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Electrophoretic Deposition of Nanoparticles as Electrocatalysts for Electrolysis in the Solar Sulfur Ammonia Hydrogen Production

Nicole S. Pacheco, Neil Verma, Komail Haider and Jan B. Talbot[a,*]

Chemical Engineering Program
Department of NanoEngineering
University of California, San Diego
La Jolla, California 92093, USA
[a]jtalbot@ucsd.edu

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Abstract. Cobalt ferrite nanoparticles were deposited using electrophoretic deposition from two different bath chemistries, 90 vol.% water and 10 vol.% isopropanol with hexadecyltrimethlyammonium bromide (CTAB) and 100 % ethanol. The deposits were tested for electrocatalytic activity for the oxidation of ammonium sulfite to ammonium sulfate as part of a solar sulfur ammonia thermochemical cycle to produce hydrogen.

Introduction

The solar sulfur ammonia (SA) thermochemical cycle is a potential process for splitting water to produce hydrogen [1, 2]. The hydrogen production sub-cycle in the SA cycle consists of the electrolytic oxidation of ammonium sulfite to ammonium sulfate. The reactions, in basic medium, are as follows:

Anode reaction: $SO_3^{-2} + 2OH^- \rightarrow SO_4^{-2} + H_2O + 2e^-$ $E^o = -0.936V$ (1)

Cathode reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^o = -0.828V$ (2)

Overall reaction: $SO_3^- + H_2O \rightarrow SO_4^{-2} + H_2$ $E^o = -0.108V$ (3)

The anodic reaction is kinetically slow; both cobalt ferrite ($CoFe_2O_4$) and platinum cobalt (Pt_3Co) films have proved to be good electrocatalysts [1]. Therefore, $CoFe_2O_4$ and Pt_3Co nanoparticles have been investigated in attempt to improve this reaction rate and also to utilize less catalytic material. In our preliminary work, Tanakit et al. [3] used two different baths of 90/10 vol. % water/ isopropanol (IPA) with 1 mM CTAB and 100 % ethanol bath to deposit these particles on graphite paper using electrophoretic deposition (EPD). Additionally, it was determined that sonication of the baths during EPD led to more uniform deposits. For this study, the EPD of $CoFe_2O_4$ nanoparticles was further investigated. The substrates used for EPD were graphite paper and felt. The samples were tested for electrochemical activity in 2 M ammonium sulfite using linear sweep voltammetry.

Experimental

Zeta Potential. The concentration of particles in the solution was diluted to between 0.04 - 0.1 g/L. The pH value was changed with the addition HNO_3 or NaOH. A beaker containing 40 mL of the diluted bath was sonicated for 1 min. After sonicating, zeta potential measurements were taken of a sample with a Brookhaven Instruments Corporation ZetaPlus.

Electrophoretic Deposition. Cobalt ferrite nanoparticles were made from a co-precipitation method [4]. Then 2 g/L of $CoFe_2O_4$ nanoparticles were placed in 3 different baths each of 200 mL: 100 % ethanol, 90/10 vol. % water/IPA with 0.05 mM or 1 mM CTAB. These different baths were used for EPD on aluminum foil, as well as graphite paper and felt substrates.

Before performing EPD, the suspension was sonicated for 2 min, followed by placing a 15 cm^2 aluminum anode and the substrate (cathode) into the suspension to deposit the nanoparticles onto the substrate with sonication. A constant voltage was applied between the two electrodes from 16 -

54 V for 1 or 2 min. The deposited mass was determined by weighing before deposition and after baking the deposit at 200 °C in a vacuum oven baked for one hour.

For EPD, the substrate was positioned between two insulating Teflon plates, which were electrically connected to the anode placed parallel 2 cm away. When performing EPD on graphite felt, an anode was placed 2 cm from each side of the felt, which allowed the particles to deposit on both sides of the felt. The substrate areas for EPD were 4.91 cm^2 for aluminum, 3.14 cm^2 for graphite paper and 12 cm^2 for graphite felt (6 mm thick). Deposits were examined with a Phillips XL30 ESEM scanning electron microscope (SEM).

