Abstract: A composite nanoparticle of silica/polyaniline was synthesized from a microemulsion and it was tested as an electrochromic film. The compositions for the stable microemulsion system was selected as 65.4 wt% cyclohexane, 30.4 wt% surfactant and 4.2 wt% aqueous phase, where the surfactant was a mixture of 1-hexanol and Triton X-100. Hexanol-to-Triton X-100 mixing ratio in weight was selected as 2. Microstructure analysis such as TEM and BET surface area measurement were performed with the obtained particles. It was demonstrated that the composite structure of the nanoparticle was successfully obtained using the microemulsion synthesis method. The electrochromic properties of the composite electrochromic film were compared with pure polyaniline. The composite film showed the enhanced electrochemical durability. The stability enhancement could be understood as the protective effect of the composite structure.

Key-Words: electrochromic; nanoparticle; operation life time; polyaniline; silica; inorganic-organic hybrid

1 Introduction
The electrochromic materials can be applied to smart windows and display devices. For these applications high electrochromic efficiency, short response time, long operation life time and reduction of energy consumption are the most important requisites of the materials [1, 2]. There are two types of electrochromic materials: inorganic transition metal oxides, organic polymer (mostly conducting polymers). Nowadays, organic electrochromic materials are gaining more attention, because of their faster response and longer operation life time.

However, the operation life time of polyaniline is still limited to $10^5$ cycles while $10^8$ cycles are required for display applications. The limited operation life cycle is one of the main obstacles for the electrochromic materials to be used in display devices.

In general, electrochemical stability of the polymer is considered as one of the key factors determining the operation life time [3-5]. Electrochemical degradation of polyaniline is observed when sufficiently high anodic potential is applied [6]. By the application of a potential in excess of 0.8 V, oxidation can result in a positively charged form of the polymer which is more susceptible to the attack of water or other kinds of nucleophilic components from the electrolyte system [7].

Many efforts have been made to make the durability of the polymer electrochromic material available from the literatures. As an effective method to improve the mechanical and chemical stability of the polymer material the inorganic-organic hybridization can be used [8, 9]. It has been demonstrated that the electrochemical stability of polymer materials could be improved by forming composites with chemically stable inorganic particles or matrixes (i.e. SiO$_2$, Al$_2$O$_3$) [10-13].

Inorganic-organic hybrid nano composites are attracting much attention for their chemical, physical, optical, and electrical properties which are not obtainable with a single component [14]. Silica is the most frequently studied inorganic material for such composite. If the composites are used as in an optical coating, then the size of the composite particle must be controlled under 100 nm to avoid scattering of visible light.

Microemulsion method is one of the useful methods to produce monodispersed nanoparticles. When the micelles were used as the nano-reactors, it could suppress the particle growth within the range of 50 nm. Thus, in this study we demonstrated that the inorganic-organic silica/polyaniline composite nanoparticle could be obtained using a microemulsion method, and the silica/polyaniline composite nanoparticle could be applied for the electrochromic film to enhance the electrochemical stability of the material.

2 Experimental
An inverse (water in oil) microemulsion system was prepared using cyclohexane, hexanol, Triton X-100, TEOS, aniline, ammonium persulfate (APS) and HCl. They were used as received. When the co-surfactant system is used, water-to-surfactant ratio could be
increased, and hence, more aqueous phase could be dispersed with the given amount of surfactant. The composition of the prepared microemulsion was 65.4 wt% cyclohexane, 10.1 wt% Triton X-100, 20.3 wt% hexanol and 4.2 wt% water phase. The first intention of this work was to prepare the inorganic-organic hybrid particles by a simultaneous synthesis of silica and polymer in a same micelle. The polymerization of aniline usually requires acidic condition. So we proceed with the overall synthesis in the acidic solution.

The preparation starts with the mixed solution of cyclohexane, hexanol, Triton X-100, and TEOS. The concentration of TEOS in the cyclohexane was 0.1M. The aqueous solutions of HCl (0.1 M), HCl (0.1 M) + APS (0.1 M) and HCl (0.1 M) + aniline (0.01 – 0.3 M) were dispersed into the mixed solutions while being stirred. After 24 hrs of reaction, particles were extracted from the microemulsion solution. The extracted particles were washed with ethanol to remove the surfactant and the other remaining solvents.

Using the synthesized composite particles, the electrochromic films were prepared on a fluorine-doped tin oxide (FTO) coated glass by a spin coating. The coating solution was prepared by a dispersion of the synthesized composite particles into ethanol. The spin-coated sample was then heat-treated in a furnace at 150 °C for 2 hr to eliminate the remaining solvent.

Pure polyaniline film was also prepared on the FTO-coated glass for the comparison of the electrochromic properties. The pure polyaniline film was deposited by using a chemical polymerization coating method.

Electrochromic properties of the composite film and polyaniline film were compared using cyclovoltammetry, optical transmittance spectroscopy, and the measurement of coloration contrast at a fixed wavelength (600 nm).

3 Results and discussion

When the aqueous phase was completely dispersed into the microemulsion, the solution became transparent. 1 hr after the mixing the solution for the hybrid particle turned dark blue which is the typical color of polyaniline in an emeraldine phase. The size and shape of the particles obtained from the microemulsion were checked by the TEM as given in Fig. 1. The size of the particles was found to be around 10 nm. When the particles were extracted from the microemulsion, they were agglomerated into particles with diameters around 50 nm (Fig. 1b).

