



## Surface Treatment of CoS/Polymer Nanocomposite Membranes for Improving Wettability and Surface Energy

N. K. Agrawal<sup>1</sup>, R. Agarwal<sup>2</sup>, Y. K. Vijay<sup>3</sup> and K. C. Swami<sup>1</sup>

<sup>1</sup>Department of Physics, Malaviya National Institute of Technology, Jaipur 302017, India.

<sup>2</sup>Centre for Converging Technologies, University of Rajasthan, Jaipur - 302004, India.

<sup>3</sup>Department of Physics, University of Rajasthan, Jaipur-302004, India.

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### Abstract

Surface properties play important role in various biomedical and chemical applications. Chemical surface modification is most promising and simple technique for surface modifications. Quantum confinement effect changes the electronic structure of the nanocrystal, resulting in blue shift that is attributed to smaller particle size. CoS nanoparticles synthesized by chemical route gives a strong absorption peak in UV-Vis spectra at 317nm. Hence CoS nanoparticles were synthesized by wet chemical method and used with polymethyl methacrylate (PMMA) for preparation of polymer nanocomposite membranes (NCPM). These membranes were subjected for surface modification technique i.e. acid-base treatment and characterized by Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM), for identification of surface modification. Wettability and surface energy were also determined for these membranes.

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### Introduction

Polymers are important materials in modern manufacturing processes<sup>1</sup> and widely used in applications that offer various chemical<sup>2-3</sup>, mechanical<sup>4</sup> and elastic properties<sup>5</sup> along with lightweight<sup>6-8</sup>, flexibility<sup>9</sup> and good processability<sup>10</sup>. Diverse applications of polymers in every-day<sup>11</sup>, industrial<sup>12</sup> and medical<sup>13-15</sup> uses depend upon physical<sup>16</sup>, chemical<sup>17</sup> and biological interactions<sup>18</sup> of molecules or micro-organisms at their surface<sup>19</sup>. Being transparent and durable, PMMA is a versatile material that has been used in wide range of fields<sup>19</sup> and applications<sup>20</sup> such as rear-lights<sup>21</sup>, instrument clusters for vehicles<sup>22</sup>, appliances and lenses for glasses<sup>23</sup>, medical<sup>24</sup> and implants<sup>25</sup> etc.

Nanocomposites can be synthesized from clays and organoclays using the method like in-situ polymerization<sup>26</sup>, solution<sup>27</sup> and latex<sup>28</sup>. Polymer nanocomposites are materials in which nanoscopic inorganic particles, typically 10-100 nm in at least one dimension, are dispersed in an organic polymer matrix in order to dramatically improve the properties of the polymer<sup>29-30</sup>. The synthesis of polymer nanocomposites is an integral aspect of polymer nanotechnology<sup>31</sup>. Polymer nanocomposites represent a new alternative to conventionally filled polymers because of their nanometer size<sup>32</sup> filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites<sup>33</sup>. These include increased modulus<sup>34</sup>, strength<sup>35</sup>, outstanding barrier properties<sup>36</sup>, improved solvent<sup>37</sup>, heat resistance<sup>38</sup> and decreased flammability<sup>39</sup>.

Usually, polymer does not have these properties for various applications<sup>40</sup> resulting in undesired surface events that can lead to failure of materials and device or system containing it<sup>41</sup> for ex. delamination of adhesive bonds<sup>42</sup>, permanent staining of a fabric<sup>43</sup>, fouling of membranes<sup>44</sup> with proteinaceous films, a false positive

or false negative immunoassay results<sup>45</sup> and bacterial grown on catheters<sup>46</sup>.

Polymeric Nanocomposites are used almost in all industries ranging from semiconductors<sup>47</sup>, coatings<sup>48</sup>, household appliances<sup>49</sup>, automotive and biomedical implants<sup>50</sup>. They generally have excellent bulk physical<sup>51</sup> and chemical properties<sup>52</sup>. However, certain properties such as low surface energy<sup>53</sup>, low wettability<sup>54</sup> and high electrical resistivity sometimes limit their applications. To get rid of this, surface modification techniques are used to alter polymer surfaces without affecting the bulk properties of the material<sup>55</sup>.

