

# Nanotechnology for Smart Textile

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**Abstract:** Series of metal and metal oxide and core@shell nanoparticles have been prepared using microemulsions as nanoreactors. The microemulsion method has been found to be very efficient to prepare a wide range of metal, metal oxides, metal@metal, metal oxide@metal core@shell nanoparticles at low-cost. The size, shape and morphology of the nanoparticles can be tuned by changing the composition of the microemulsions or the nature of the constituent surfactant, cosurfactant or oil phase. The properties of the nanoparticles may be tuned and nanoparticles with desirable properties may be incorporated in fabrics for smart textiles. The prospects of the nanoparticles and their functionality to design and fabricate smart textiles have been discussed.

**Key Words:** Metal and metal oxide nanoparticles; core@shell nanoparticles; smart textiles

## 1. INTRODUCTION

Smart textiles, i.e. textiles capable of sensing and reacting to environmental conditions or stimuli from mechanical, thermal, chemical, electrical, optical, magnetic or other sources, have received significant attention in recent days [1]. Smart textiles can be referred to smart clothing that makes us feel comfortable at all times, during any activity and in any environmental conditions, a suit that protects and monitors, that warns in case of danger and even helps to treat diseases and injuries. Some of the more recent developments include: patient health monitoring through sensor embedded garments that track and record biometric data, improvement of athletic performance both by analyzing sensor data and adapting to changing conditions so as to improve performance over the time, environmental sensing and communication technologies for military defense and other security personals, new structural and decorative solutions for fashion design.

Smart textiles, in general comprises three components: sensors, actuators and controlling units. The sensor provides nerve system to detect signals. Materials may act only as sensors or as both the sensors and actuators. Smart textiles are combination of textile and electronics. Modified textile material and miniaturized electronic devices create smart cloths, which provide special function in various situations according to the design and application. The response carried out can be either direct visible or indirect. The direct visible responses include property changes, such as change in color, or size/location changes like shape, geometry and volume. Indirect responses may include property changes or energy exchanges at a molecular level, magnetic or electrical level. Such responses, are not in general, visible to the naked eye, but they can trigger other controlled reactions or functions [1].

Nanotechnology has been found to be very promising for smart textiles. Making fabric with nanoparticles creates many desirable properties without a significant increase in weight, thickness or stiffness. The incorporation of nanoparticles to fabric usually gives advantageous properties such as extreme water resistance, odor and moisture elimination, increased elasticity and strength, bacterial, microbial and fungal resistance, flame retardation, wrinkle resistance, odor and moisture elimination and self-cleansing

action [1]. It is, therefore, very crucial to prepare nanoparticles of metals, metal oxides, clay, zeolites and carbon nanotubes, carbon black nanoparticles, nanocomposites and nanofibres and core@shell nanoparticles and efficiently 'nanofinish' the fabric to exploit the stimuli sensitivity and functionality of the nanoparticles.

In this study, we aim at preparing metal, metal oxide and core@shell nanoparticles using a cost-effective and simple means, which may be successfully applied to fabric to produce smart textiles. Our main goal is to establish common methodologies that may be used for preparation of a wide variety of nanoparticles with desirable properties for smart textiles.

## 2. EXPERIMENTAL

Reduction of the silver and copper salts was carried out with reducing agent, NaBH<sub>4</sub> in w/o microemulsions, comprising an anionic surfactant, sodium dodecyl sulfate (SDS), 1-pentanol, cyclohexane and water to prepare silver and copper nanoparticles [2]. The composition of the quaternary microemulsion system was varied to change the microenvironment. The microemulsions were prepared by mixing SDS, 1-pentanol, cyclohexane followed by the addition of pure deionized water. The final mixture was a clear microemulsion system.

Single microemulsion reactant addition scheme was applied to prepare Fe@Cu core@shell nanoparticles which involved sequential addition of precursors to the microemulsion of same type [3]. Triton X-100 and cyclohexane were used as surfactant and oil phase, respectively for preparation of w/o microemulsions. Hexanol was used as a co-surfactant which eventually acted as an 'anchor' and hence played an important role for the stabilization of microemulsion. The completion of the reaction was characterized by observing in the change in the color of the reverse microemulsions containing the synthesized NPs.