Electrochemical Testing. A standard three-compartment electrode system with a standard calomel electrode (SCE) as the reference electrode was used for electrochemical testing of the EPD deposits in 2 M ammonium sulfite. The working electrodes (EPD samples) were first soaked for either 24 h or 72 h in the electrolyte before testing, in order to attain reproducible results. The area of the graphite paper counter electrode was 8 cm^2, whereas the area of the EPD deposit on graphite paper was 3 cm^2 and on felt was 2 cm^2. The sample was cut from the middle of the EPD deposit. Linear sweep voltammetry (LSV) was conducted from 0.0 to 1.0 V vs SCE using a Princeton Applied Research VeraSTAT 3 potentiostat at a scan rate of 50 mV/s to test the electrocatalytic activity of the deposits compared to blank graphite substrates.

Results and Discussion

The zeta potential of CoFe2O4 nanoparticles in 90% water/10% isopropanol solution with 1 mM CTAB and in ethanol as a function of pH is shown in Fig. 1. In ethanol, the zeta potential decreased from 17 mV at pH 3 to -7 mV at pH 10. The zeta potential remained positive from 12 to 32 mV for the entire pH range in the CTAB bath. CTAB is a cationic surfactant, which helps disperse the nanoparticles in suspension. Additionally, the zeta potential of the $CoFe_2O_4$ nanoparticles increased from 8 to 29 mV as the CTAB concentration was increased from 0.05 to 1.1 mM at pH 5 as shown in Figure 2.