Therefore, it is not only desirable but also vital to modify polymer surfaces, whether merely to clean them or to modify them physically, chemically, mechanically or biologically, in order to control the subsequent surface interactions and responses which are required for various applications<sup>56-58</sup>.

Hence, in this study we have synthesized nanocomposite polymethyl methacrylate membranes by solution casting method. These membranes were subjected to surface modification using acid-base etching. The modified surface was characterized by various techniques. Contact angle measurements were also performed for these membranes to determine the wettability of the modified surface.

### Experimental

CoS nanoparticles were synthesized using wet chemical method. Cobalt acetate, Na<sub>2</sub>S and Ethylene diamine tetra acetic acid (EDTA) of sigma Aldrich AR grade were used for synthesis. 0.2 molar solutions was prepared for each of the above mentioned salt, then the solution of cobalt acetate and Na<sub>2</sub>S were mixed slowly into the solution of EDTA with the mixing rate of 5 ml/min. The solution was continuously stirred for two hours using magnetic

stirrer at 800 rpm. Brown coloured CoS nanoparticles were obtained after the completion of the reaction. These nanoparticles were washed with distilled water and ethanol using centrifuge and then dried at room temperature. These dried nanoparticles were characterized by UV Vis spectroscopy and TEM and then used for preparation of polymer nanocomposite membranes.

Polymer membranes were prepared using solution-casting method, which is one of the easiest and less time consuming methods. In this method, the PMMA granules were weighed, dissolved in dichloromethane and stirred using magnetic stirrer at room temperature for 3 hours to obtain the uniform dissolution. The hence obtained clear solution was poured into the petri-dishes floating on mercury. Mercury was used to obtain the uniform thickness of the membranes. Now, the solvent in the petri-dishes was allowed to evaporate for 10- 12 hrs. resulting in films that were peeled off using forceps.

Polymer nanocomposite membranes were also prepared using solution casting method. The CoS nanoparticles were dispersed in dichloromethane using ultrasonicator followed by mixing of this dispersed solution with PMMA solution prepared using above mentioned method. Now, this solution was stirred, poured into petri-dishes, solvent was allowed to evaporate and hence obtained membranes were peeled off using forceps.

Surface modification is quite often used to create surfaces with properties considerably different from that of the bulk of the polymeric materials. Acid-base etching is one of the most widely used surface treatment technique. In this study, 1N HCl and 1N NaOH solution in water was prepared. Then, pristine and nanocomposite membranes were dipped into the HCl and NaOH solution. After 20 minutes membranes were taken out of the solution and washed with distilled water. To study the surface modification, these membranes were characterized by SEM and AFM.

Nanoparticles and membranes were characterized using UV Visible spectrophotometer (Shimadzu, UV-2100). PL emission spectrum of nanoparticles was recorded by (Shimadzu, PL-RF5301) spectrofluorometer. Particle size and morphology of nanoparticles was determined using Technika TEM instrument operating at 200 KV. Study of surface morphology of the membranes was done using Scanning Electron Microscope (SEM)(Carl ZEISS EVOR-18) operated at 20 KV. Surface roughness of the polymer surface was observed using Atomic Force Microscopy (AFM).

## Results and Discussion

Morphology and size of the synthesized CoS NPs were observed using transmission electron microscope (TEM). Sample was prepared by placing few drops of ethanol dispersed nanocrystalline on carbon coated copper grids. Figure 1 shows the TEM image of the synthesized CoS nanoparticles. Image shows 5-8 nm size of CoS nanoparticles. From Fig.1 it is clear that the particles are almost of spherical and uniform distribution.