Direct synthesis of ZnO@Ag core@shell nanoparticles was carried out for the first time using a double scheme microemulsion method [4]. Triton X-100/hexanol/cyclohexane/water microemulsion system was used for the preparation of the nanoparticles. TX-100 solution was prepared in hexanol/cyclohexane and a molar ratio of 1:4 of TX-100: hexanol was maintained. Equal volumes of microemulsions were taken in two stoppered vials. Zn(NO<sub>3</sub>)<sub>2</sub> was incorporated in one microemulsion, and was mixed with another microemulsion with NH<sub>4</sub>OH incorporated in it. The mixture was shaken until a transparent microemulsion was obtained. The resultant mixture was then kept overnight. The w/o microemulsion containing AgNO<sub>3</sub> with respect to the total microemulsion volume was then transferred to a vial containing ZnO nanoparticles synthesized in w/o microemulsion followed by addition of NaBH<sub>4</sub> incorporated in an equal volume of microemulsion of TX-100. Dark brown

solution was formed which faded with time and thus gave a reddish brown coloured solution.

ZnO nanoparticles (NPs) have also been synthesized via a simple chemical reaction using zinc acetate as a precursor in mixtures of propanol-2 and water at different volume ratios [5]. The influence of reverse micellar solutions of SDS and a cationic surfactant cetyltrimethyl ammonium bromide (CTAB) on the growth process of the prepared ZnO NPs was also investigated.

Spectral analyses were carried out in a Labomed double beam UV-Vis spectrophotometer, model UVD-3500. Rectangular quartz cells of path length 1 cm were used throughout the investigation. Malvern ZS90 was used for study of the particles size distribution of the nanoparticles confined in the microemulsion. The average particle size and morphology of the nanoparticles were also investigated by scanning electron microscopy (SEM) (Model JSM-6490LA). Energy dispersive X-ray (EDX) spectral analyses were also carried out (JSM-6490LA) for elemental analysis.

### 3. RESULTS AND DISCUSSION

#### 3.1 Metal nanoparticles

The synthesis of nanoparticles of silver and copper were carried out in w/o microemulsions of SDS. The aqueous cores of microemulsion systems serve as compartmentalized media (nanoscaled reactors) for chemical reactions in a controlled manner resulting in the formation of nanoparticles. The size (diameter of the core) of the nanoreactors was controlled by changing the composition of w/o of the microemulsions during the preparation of metal particles in order to control the size of the metal particles. The UV spectrum of resultant silver nanoparticles obtained in microemulsions revealed formation of nanosized particles. The spectrum shows a band around 400 nm caused by plasma resonance absorption of

silver nanoparticles. The UV spectrum of copper nanoparticles does not exhibit the expected plasmon peak due to the plasma oscillation characteristic of copper surface.

It is evident from the SEM images (Fig. 1), that silver (a,b,c) and copper (d,e,f) particles at different water to surfactant molar ratio,  $W_0$  are formed in nanodimensions. The size of the nanoparticles can be tuned by changing composition of microemulsions. Smaller particles are obtained at low  $W_0$ , while the higher  $W_0$  yields larger particles with large distribution. The shapes of silver and copper nanoparticles (Fig. 1) are spherical. The EDX spectra confirm the presence of metallic silver and copper. The size of the particles formed in the microemulsion environment and bound by the micellar 'cage' is governed by the value of  $W_0$ . From the average particle size of silver and copper estimated from SEM images (Fig. 1), it is apparent that an increase in  $W_0$  causes a linear increase in the particle size in the microemulsions of SDS.

The method has been proved to be efficient in preparation of nanoparticles with tunable size for other metal nanoparticles and as per the demand of the smart textiles metal nanoparticles with desirable size and properties may be easily prepared.

#### 3.2 Metal@metal core@shell nanoparticles

Fe@Au core@shell nanoparticles (CSNPs) were synthesized in reverse microemulsion-based nanoreactors. Fig. 2 shows the SEM micrographs, which depicts dark and bright contrast for both Fe and Au nanoparticles respectively to confirm the coating of the Au NPs over the core Fe NPs. This is supported by DLS and EDX results. In addition, distinct surface plasmon resonance (SPR) of Fe@Au CSNPs at different mole ratio of the precursor salts also supported the formation of hybrid CSNPs. Control over the core to shell ratio was proved to be vital for the tunability of optical properties of Fe@Au CSNPs which was achieved by optimizing size controlling parameters of microemulsions i.e. the nanoreactors. Type of surfactants (based on their nature), type of co-surfactants (based on their chain length/chain branching), and  $W_0$  were optimized and DLS results excellently corroborated the fact the variation in size and size distributions of these nanoreactors were consequence of the fine-tuning of interfacial fluidity governed by the parameters of microemulsions. The tunability of the dimension of Fe@Au CSNPs exhibited wide spectrum of tunable optical properties.

