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# The effects of nanoparticles on the physical properties of type I collagen

A thesis presented in partial fulfilment of the requirements for the degree of

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#### Abstract

This thesis concerned with the interactions of surface functionalized TiO<sub>2</sub> and ZnO NPs with type I collagen. The collagen nanocomposites formed with TiO<sub>2</sub> and ZnO NPs may be potential candidates for some biomedical applications thanks to the synergetic effects between two materials. How the physical properties of collagen have been changed when interacting with TiO<sub>2</sub> and ZnO NPs has been investigated in this project. The general background and research objectives of this study are introduced in Chapter 1, followed by Chapter 2 which gives details about the preparation of the samples, in addition to the characterization techniques and protocols. The TiO<sub>2</sub> and ZnO NPs were synthesized by colloidal synthetic methods and their surfaces were functionalized with different functional groups. The physical properties of the TiO<sub>2</sub>-collagen nanocomposites and ZnO-induced collagen gels were studied by rheology, DSC, swelling ratio assay, FTIR and confocal microscopy. The mechanical studies are the main focus of this studys.

In Chapter 3,  $TiO_2$  NPs coated with chitosan and PAA were introduced into collagen solutions before fibrillogenesis was carried out. They were found to affect the linear rheology of the collagen gels as a function of their concentration. There were no significant differences in the strain-stress response in the non-linear rheology. It was found that the PAA coated  $TiO_2$  NPs promoted collagen fibrillogenesis, resulting in thin fibrils, and a dense and more crosslinked structure, while the chitosan coated  $TiO_2$  NPs slowed down the collagen fibrillogenesis and created a heterogeneous network with thick fibrils and less crosslinks.

ZnO-PVP NPs were found to induce collagen gelation without the use of the conventional fibrillogenesis involving gelation buffer, as reported in Chapter 4. The

hydrogel formed with this method was found to be three times as strong as the gel formed with conventional gelation buffer at the same collagen concentration. Confocal images indicated those two gels have different molecular assembly states. A group of experiments showed ZnO acted as a neutralizing agent here to raise the pH of the collagen solution to the pH close to the isoelectric point of the collagen.

Both the  $TiO_2$  and ZnO NP-collagen systems have demonstrated that different collagen networks can be created by the direct or indirect interactions between collagen monomer solution and the nanoparticles. By manipulating the assembly of collagen to design different networks, it is possible to achieve the physical properties required for different applications.

The results are followed by the conclusions and future perspectives of this study.

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### Abbreviations

Col	Collagen
CS	Chitosan
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
G'	Storage modulus
G <sub>o</sub> '	Equilibrium storage modulus
G"	Loss modulus
γc	Critical strain
$\gamma_y$	Yield strain
HCl	hydrochloric acid
HOAc	Acetic acid
К	Differential shear modulus
min	Minute
NaOH	Sodium hydroxide
NaCl	Sodium chloride
NP	Nanoparticle
PAA	Poly (acrylic acid)
PBS	Phosphate buffered saline
PVP	Polyvinylpyrrolidone
S	Second
SAED	Selected area electron diffraction

σ Stress

TEM Transmission electron microscopy

- TGA Thermogravimetric analysis
- THF Tetrahydrofuran
- TiO<sub>2</sub> Titanium dioxide
- TiO<sub>2</sub>-CS Chitosan coated TiO<sub>2</sub>
- TiO<sub>2</sub>-PAA PAA capped TiO<sub>2</sub>
- TiO<sub>2</sub>-UM Surface un-modified TiO<sub>2</sub>
- TiCl<sub>4</sub> Titanium tetrachloride
- ZnO Zinc oxide