The UV Visible absorption spectrum peak for CoS nanoparticles was obtained at 317 nm as shown in Fig. 2(a). Nanoparticles are found optically stable in visible range and can be used in optical devices, having linearity in visible range<sup>15</sup>. The UV Vis absorption shows that the absorption edge of CoS nanoparticles exhibit the significant blue shift as compare to bulk CoS. Bulk CoS show semiconducting properties, hence its band gap can be calculated using Tauc relation, that relates the optical absorbance coefficient ( $\alpha$ ) of a semiconductor with the band gap of material. Tauc relation can be expressed as:  $\alpha h\nu = A(h\nu - E_g)^n$ , where  $\alpha$  is the absorption coefficient,  $E_g$  is the absorption band gap, A is constant, n depends on the nature of the transitions and can have values  $1/2, 1, 3/2$  and 2

corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively.

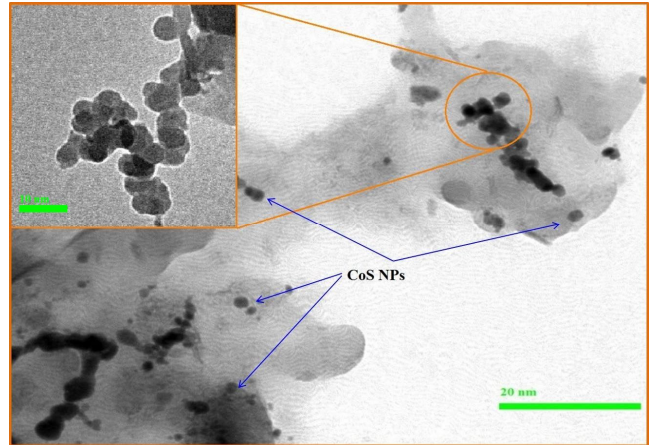


Figure 1: TEM image of synthesized CoS nanoparticles

In this case  $n=1/2$ , as CoS shows direct allowed transition. The absorption spectra of CoS based on Tauc relation is shown in Fig.2(b).

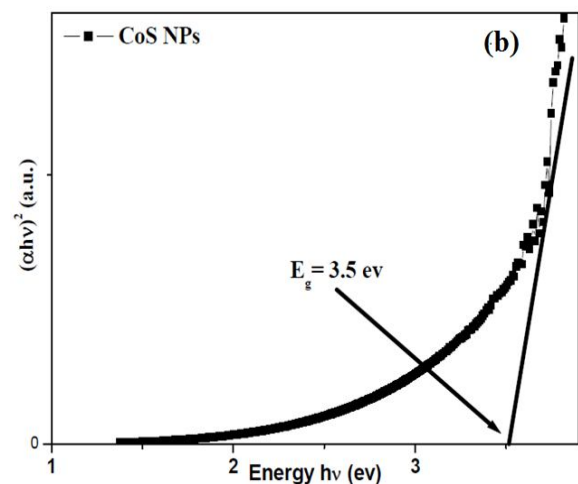
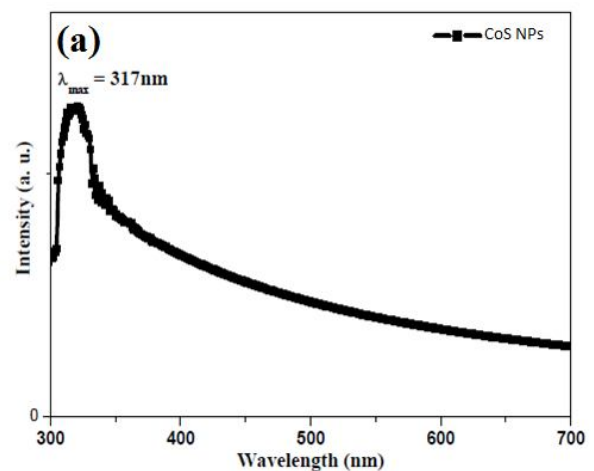


Figure 2: (a) UV Vis spectra of CoS nanoparticles, (b) Plot using Tauc relation for determination of band gap of CoS nanoparticles