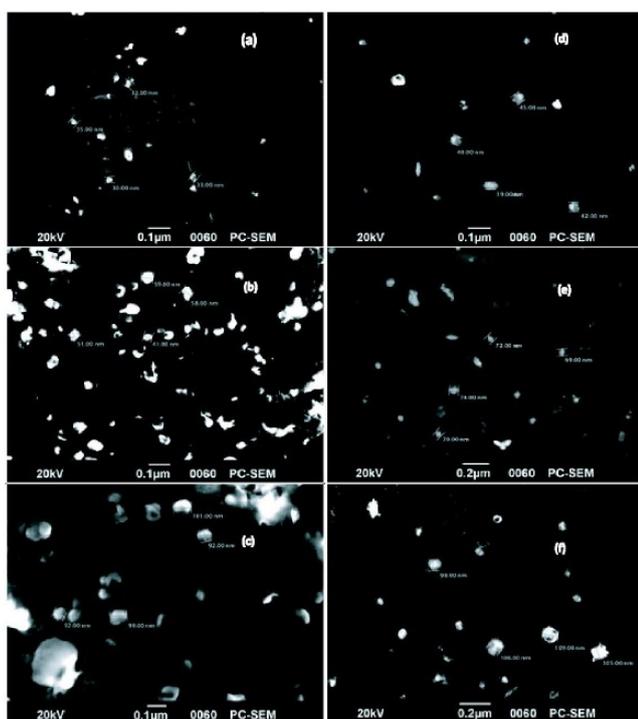


Fig. 1 SEM images of silver (a,b,c) and copper (d,e,f) nanoparticles obtained in SDS/1-pentanol/cyclohexane/water microemulsions at different  $W_0$ : (a), (d) 15.7; (b), (e) 20.8; (c), (f) 28.7 [2].

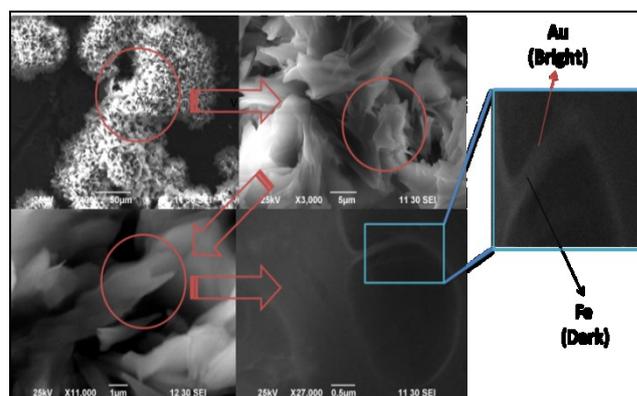


Fig. 2 SEM micrographs of Fe@Au CSNPs [3]

### 3.3 Metal oxide and metal oxide@metal core@shell nanoparticles

At a constant  $W_o$  of 13.34, under the highly basic condition,  $[\text{Zn}(\text{OH})_4]^{2-}$  ions formed (due to basic hydrolysis of zinc nitrate precursor) easily in the water pools of w/o microemulsion was converted to ZnO since the coordination state of  $\text{Zn}^{2+}$  and  $\text{O}^{2-}$  is considerably similar in both ZnO and  $[\text{Zn}(\text{OH})_4]$ . Thus ZnO nanoparticles could be prepared using microemulsions. The *in situ* reduction of  $\text{Ag}(\text{NO}_3)_2$  resulted in the production of silver which *via* the process of nucleation deposited as a layer of silver on ZnO nanoparticles.

Uniform coating of silver could be successfully performed on ZnO nanoparticles and the properties might be systematically tuned by varying the thickness of the core and the shell. Direct synthesis of ZnO@Ag core@shell nanoparticle have been carried out for the first time using a double scheme microemulsion method and the limiting factor of crystalline mismatch could be successfully overcome.

