Silica-coating as protective shell for the risk management of nanoparticles

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Abstract. Nanoparticles (NPs) surface functionalization with silica (SiO₂) has attracted high attention due to hydrophilicity, biocompatibility, chemical and thermal stability of silica. The present work is addressed to the production and characterization of SiO₂-coatings on titanium dioxide (TiO₂) and silver (Ag) NPs dispersed in aqueous solutions (commercial nanosols) with the aim to manage the potential risk that such NPs could generate in occupational exposure scenarios. A colloidal approach, based on principles of heterocoagulation in which opposite charged NPs are forced to coagulate in hierarchical structures, imposed by their relative size and weight ratio, was followed. The results were compared with a chemical approach, based on nucleation of silica phase from silica precursor solutions on the surfaces of TiO₂ or Ag NPs seeds. In order to increase the adhesion of silica on TiO₂ and Ag surfaces, heterocoagulated sols were spray-dried and subsequently redispersed in water to check the feasibility of such approach at industrial level. Physicochemical properties such as zeta potential, electrical conductivity, particle-size distribution, specific surface area and morphology of the samples produced with different SiO₂:TiO₂ and SiO₂:Ag weight ratios were collected and compared. Indirect evidences of silica coating were obtained.

1. Introduction

The present work is performed on behalf of SANOWORK (FP7-NMP4-SL-2011-280716) project that addresses the following objectives.

- Promoting, developing and implementing “DESIGN OPTION BASED” risk remediation strategies.
- Integrating such strategies within MANUFACTURING PROCESSING LINES.
- Implementing EXPOSURE assessment methodologies in the WORKPLACES.
- Performing a RISK analysis BEFORE and AFTER the application of the proposed strategies.
- Analyzing COST / BENEFIT on the basis of the risk analysis results and nanomaterials (NMs) performance.

The development of “DESIGN OPTION BASED” risk remediation strategies is a challenging and beyond the state of the art objective aimed to design out risks rather than address them when they occur.
The main strategy developed by SANOWORK project is based on surface NMs engineering through inorganic/organic surface coating by playing with mechanism and kinetics of self assembled monolayer (SAM) formation [1]. SAMs on NPs, including colloids and nanocrystals, stabilize the reactive surface of the particles and represent a simple way to control the surface reactivity at the particle-solvent interface. Adsorbate molecules adsorb readily because they lower the surface free-energy of the substrate and are stable due to the strong specific adsorption of the “head groups.” These bonds create monolayers that are more stable than the physisorbed bonds of Langmuir–Blodgett films [2] and still remain bonded to the surface even when the solid substrate is removed from the solution. The colloidal functionalization of nanoparticles by electrosteric self-assembling is particularly attractive [3] due to the ease of preparation, the tunability of solid/liquid dispersion state and of surface properties via modification of adsorbed layer molecular structure and functions, and the use of adsorbed layers as building blocks in more complex structures, e.g. for ‘grafting’ additional layers to a surface. Within possible coatings, those based on silica (SiO₂) have attracted high attention due to their hydrophilicity, biocompatibility, chemical and thermal stability, even in aqueous media.

The present work is addressed to the production and characterization of SiO₂-coatings on titanium dioxide (TiO₂) and silver (Ag) NPs dispersed in aqueous solutions (commercial nanosols). A colloidal approach, based on principles of heterocoagulation in which opposite charged NPs are forced to coagulate in hierarchical structures, imposed by their relative size and weight ratio, was followed. The results were compared with a chemical approach, based on nucleation of silica phase from silica precursor solutions on the surfaces of TiO₂ or Ag NPs seeds.

Physicochemical properties such as zeta potential, electrical conductivity, particle-size distribution, specific surface area and morphology of the samples produced with different SiO₂:TiO₂ and SiO₂:Ag weight ratios were collected and compared.