The intercept of the tangent to the plot  $(\alpha h\nu)^2$  versus  $h\nu$  gives a good approximation of the band gap energy for this direct band gap material. The band gap energy can be determined by extrapolation of curve to the zero absorption coefficients. Fig. 2(b) as plotted using Tauc relation shows band gap  $E_g = 3.5$  eV of the synthesized CoS NPs. This band gap energy ( $E_g = 3.5$  eV) of CoS nanoparticles are much larger than the value of the bulk CoS ( $E_g = 2.1$  eV). This can be explained because the band gap of the semiconductors has been found to be particle size dependent. The band gap increases with decreasing particle size and the absorption edge is shifted to a higher energy (blue shift) with decreasing particle size. Considering the blue shift of the absorption position as compare to bulk CoS, the absorption onset of the present samples can be assigned to the direct transition of electrons in the CoS nanoparticles.

The photoluminescence (PL) spectrum of CoS nanoparticles is shown in Fig. 3. The emission peak occurs at 360 nm that is also blue shifted when compared to the bulk CoS. This emission is due to the recombination of electron and hole pairs. The blue shift demonstrates the strong quantum confinement.

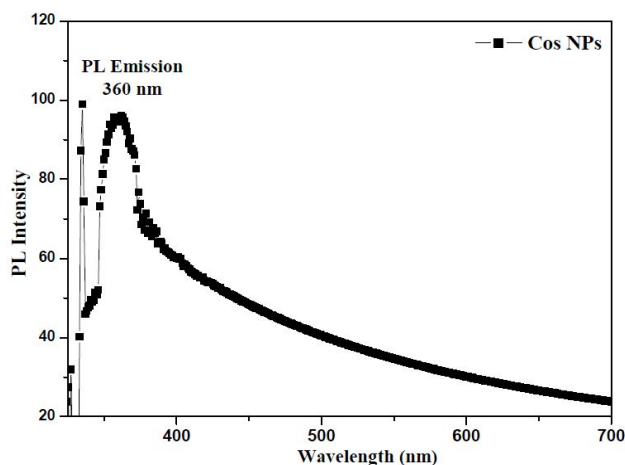


Figure 3: Emission spectra of synthesized CoS nanoparticles

Surface morphology of the membranes was observed using SEM. Fig. 4 presents surface morphologies of PMMA membranes and nanocomposite membranes. It shows that SEM image of untreated membrane was smooth and when the membranes were treated with acid and base solutions membrane surfaces became rough, showing increase in porosity in the treated membranes than in the untreated membrane. Influence of the surface treatment on the morphology of nanocomposite membranes, surface topography and roughness analysis of modified surface was carried out by atomic force microscopy (Nano Surf Easy Scan 2). From the analysis of the images surface roughness was found to be increased after acid, base treatment as clear from Fig. 5. Further, higher surface roughness was observed after base treatment in compare to acid treatment. Similar facts were observed in case of the nanocomposite membranes. It is clear from images that the pristine membrane has smooth surface and become rough after treatment.

### Wettability

Hydrophobic materials are not favourable for many of the biomedical applications, cell adhesion, bacterial attachment and proliferation. Hence most of material required high wettability and high surface energy to be used as biomaterial, which could be measured by measuring water contact angles<sup>57</sup>. Here, the water contact angle and water absorption ratio of the untreated and treated membranes is studied. The theory of contact arises from the

consideration of a thermodynamic equilibrium between the three phases: the vapor phase (V), liquid phase (L), the solid phase (S). If the solid–vapour interfacial energy is denoted by  $\gamma_{sv}$ , the solid–liquid interfacial energy by  $\gamma_{sl}$ , and the liquid–vapour interfacial energy (i.e. the surface tension) by  $\gamma_{lv}$ , then the contact angle  $\theta$  is determined using Young's Equation for Measurement of Contact Angle  $\{\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta\}$ <sup>58</sup>. We have measured water contact angle for these surfaces and calculated the surface energy for the acid-base treated polymer nanocomposite membranes. Surface energy and contact angle are shown in table 1. It was observed that the water contact angle for treated membranes was lowered and water absorption ratio was increased. This means, the surface wettability of the treated membranes were enhanced showing the improved hydrophilicity of the membranes.