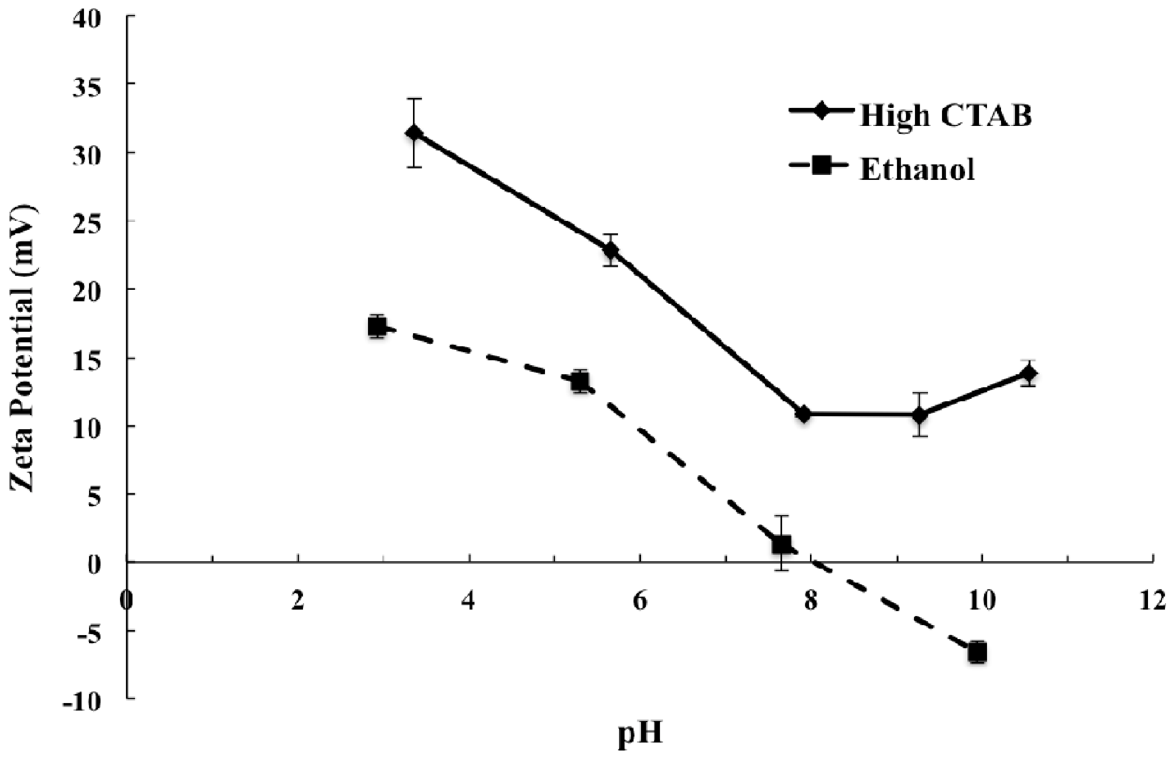

Figure 1: Zeta potential of cobalt ferrite particles in 90/10 vol. % water/IPA with 1 mM CTAB and in ethanol.

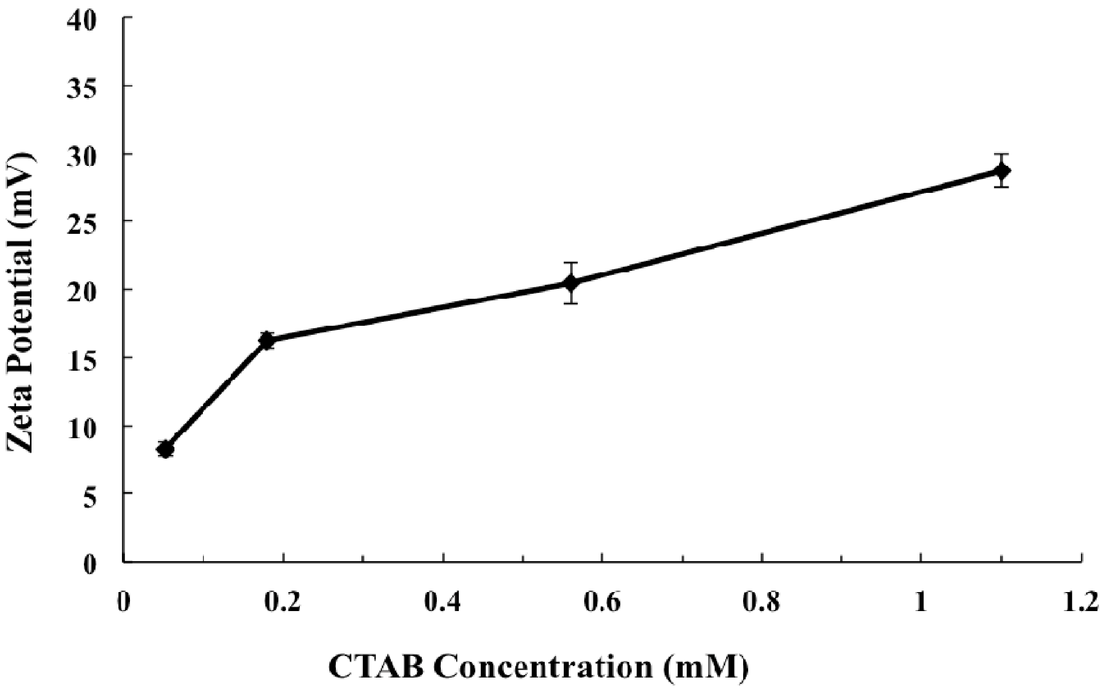

Figure 2: Zeta potential of cobalt ferrite particles in 90/10 vol. % water/IPA at pH 5 with varying CTAB concentration.

EPD of $CoFe_2O_4$ nanoparticles in 100 % ethanol bath was performed at a pH of 5 and in both 1 mM and 0.05 mM CTAB bath at a pH of 6 onto both graphite paper and felt substrates. Initially, EPD was performed on aluminum foil substrates to test the deposition conditions and adhesion. For reference, the mass of a monolayer of cobalt ferrite spherical nanoparticles with a diameter of 20 nm on an area of 4.91 cm^2 was calculated to be 0.03 mg assuming hexagonal close packing, or 6.1 $\mu g/cm^2$. EPD in 100 % ethanol bath at pH 5 was done on aluminum at varying times from 35 to 55 s at 5 V with sonication. Figure 3 shows the cobalt ferrite deposit density (mass per area) as a function of time at 5 V in which the deposit weight increases linearly. Thus, a monolayer of $CoFe_2O_4$ nanoparticles can be deposited on aluminum by EPD in ethanol at conditions of 5 V for ~45 s.

