

# Preparation of Copper Sulfide Deposition on Modified Poly(Ethylene Terephthalate) Fibres with Good Conductivity

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## Abstract

*The immobilization of CuS on the surface of poly(ethylene terephthalate) (PET) fibres was carried out by the functionalization of PET fibres with chitosan (CS), followed by the chemical deposition method. Crosslinked chitosan with NH<sub>2</sub> functionality was used as a chelator to absorb copper ions, which can successfully initiate CuS deposition in the following chemical deposition stage. The CuS-loaded fibres were characterised by scanning electron microscopy, X-ray diffraction, infrared spectroscopy and thermal gravimetry, respectively. The properties of tensile and conductivity were also investigated. The lowest surface resistance 42 Ω/cm of the treated PET fibres was obtained when the CS concentration was 1.0%.*

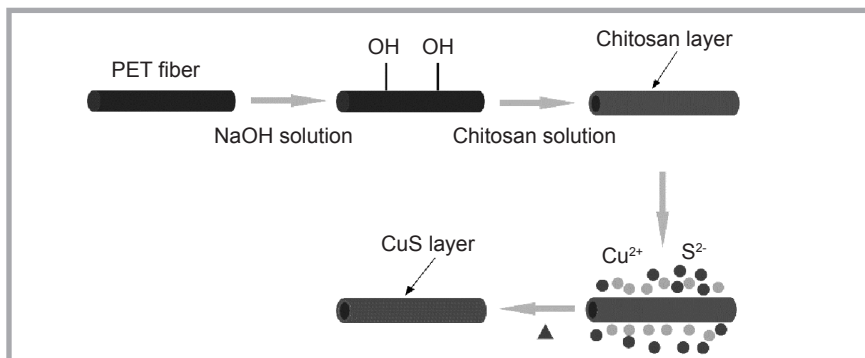
**Key words:** poly(ethylene terephthalate), CuS, conductive fibres.

## Introduction

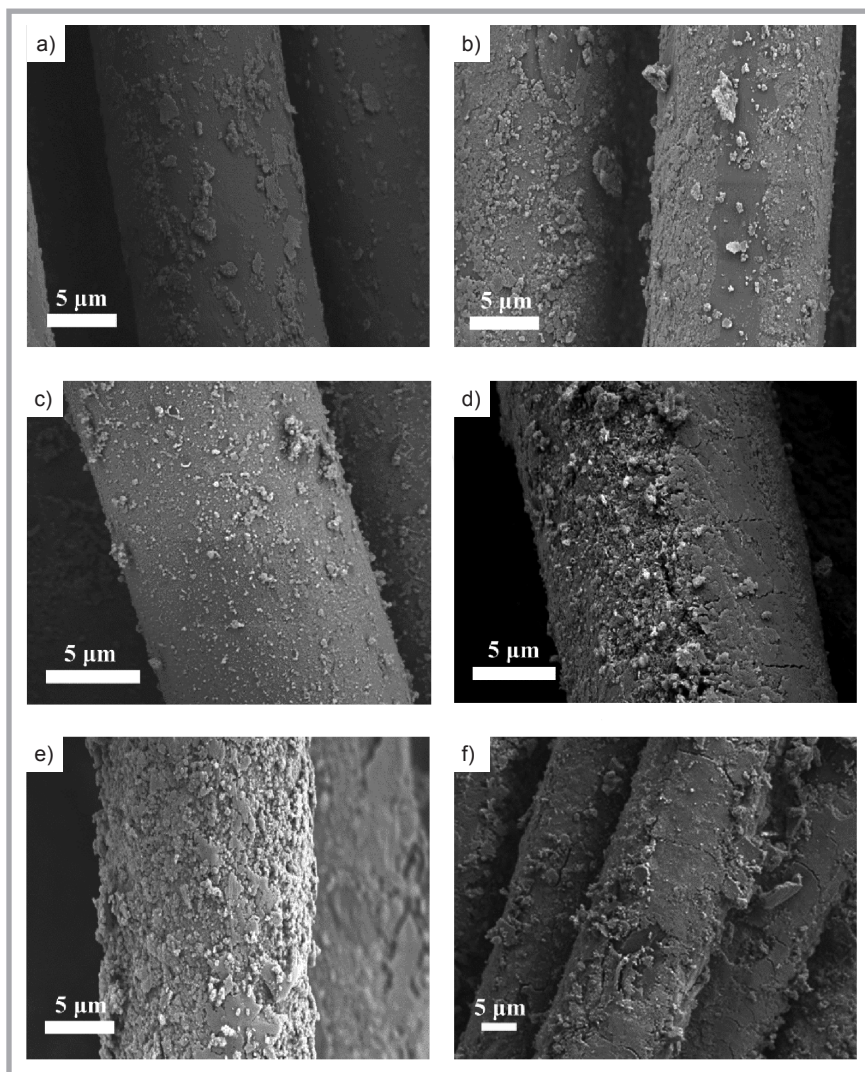
Copper sulfide is a p-type semiconductor and has been used in light emitting diodes, solar cells, biology markers, EMI shielding and photocatalytic [1]. Besides this, the CuS compound is environmental friendly, the price of which is also much lower than for noble metals such as Ag and Pd. All that has made CuS more economical and feasible in industrial applications. So far, a variety of methods have been employed for the deposition of CuS thin films, such as chemical vapour deposition [2], thermal co-evaporation [3], successive ionic layer adsorption and reaction (SILAR) [4], photochemical deposition [5], the electrochemical method [6] and chemistry bath deposition (CBD) [7-10]. Among these, chemical bath deposition is an attractive technique for the deposition of semiconductors as it does not require sophisticated instrumentation like a vacuum system and other expensive equipment. With the CBD method, the electrical conductivity of the substrate is not a necessary requirement. Low temperature deposition also avoids the oxidation and corrosion of metallic substrates. Better orientations and improved grain structure can be obtained under easily controlled deposition parameters. Poly(ethylene terephthalate) fibre is one of the most widely used polyester fibres, which are the world's largest and most commonly used synthetic fibres due to their high strength, high modulus, low-shrinkage, heat set stability, light fastness, chemical resistance, and so on [11-15]. Nevertheless poor moisture absorption, high specific resistance and the serious electrostatic phenomenon all limit the application of PET fibre. The dep-