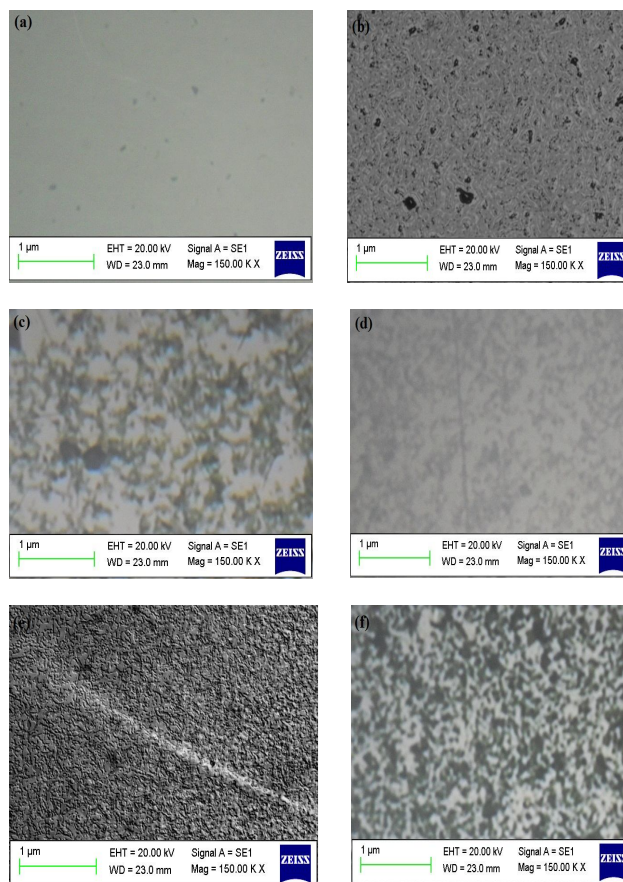
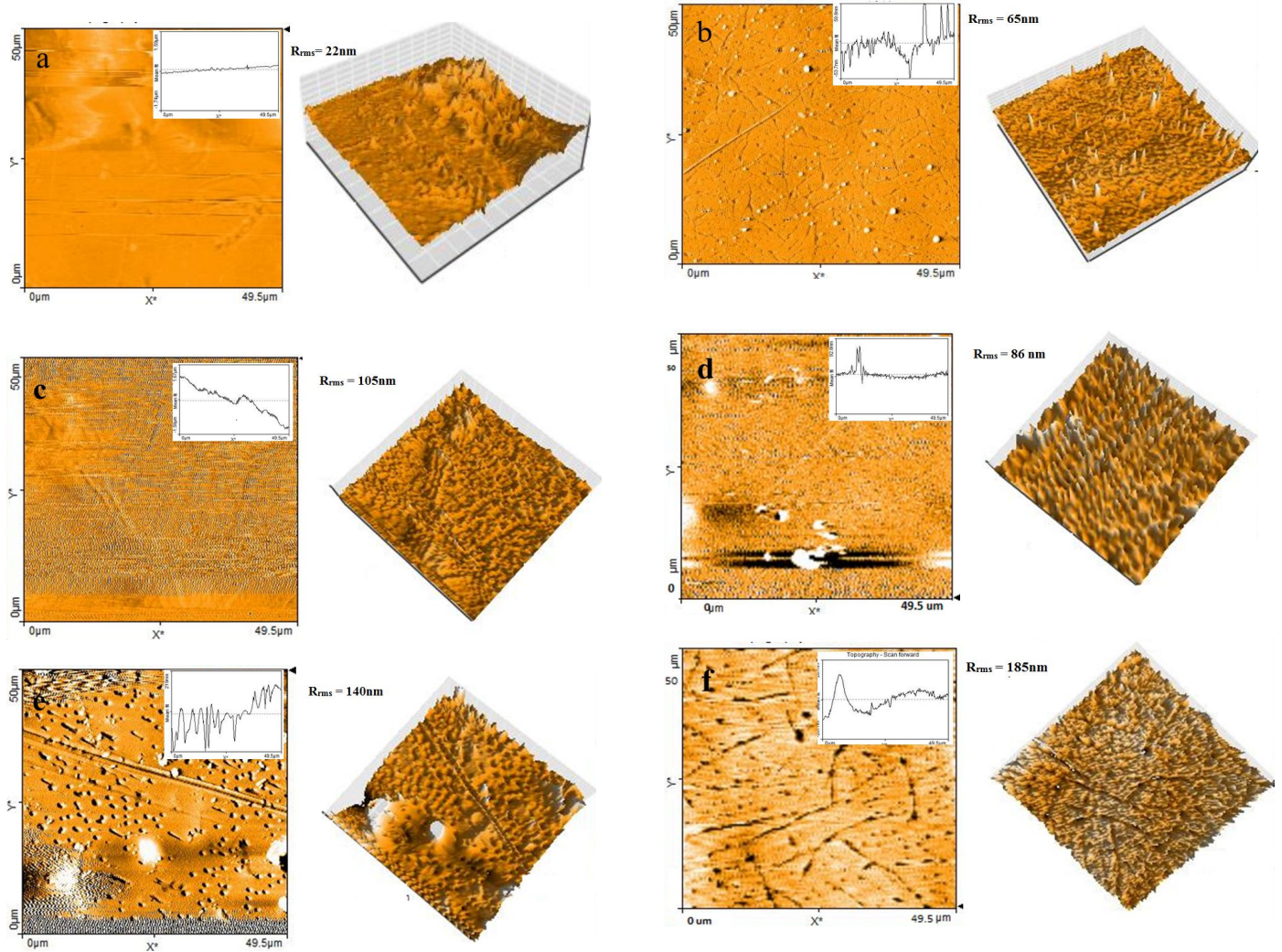