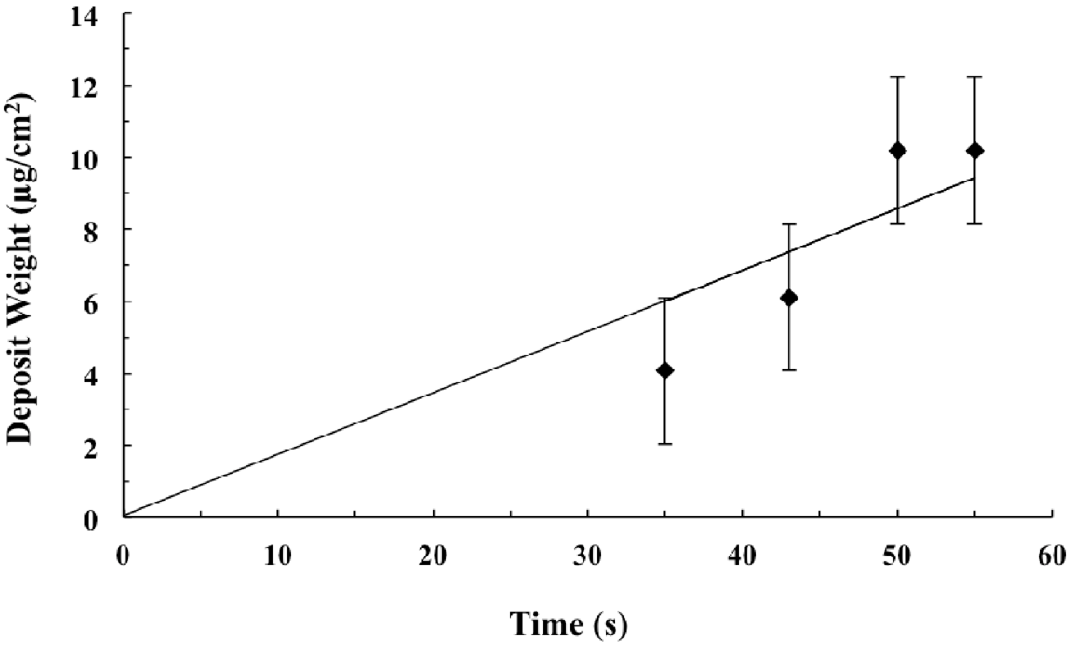

Figure 3: Deposit weight vs. deposition time at 5 V for cobalt ferrite in 100% ethanol.

Depositions were performed on aluminum for 1 min at 10 - 40 V in a 100 % ethanol bath at pH 5 and cobalt ferrite in 0.05 mM CTAB bath at pH 6. Then all of these samples were baked at 200 ^{o}C in a vacuum oven for 1 hr. Samples were soaked in water for 24 hours and weighed to assess wet adhesion. Also, baked samples were subjected to a tape test to assess dry adhesion. There was no detectable loss by soaking in water and about 0 to 25 % of the particles deposited were removed by the tape test, signifying good wet and dry adherence. The EPD conditions for graphite substrates were an applied voltage of 21 - 40 V for 1 min. The measured current ranged from 10 - 219 mA with deposit weights ranging from 0.24 to 14.6 mg. A much large amount of nanoparticles could be deposited on the 3-dimensional felt. These conditions were chosen in attempt to attain complete coverage with minimal layers of particles.