To investigate the components of the obtained particles FTIR spectra were measured on both the pure silica and the composite particles. As shown in Fig. 2, characteristic absorption bands were observed at 1637 (OH groups from water or ethanol), 1208 (Si-O), 950 (Si-OH), and 800 cm\(^{-1}\) (Si-O-Si), which are assigned to the characteristic absorption stretches for silica. The additional peaks at 1588 (N=Q=N), 1505 (N-B-N), 1452 (benzene ring), 1390 (C-N), and 1304 cm\(^{-1}\) (C-N) were observed for the composite sample. These bands are assigned to the characteristic peaks from polyaniline.

![Fig. 1 TEM photo of the composite particles: TEM samples were prepared on a carbon coated Cu grid from a) one drop of microemulsion solution and from b) one drop of ethanol solution dispersed with the particles extracted from the microemulsion.](image)

![Fig. 2 FTIR spectra for pure silica and silica / PANI composite particles obtained from microemulsion solutions.](image)
aqueous phase. As shown in Fig. 3, a decrease of surface area was observed when aniline content is increased higher than 0.2 M. At lower concentration of aniline (< 0.15 M), the measured surface areas were almost the same as that of the pure silica particles obtained from SE.

![Fig. 3 Surface area change during the increase of aniline load to the hybrid particle.](image)

It seems that polyaniline from the added aniline is filling into the pores of silica particle. Since the surface area is decreased because of the polyaniline filling, it should be restored by a removal the polyaniline from the pores. So, the surface area change was also monitored during a heat treatment up to 500 °C. As shown in Figure 5, during the heat treatment increase of surface area was clearly shown. It could be interpreted that a thermal decomposition of polyaniline restored the original surface are of the pores. On the contrary, the pure silica particle showed only a slight decrease of surface area.

![Fig. 4 BET surface area change during the thermal decomposition of polyaniline at 300 C and 500 C in air (Silica/polyaniline sample with aniline content of 0.3M).](image)

The overall observation results support that the polyaniline could possibly be incorporated into the void space of the silica skeleton. This could once again be explained with a microstructure model as in Fig. 5.

![Fig. 5 Idealized models for the structures of the composite and porous silica particle](image)

When polyaniline is filling up the void space of porous silica (Fig. 5a), the surface area of the particle should decrease with an increasing content of aniline. Then the surface area should also be restored after the complete removal of the polymer from the particles as shown in (Fig. 5b). On the contrary, for the pure silica particles no increase of surface area after the heat treatment was observed. After the same thermal treatment, the pure silica particles showed rather a slight decrease of surface area, which could be interpreted as a sintering effect. Electrochromic films were then prepared by using the composite nanoparticle. As described in the experimental section both the composite film and pure polyaniline film were prepared for a comparison. To eliminate the thickness effect on the electrochromic properties, samples with the similar thicknesses of 200 – 300 nm were selected for further experiments. The cyclovoltammograms for the composite film and the polyaniline film are given in Fig. 6. As can be seen from the curves, the two samples showed almost the same shape of cyclovoltammograms. Two anodic peaks and two cathodic peaks were observed at the same region of potentials. However, they showed a little difference of peak height. For the composite film the peak at a lower anodic potential (~0.2 V, Ia) is higher than the peak at a higher anodic potential (~0.75 V, Ib), whereas the composite film showed lower peak at a higher anodic potential (~ 0.8 V, Ib).

The peaks at higher anodic potential represent the oxidation reaction to form nigraniline and pernigraniline of polyaniline [15]. In this respect, it could be said that in the composite film the pernigraniline formation was
depressed as compared with the polyaniline film. Nigraniline phase usually exhibits dark blue color whereas pernigraniline shows dark gray or black. They are the highly oxidized form of polyaniline. The highly oxidized form at high anodic potential is generally weak against chemical attack from the electrolyte and is the main cause of the electrochemical degradation of polyaniline [16]. Therefore, it is noticeable that in the composite film formation of the highly oxidized and chemically less stable form is reduced.

![Graph](image_url)

Fig. 6 Cyclovoltammograms of the prepared cells with the working electrodes made of a) silica/polyaniline composite and b) polyaniline, both with a scan rate 50 mV/s.

Since the formation of pernigraniline was reduced in the composite film, it can be expected that the degradation will be slower than in the polyaniline film. The degree of degradation was checked by measuring the color contrast change with the number of potential switching between -0.2 V and +1.0 V with 30 seconds delay. As can be seen from Fig. 7, the composite film maintained larger color contrast than the polyaniline film after the same number of switching. This means the degradation of composite film was slower than that of the polyaniline film. The color contrast of the composite film decreased from 15.1% to 8.24% after 80 switching whereas that of the polyaniline film decreased from 18.5% to 5.5%.

![Graph](image_url)

Fig. 7 Color contrast (at 600 nm) decrease during potential switching between -0.2 V and +1.0 V: a) silica/polyaniline composite film, b) polyaniline film.

With the electrochromic characterization results, it could be said that the composite film has higher durability than the polyaniline film which is supposed to be due to the suppression of the highly oxidized and less stable form of polyaniline at high anodic potential.

4 Conclusion

The composite nanoparticle of silica/polyaniline was synthesized from aqueous micelles of an inverse (water-in-oil) microemulsion using HCl as catalyst. Obtained particles were characterized by comparing the surface area change of the composites with that of the pure silica particles during heat treatment. It was shown that the obtained particles are in the form of composite nanoparticles. The enhancement of durability and stability was shown from the film made of silica/polyaniline composite nanoparticle. The stability enhancement was supposed to be due to the suppression of the highly oxidized and less stable form of polyaniline. The enhancement is believed to be caused by the protective effect of the composite structure of the nanoparticle.

References:


