

# Determining Surface Energies of Nanoparticles from the Contact Angles Measured with the NanoTraPPED Method

**Andrei Honciuc<sup>1</sup>, Oana-Iuliana Negru<sup>1</sup>**

<sup>1</sup>Electroactive Polymers and Plasmochemistry Laboratory, “Petru Poni” Institute of Macromolecular Chemistry  
Aleea Gr. Ghica Voda 41A, 700487 Iasi, Romania  
honciuc.andrei@icmpp.ro; negru.oana@icmpp.ro

## Extended Abstract

Nanoparticle behaviour in bulk and interaction with the environment could be in part determined by their surface physicochemical properties, or surface functional groups. Characterization of the physicochemical state of the surface of nanoparticles can be important for predicting and understanding their bulk behaviour, in powders, such as dispersibility in water, or solvents, flowing ability, pelleting ability, aggregation, etc., which can be useful for many industries. In fundamental science, establishing a correlation between surface properties and nanoparticle bulk behaviour powders represents an ongoing challenge. One parameter that could give important insights into physicochemical state of the nanoparticles and their capability to interact with the environment through physical forces is the surface energy and its components. The magnitude of the surface energy can be interpreted as the ability of the surface to interact through physical forces. Surface energy can be broken down into components, such as polar, dispersive, hydrogen bonding, acid, base, etc., and their relative magnitude describes the preferred way, following the principles of independent action, through which a surface can interact with a solvent, an adsorbate, etc.[1]. For macroscopic surfaces, the surface energy components can be trivially determined by measuring the contact angles of several solvents and with the help of existing surface energy models, such as Owens-Wendt-Rabel-Kaelble OWRK (dispersive and polar), van Oss-Chaudhury-Good (OCG) (dispersive, acid and base); extended Fowkes (dispersive, polar and hydrogen bond)[2], [3]. Determining the surface energies of nanoparticles from contact angles with different liquids is not trivial, see the Washburn or thin-layer wicking methods[4], [5]. Several other methods have been recently developed, but still represent a challenge in terms of implementing them with different liquids[6], [7]. Here we present a comparative study on the surface energies of a series of silica nanoparticles synthesized from the same batch and modified with different surface functional groups, such as -NH<sub>2</sub>, -SH, -CN, -OH, -alkyl and -Gly(glycidyl). The surface energy components were determined with the recently developed NanoTraPPED (Nanoparticles Trapped on Polymerized Pickering Emulsion Droplets) technique[8], which relies on trapping the silica nanoparticles at the oil/water interface of a Pickering emulsion droplet; in this case, the oil is a polymerizable monomer, immiscible with water. Upon polymerizing the Pickering emulsion, the nanoparticles are trapped at the interface and with the help of electron microscopy, the contact angles can be measured. The results of surface energies and components obtained with different surface energy models, such as OWRK, Chaudhury van Oss, and extended Fowkes, for the mentioned nanoparticles are compared. Among the surface energy models used for modelling the obtained data, we find the OWRK method to yield the most meaningful results. Further, we attempt to correlate the role of the different magnitudes of surface energy components, with the bulk behaviour of nanoparticles bearing different surface functional groups function of their dispersibility in water, sedimentation, or pelleting ability, emulsification ability, etc.

## References

- [1] A. Honciuc, *Chemistry of Functional Materials Surfaces and Interfaces: Fundamentals and Applications*, 1st ed., 1 vols. Amsterdam: Elsevier, 2021.
- [2] D. K. Owens and R. C. Wendt, ‘Estimation of the surface free energy of polymers’, *Journal of applied polymer science*, vol. 13, no. 8, pp. 1741–1747, 1969.
- [3] C. J. van Oss, ‘Acid–base interfacial interactions in aqueous media’, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 78, pp. 1–49, Oct. 1993, doi: 10.1016/0927-7757(93)80308-2.

- [4] S. Kirdponpattara, M. Phisalaphong, and B. Z. Newby, ‘Applicability of Washburn capillary rise for determining contact angles of powders/porous materials’, *Journal of Colloid and Interface Science*, vol. 397, pp. 169–176, May 2013, doi: 10.1016/j.jcis.2013.01.033.
- [5] E. Chibowski and F. Gonzalez-Caballero, ‘Theory and practice of thin-layer wicking’, *Langmuir*, vol. 9, no. 1, pp. 330–340, Jan. 1993, doi: 10.1021/la00025a062.
- [6] L. N. Arnaudov, O. J. Cayre, M. A. Cohen Stuart, S. D. Stoyanov, and V. N. Paunov, ‘Measuring the three-phase contact angle of nanoparticles at fluid interfaces’, *Phys. Chem. Chem. Phys.*, vol. 12, no. 2, pp. 328–331, 2010, doi: 10.1039/B917353F.
- [7] L. Isa, F. Lucas, R. Wepf, and E. Reimhult, ‘Measuring single-nanoparticle wetting properties by freeze-fracture shadow-casting cryo-scanning electron microscopy’, *Nature Communications*, vol. 2, p. 438, Aug. 2011, doi: 10.1038/ncomms1441.
- [8] A. Honciuc and O.-I. Negru, ‘NanoTraPPED—A New Method for Determining the Surface Energy of Nanoparticles via Pickering Emulsion Polymerization’, *Nanomaterials*, vol. 11, no. 12, p. 3200, 2021, doi: 10.3390/nano11123200.