The deposits were tested for electrochemical activity in 2 M ammonium sulfite. Figure 4 compares the LSV (current density vs applied voltage) of $CoFe_2O_4$ nanoparticles deposited on graphite paper and felt using EPD from ethanol (E) and CTAB baths at a concentration of 1 mM (CHigh) or 0.05 mM (CLow), which showed the highest electrochemical activity. All of the samples were soaked for 24 h in the electrolyte, except for the samples on felt from the ethanol and CLow suspensions, which were soaked for 72 h. All deposits showed electrochemical activity greater than the blank graphite substrates. For EPD on graphite paper, the deposits from the ethanol and high concentration CTAB baths gave the highest electrochemical activity (in Fig. 4a), whereas on felt the deposit from the low concentration CTAB bath showed the highest electrochemical activity (in Fig. 4b), which also was the highest overall.

The deposits were examined by SEM, as shown with representative images of samples in Fig. 5, which compares the images of the cobalt ferrite samples which were the most electrochemically active with blank substrates. Also, further SEM analysis showed that the synthesized $CoFe_2O_4$ particles were 22 ± 3 nm in size. As shown in Fig. 4, the graphite paper has a rough, irregular surface, whereas the felt has many fibers in a mat. From these micrographs and others, it was concluded that deposits with minimal exposed substrate, as a result of thick deposits with slight cracking, tended to have better electrocatalytic activity compared to sparse, thin deposits. The higher surface area of felt from the paper substrate and the morphology of the deposits from the different baths could explain the difference in electrochemical activity in Fig. 4, but more research must be done to understand this better.

Conclusions

EPD conditions to deposit cobalt ferrite nanoparticles onto graphite paper and felt from two bath chemistries were determined. The deposits showed adequate wet and dry adherence to the substrates. The thick deposits with slight cracking tended to have better electrocatalytic activity compared to sparse, thin deposits. Further work will investigate EPD conditions for complete infiltration of the particles into the felt mat and optimization of the amount of nanoparticles on the substrate to improve electrocatalytic activity for the anodic reaction for hydrogen production.

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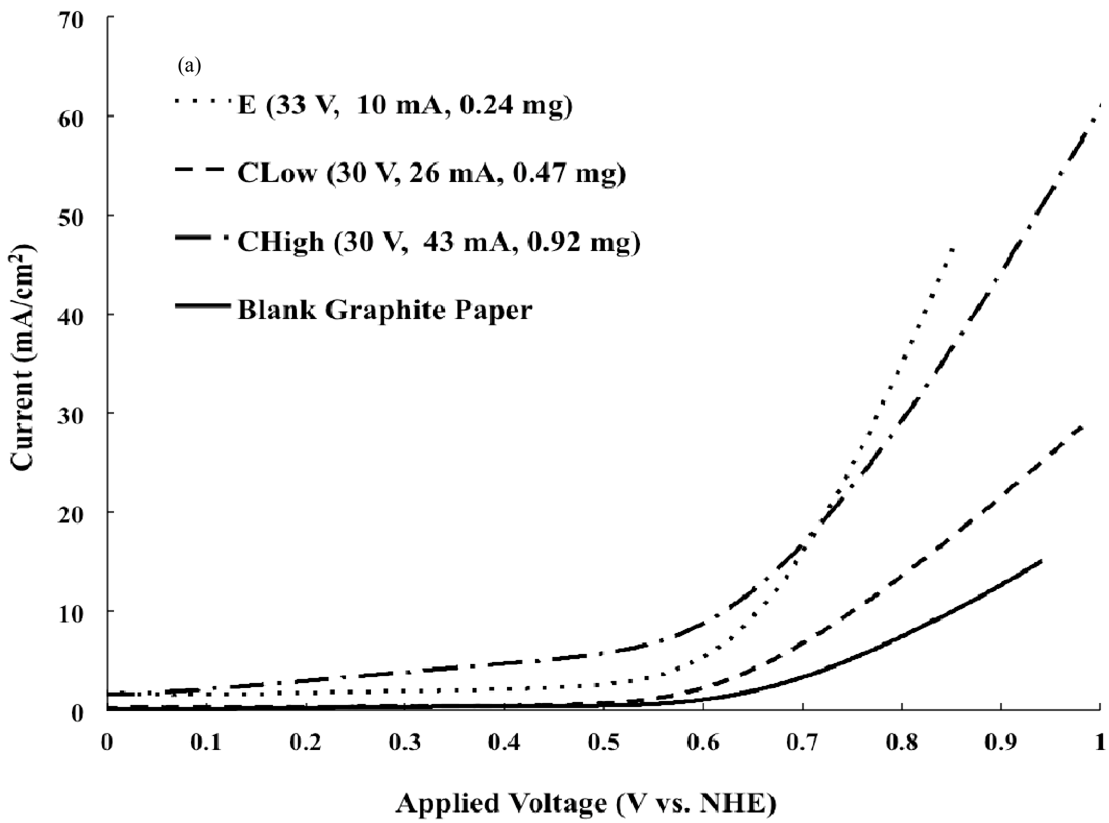

