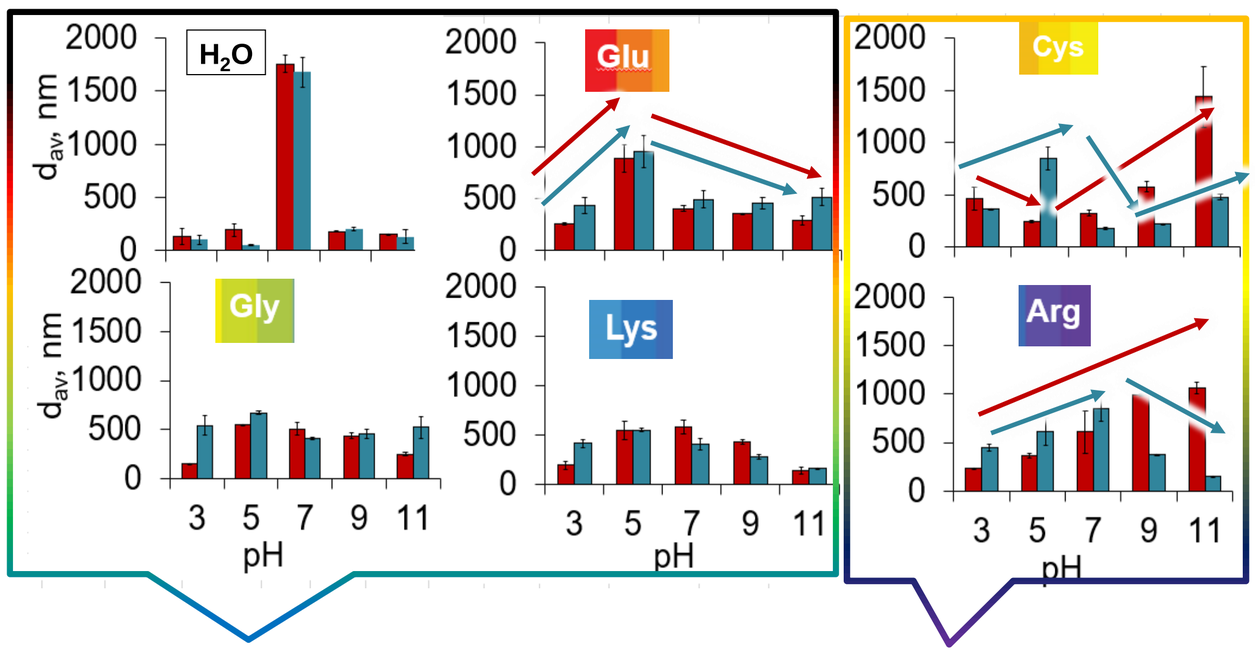
- Plasmatherm, Russia
- S = 10.05 m^2/g
- BET: d_{av} = 141.1 nm
- TEM: d_{av}=102±61 nm



- PlasmaChem, Germany
- S = 46.02 m^2/g
- BET: d_{av} = 31 nm
- TEM: d_{av}=26±9 nm



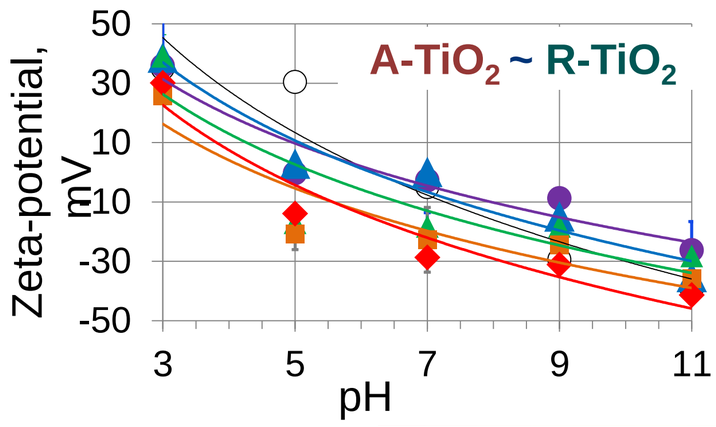
Effect of AAs on aggregation



For both particles the highest aggregation is achieved reasonably at a pH close to the pH of the isoelectric point (pH_{IEP}).

Contrasting effect of pH on the behavior of rutile and anatase NPs.

Effect of AAs on colloidal stability



- In the presence of AAs pH_{IEP} shifts to acids
- Curves are located from top to bottom according to its acidity

pH_{IEP}: Glu < Cys < Gly < Lys < Arg

CONCLUSION

Our findings showed that:

- **in an acidic medium (pH 3–5), aggregation depends more on pH**;
- in a weakly acidic medium (5–7), it depends more on the surface of the particles;
- in an alkaline medium (7–11), it depends more on the nature of the amino acids.