From the SEM image of ZnO@Ag core@shell nanoparticle formed in w/o microemulsion with  $W_o = 13.34$  it is clear that the core@shell nanoparticles formed are nearly spherical in shape (Fig. 3). Magnification of a selected part reveals two distinct regions; the inner dark part and a shiny portion surrounding the dark region. This indicates the formation of a very thin layer of metallic silver around the semiconducting ZnO core. The absorbance spectra of ZnO, silver and ZnO@Ag core@shell nanoparticles synthesized at  $W_o = 13.34$  were recorded. The absorption maximum at 326 nm is attributed to the absorption of ZnO nanoparticles. The SPR of ZnO@Ag core@shell nanoparticles is shifted to longer wavelength i.e. 420 nm (bathochromic shift) compared to the plasmon resonance of silver nanoparticles showing absorption maximum at 408 nm. Interfacial coupling between silver nanoparticles may be the reason for the broadening and red shift of the surface plasmon absorption.

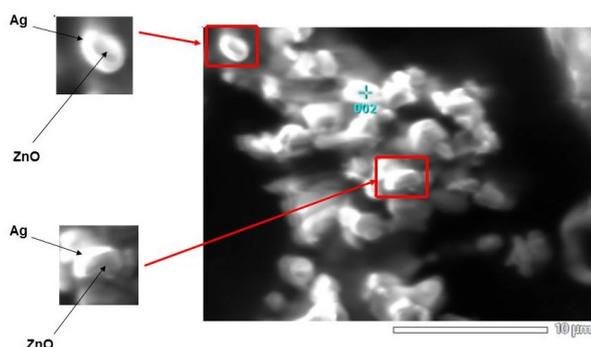


Fig.3 SEM image of ZnO@Ag core@shell nanoparticles synthesized at  $W_o = 13.34$  [4].

Since the precursor salts of zinc and silver used are both water soluble, basic hydrolysis of  $\text{Zn}^{2+}$  and reduction of  $\text{Ag}^+$  salts occur in the hydrophilic water pool of the nanoreactors. Both ZnO and the silver nanoparticles remain confined in the hydrophilic core which is said to contain water of special properties, such as lower micropolarity, altered nucleophilicity and viscosity, which makes it a medium different from ordinary water. More energy is required for silver to undergo free nucleation. However, in these confined water pools of the reverse micelle which has a 'cage-like' effect, lesser Gibbs energy is required for silver nanoparticles to undergo heterogeneous nucleation on the surface of ZnO

nanoparticles. Surface reconstruction would further decrease their energy and thus provide active site for heterogenous nucleation and growth of silver nanoparticles.

### 3.4 Metal oxide nanoparticles

Reverse micellar solutions of SDS and CTAB served as nanoreactors to influence the growth process of ZnO NPs. The growth kinetics of ZnO NPs was studied in reverse micellar solutions of SDS and CTAB.

Particle size estimated from the cut-off wavelength of UV-visible absorption spectra by using effective mass model indicates a uniform particle size distribution of ZnO NPs in reverse micellar solutions and both SDS (anionic) and CTAB (cationic) surfactants effectively influenced the growth kinetics of ZnO NPs. The growth process occurs in the diffuse layer of the reverse micelles and the growth kinetics is likely to be determined by the surface activity and the aggregation behavior. The ZnO NPs prepared (using propanol-2/water = 18/2) without surfactant had the final particle radius of 2.168 nm, which increased by 11 % and 14 % for SDS and CTAB reverse micellar solutions respectively. Irrespective of the type of the surfactants, uniform particle growth of ZnO NPs may be achieved by manipulating the hydrophilic core of the reverse micelles [5].

## CONCLUSIONS

A range of metal, metal oxides, metal@metal, metal oxide@metal core@shell nanoparticles could be synthesized using reverse micelle dominated microemulsions as nanoreactors. The concept may be successfully applied to prepare nanoparticles of a wide variety of nanoparticles with tunable size and distribution by proper choice of surfactants, cosurfactants, oil phase and composition to control the dimension of the hydrophilic core of the reverse micelles. This offers the tunability of size-dependent properties of the nanoparticles. The methodology is very promising to fabricate smart textiles with desirable properties and stimuli sensitivity through simple tuning of the size and distribution of the nanoparticles prior to fabrication.

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