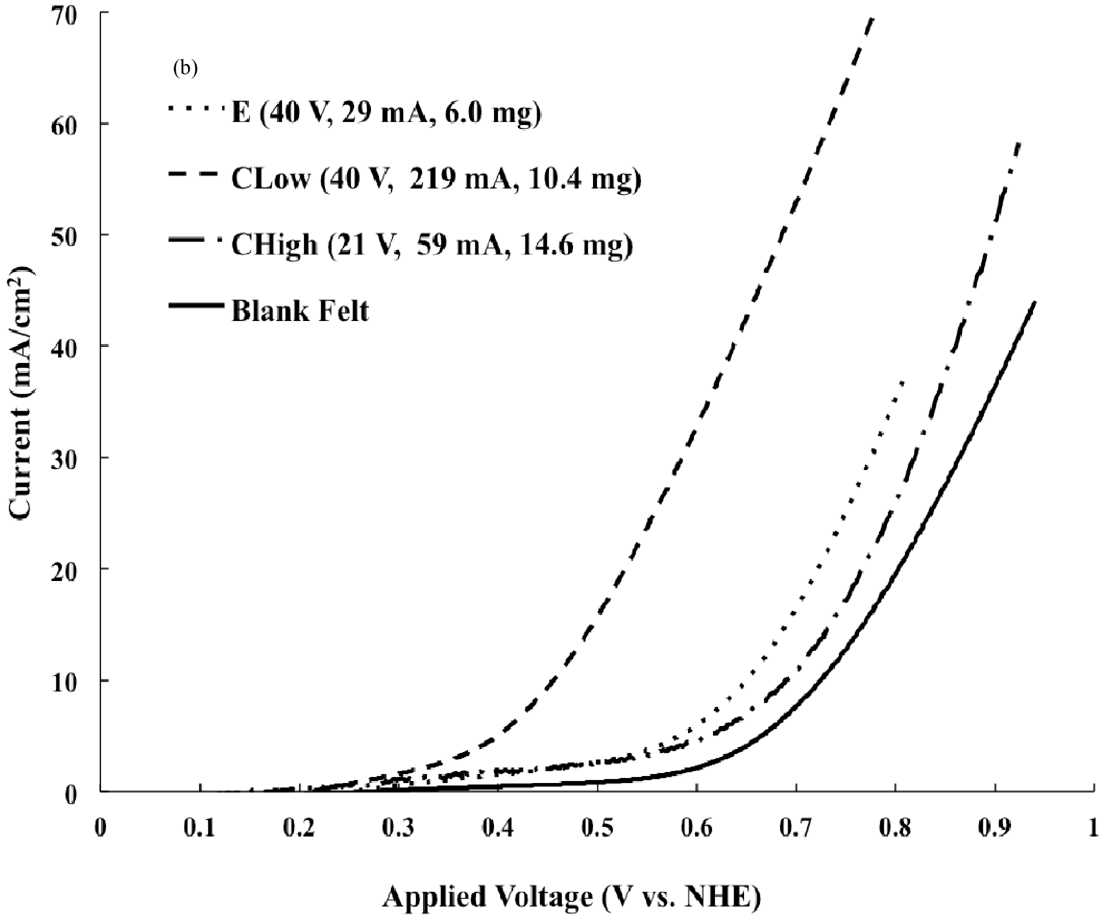

Figure 4: Electrocatalytic activity showing current density vs. voltage of EPD deposits in 2 M ammonium sulfite on (a) graphite paper and (b) felt comparing the various baths and EPD conditions.