2. Experimental

2.1. Materials
Titanium dioxide (TiO₂) sol (NAMA41, 6 wt%, 40 nm), silver (Ag) sol (NAMA39, 4 wt%, 125 nm), both from Colorobbia Italia, and silica (SiO₂) sol (LUDOX HS-40, 40 wt%, 20 nm) from Grace Davison were used for heterocoagulation process. For the silica coating of titanium dioxide and silver NPs by chemical synthesis (according to Stöber method), tetraethyl orthosilicate (TEOS) from Sigma-Aldrich as precursor of silicon and ammonium hydroxide (NH₄OH) solution at 30 wt% from Carlo Erba as basifying agent were used.

2.2. Methods of production of heterocoagulated and synthesized sols
The commercial sols were diluted with water (TiO₂ and SiO₂ sols to 3 wt% and Ag sol to 2 wt%) and, in the case of SiO₂ sol, acidified by cationic exchange on resin till pH 4. After such treatments, the titania and silica sols, as well as the silver and silica sol, were mixed in well-defined ratios (indicated in Figure 1 as SiO₂:TiO₂ and SiO₂:Ag weight ratios) and ball milled (BM) for 24 hours with alumina spheres as milling media.

In addition to the heterocoagulated (HC) sols some synthesized sols were also prepared by diluting the TiO₂ and Ag commercial sols, adding TEOS in well-defined amount in basic environment and leaving the reaction to occur for 24 hours. After that time the reaction systems were washed three times with ethanol. In Figure 2 are shown the sols produced in this way.

2.3. Heterocoagulated sols treatments
In order to increase the adhesion of silica NPs on the surfaces of TiO₂ and Ag NPs, the heterocoagulated sols were spray-dried in counterflow with a stream of hot air (at 220 °C) through a nozzle of 500 µm of diameter (Figure 3).
Figure 1. Diagrams showing the method of production of heterocoagulated (a) TiO$_2$-SiO$_2$ and (b) Ag-SiO$_2$ sols. SiO$_2$:TiO$_2$ and SiO$_2$:Ag weight ratios and nomenclature used are indicated.

Figure 2. Diagrams showing the method of production of synthesized (a) TiO$_2$-SiO$_2$ and (b) Ag-SiO$_2$ sols. SiO$_2$:TiO$_2$ and SiO$_2$:Ag weight ratios and nomenclature used are indicated.

Figure 3. Spray-drying technique applied to heterocoagulated sols.

The spray-dried powders were subsequently redispersed in water by ball milling or ultrasonication with a solid content of 0.5 wt%. The spray-dried powders and the corresponding redispersed sols were indicated with the name of the starting sols followed by SD or RED, respectively. Redispersed sols were compared with the starting ones to study the effect of spray-drying on the silica coating.
2.4. Measurements
The particle-size distribution of sols was measured by dynamic light scattering (DLS) (ZetaSizer, Malvern). The zeta potential of the particle in suspensions was determined by electroacoustic method (AcoustoSizer II, Colloidal Dynamics). Surface area of spray-dried powders was measured by nitrogen adsorption (BET) (Sorpty 1750, Carlo Erba). Powder size and shape were measured by scanning electron microscopy (SEM) (Stereoscan 360, Cambridge Instruments). The electrical conductivity of sols was measured with a conductimeter (AMEL 134, AMEL).

3. Results and discussion
In order to get information about the occurrence of silica coating on titania or silver NPs surfaces, particle-size distribution by dynamic light scattering (DLS) and zeta potential by electroacoustic measurements on the heterocoagulated sols were carried out. Moreover, the spray-dried powders obtained from such sols were observed by SEM before and after redispersion in water. Zeta potential and electric conductivity of the redispersed sols were also measured.

3.1. Particle-size distribution
The dynamic light scattering (DLS) spectra of commercial and heterocoagulated sols are reported in Figure 4. Titania sol (T) has an average hydrodynamic diameter of 32 nm, whilst silica sol spectra (S) is characterized by two peaks at 20 and 330 nm. Silver sol spectrum (A) shows a peak at 125 nm. As comparison, STEM analysis performed on Ag sols shows a diameter size distribution between 20-60 nm, confirming an overestimate of real Ag diameter due to the presence of organic capping agent.

The DLS pattern of TiO$_2$-SiO$_2$ sol 2 (SiO$_2$:TiO$_2$ weight ratio 3:1) shows essentially a peak at 297 nm. Ag:SiO$_2$ sols 5 (SiO$_2$:Ag weight ratios 0.2:1) and 6 (SiO$_2$:Ag weight ratios 1:1) show peaks at 220 and 190 nm, respectively. Basing on these results, the presence of silica seems to strongly affect only the size of TiO$_2$ (Figure 4).

The different behavior of the two systems could be due to different affinity between oxide (TiO$_2$) and metal (Ag) surface towards silica, but also to the presence of a capping agent (polyvinyl pyrrolidone, PVP) on Ag surface that could hide the increase of Ag particle diameter expected by the formation of silica coating, as briefly schematized in Figure 5.

![Figure 4](image_url)  
**Figure 4.** DLS pattern for (a) TiO$_2$-SiO$_2$ sol 2 and (b) Ag-SiO$_2$ sols 5 and 6 compared with the DLS pattern for the commercial titania, silica and silver sols.

![Figure 5](image_url)  
**Figure 5.** Possible explanation of missed increasing of hydrodynamic size for SiO$_2$-coated Ag NPs.
3.2. Zeta potential measurements

Zeta potential of heterocoagulated and redispersed sols are plotted in Figure 6. By increasing the weight ratio of silica with respect to titania, the zeta potential value decreases from the value of titania sol towards that one of silica sol (-23 mV); the same occurs for the silver sols (Figure 6a). However, considering that the resulting zeta potential is a combination of the signals arising from the two NPs dispersed, it is difficult to ascribe the decrease of zeta potential only to the formation of silica coating.

As far as the redispersed sols are concerned (Figure 6b), a first evidence is that zeta potential values are systematically lower than the ones of the heterocoagulated starting sols. Such a result could be explained by agglomeration occurring during spray-drying that decreases the number of acid and basic surface sites available for protons exchange with water. Furthermore, it can be seen that the addition of small amount of silica abruptly decreases the zeta potential towards the value of silica at the same pH condition (~ 2). This allows to identify the minimum amount of silica that should completely coat the surfaces (SiO$_2$:TiO$_2$ ~ 3, SiO$_2$:Ag ~ 1), corresponding to the onset of plateau characterized by small variations of zeta potential.

Figure 6. Zeta potential of (a) heterocoagulated and (b) redispersed sols.

3.3. Morphologic characteristics of spray-dried powders

The size and morphology of the powders obtained from the commercial and heterocoagulated sols after spray-drying were observed by scanning electron microscopy. The spray-dried powder obtained from the commercial titania sol is micrometric in size and characterized by irregular shapes and hollows. However, the specific surface area (from BET measurements) is 237 m$^2$/g proving that the micrometric particles are actually nanostructured. On the other hand, the spray-dried powders obtained from the commercial silica are micrometric in size, as well, with high specific surface areas (201 m$^2$/g), but their shape is much more regular being circular with a hole in the middle. The spray-dried powders obtained from the heterocoagulated SiO$_2$-TiO$_2$ sols show regular morphologies, like spheres or hollowed spheres, high BET specific surface area (255 and 177 m$^2$/g), with smooth surfaces, similar to the spray-dried silica powders, suggesting the probable formation of silica coating (Figure 7).

The spray-dried powders from the commercial silver sol are spherical with holes due to the evaporation of organics. The spray-dried powders from the heterocoagulated SiO$_2$-Ag sols have irregular shapes with average diameter that increases with the SiO$_2$:Ag weight ratio.
3.4. Electrical conductivity of heterocoagulated and redispersed sols

The electrical conductivities of heterocoagulated sols result higher than those of redispersed sols, due to the spray-drying treatment, which probably causes the immobilization of the salts present in the sols on the particle surfaces (Figure 8). The good fitting between experimental and weighted mean conductivity data and the very low value of conductivity measured for the spray-dried silica sol (0.04 mS/cm) make difficult to establish if the observed decrease as a function of silica content is due to the formation of a silica coating or to the presence of free silica nanoparticles.

Figure 8. Electrical conductivity of HC and redispersed (a) TiO$_2$-SiO$_2$ and (b) Ag-SiO$_2$ sols.
3.5. Size and shape of redispersed powders
SEM images show that in order to get well-dispersed sols after redispersion in water of the spray-dried powders a long ball milling treatment (100 h) is required for TiO$_2$-SiO$_2$ sols, while a simple ultrasonication treatment (10 min) is enough for Ag-SiO$_2$ sols (Figure 9).

![Figure 9](image)

**Figure 9.** SEM images of redispersed TiO$_2$-SiO$_2$ 3_RED sol after (a) 10 min of ultrasonication and (b) 100 hours of ball milling and (c) redispersed Ag-SiO$_2$ 5_RED sol after 10 min of ultrasonication.

The redispersion of the spray-dried powders represents a fundamental goal. In fact, spray-drying provides highly reactive and nanostructured micrometric powders, which are more stable over time with respect to nanosols, more easily stored and transported. For these reasons to be successful in maintaining the same characteristics of the starting sol with the redispersed powder is a great achievement.

3.6. Synthesized sols
The TiO$_2$-SiO$_2$ sols obtained by nucleating silica from precursors on titania NPs surfaces are characterized by spherical aggregates with submicrometric primary particles, as observed by SEM on dried samples from sol 9. By increasing the silica content (sol 10) irregular aggregates with primary particles lower than 100 nm are observed (Figure 10). For the SiO$_2$-Ag sols spherical and regular shapes with nanometric structure were observed.

With respect to the corresponding heterocoagulated and redispersed sols, the electrical conductivity of chemically synthesized samples show an abrupt decrease. Particularly the measured conductivities are 0.07 and 0.09 mS/cm for the TiO$_2$ samples, and 0.04 mS/cm for both the Ag samples. These values, very close to the conductivity of the spray-dried and redispersed silica (0.04 mS/cm), may represent an indirect evidence of the presence of more compact silica layer, which limits the ion release by the particle surfaces.

Conclusions
The main strategy developed by SANOWORK project is based on surface NMs engineering through inorganic/organic surface coating by playing with mechanism and kinetics of self assembled monolayer (SAM) formation. The inorganic coating of titania and silver aqueous commercial nanosols with silica has been performed by using a colloidal approach, based on principles of heterocoagulation, in which opposite charged NPs are forced to coagulate in hierarchical structures, imposed by their relative size and weight ratio. In order to optimize the silica amount and evaluating the silica effect, several SiO$_2$:TiO$_2$ and SiO$_2$:Ag weight ratios have been considered. Moreover, the results were compared with those arising from a chemical approach, based on nucleation of silica phase from silica precursor solutions on the surfaces of TiO$_2$ or Ag NPs seeds.
Figure 10. SEM images of redispersed (a) TiO$_2$-SiO$_2$ 9 sol, (b) TiO$_2$-SiO$_2$ 10 sol, (c) Ag-SiO$_2$ 11 sol and (d) 12 Ag-SiO$_2$ sol.

The experimental evidences collected till now on the samples produced with the colloidal and chemical approaches do not allow to certainty state that a SiO$_2$-coating on TiO$_2$ and Ag occurred, but some clues are in that direction. Further investigation are in progress. However, some preliminary cytotoxicity tests proved that the spray-drying process, particularly when coupled with silica, provides an abrupt decrease of nanosilver hazard potential. Considering that the successfully achieved redispersion of nanosilver spray-dried powders represents a process improvement for this kind of nanomaterials, further investigation are in progress in order to identify key factors responsible of biological activities.

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