Figure 4: SEM images of (a) Pristine PMMA, (b) HCl treated PMMA, (c) NaOH treated PMMA, (d) CoS doped membrane, (e) HCl treated CoS doped membrane, and (f) NaOH treated CoS doped membrane.

Table 1: Study of Wettability in terms of Contact Angle and Surface Energy for NCPM

Sample	Contact Angle ( $\theta$ in degree)	Surface Energy ( $\text{mJ/m}^2$ )
Pristine PMMA	130 $\pm$ 1	31 $\pm$ 0.5
HCl treated membrane	105 $\pm$ 1	59 $\pm$ 0.5
NaOH treated membrane	95 $\pm$ 1	68 $\pm$ 0.8
CoS doped PMMA membrane	103 $\pm$ 1	60 $\pm$ 0.8
HCl treated CoS doped membrane	68 $\pm$ 1	103 $\pm$ 1.2
NaOH treated CoS doped membrane	58 $\pm$ 1	115 $\pm$ 3.2



**Figure 5:** 2D colour map, 3D roughness/view and line graph of AFM images of (a) Pristine PMMA, (b) HCl treated membrane, (c) NaOH treated membrane, (d) CoS doped membrane, (e) HCl treated CoS doped membrane, and (f) NaOH treated CoS doped membrane.

## Conclusions

Nanoparticles of CoS having spherical shape and particle size ranging from 5-8 nm were synthesized using wet chemical method. 5% CoS PMMA nanocomposite membranes were prepared by solution cast method. These membranes are subjected for acid base treatment using HCl and NaOH. Significant increase in surface roughness and changes in topography has been observed after treatment as determined by SEM and AFM measurement. Surface modification effect was more significant when treated with base solutions in compare to acid treatment. This technique can be used to prepare nanocomposite membranes with desired surface properties, important in many biomedical applications. As an application of this process we have investigated wettability of NCPM in terms of contact angle and surface energy. Contact angle was decreased while surface energy was increased that shows improvement in wettability of NCPM.

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