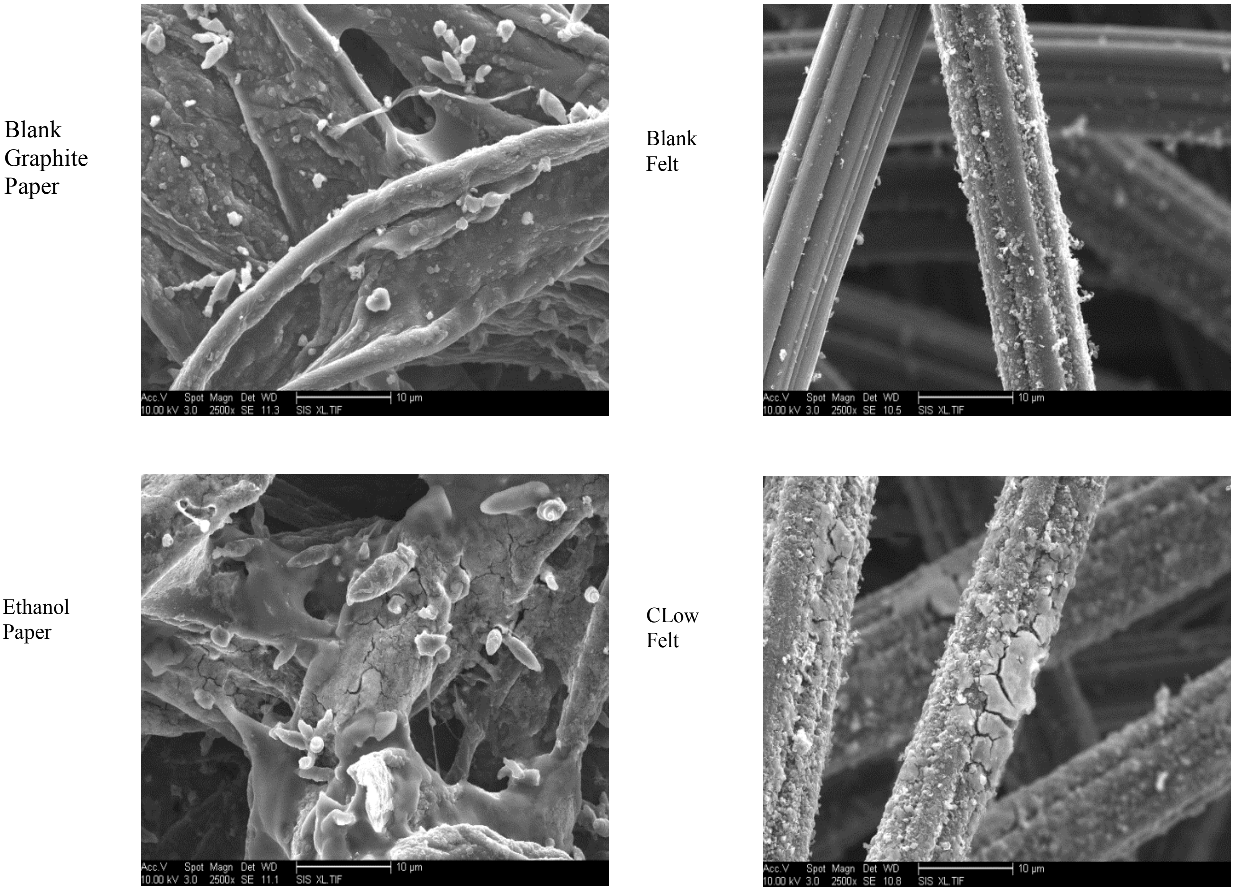

Figure 5: SEM micrographs of cobalt ferrite nanoparticles deposited on a graphite paper from ethanol and felt from a low CTAB bath (CLow) compare to the blank substrates.

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