osition of copper sulfide as fine particles onto the surface of an organic PET fibre is a promising approach to obtain electrically conductive fibres. Although this method has the advantage of giving large size electrically conductive films, there have been only a few reports [16, 17] on the subject, probably due to difficulty in obtaining good adhesion between the CuS layer and PET fibre surface.

To obtain a good electrically conductive fibre, surface treatment is an important part in obtaining firm bonding between the coating layer of the substrate and inorganic conductive materials [18-20]. Shen [21] produced electromagnetic shielding polyester fabrics by using carboxymethyl CS-palladium complexes as activation solution. It is known that with reactive groups like NH<sub>2</sub> and OH on the molecular chain, CS is prone to chelating of metal ions [22-24] such as Cu(II), Pb(II), Pd(II), Zn(II) and Hg(II) etc. To obtain conductive PET fibre with better adhesion strength, CS crosslinked by glutaraldehyde was used to form a catalyst-film on the fibre surface, which was then chelated with Cu<sup>2+</sup> ions and CuS plating subsequently initiated on the surface of the PET fibre. The benefit of this method was achieving a high quality of metal sulfide deposition thanks to the chelating interaction between CS and metal ions. The morphology of CuS-plated PET fibre was revealed by scanning electron microscopy (SEM). The crystalline structure, chemical composition and thermal stability of the conductive fibre were characterised by X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), and thermogravimetric (TG) analysis, respectively.



**Figure 1.** Schematic diagram for deposition of CuS onto PET fibres.



**Figure 2.** SEM photos of CuS-coated CS-PET fibres treated with different CS concentrations: a) 0.0%, b) 0.25%, c) 0.5%, d) 0.75%, e) 1.0%, f) 2.0%.

**Table 1.** Mechanical and conductive properties of PET fibres.

Sample	Resistance, $\Omega/\text{cm}$	Tensile strength, cN/tex	Elongation, %
Raw	–	30.2	9.5
CS 0.0% + CuS	–	28.8	10.3
CS 0.25% + CuS	5200	29.2	9.1
CS 0.5% + CuS	180	29.8.1	7.9
CS 0.75% + CuS	50	30.3	6.4
CS 1.0% + CuS	42	30.9	6.2
CS 2.0% + CuS	75	31.6	7.0

## Experimental

PET fibres were immersed in an aqueous solution of 5 wt% sodium hydroxide for 60 min at 80 °C. Then the fibres were cleaned with distilled water several times. CS solution was prepared by dissolving CS in HAc (2.0 wt%), followed by dripping 4 g/l glutaraldehyde with moderate stirring for 20 min at 20 °C. To form a film on the fibre, the fibre prepared was dipped into this solution and then cured at 120 °C for 40 min. The CS treated fibres were dried at 60 for 1 h and plated with CuS by dipping them into an aqueous solution of 2 wt%  $\text{CuSO}_4/\text{Na}_2\text{S}_2\text{O}_3$  (1:1 w/w) at 85 °C for 1 hr.

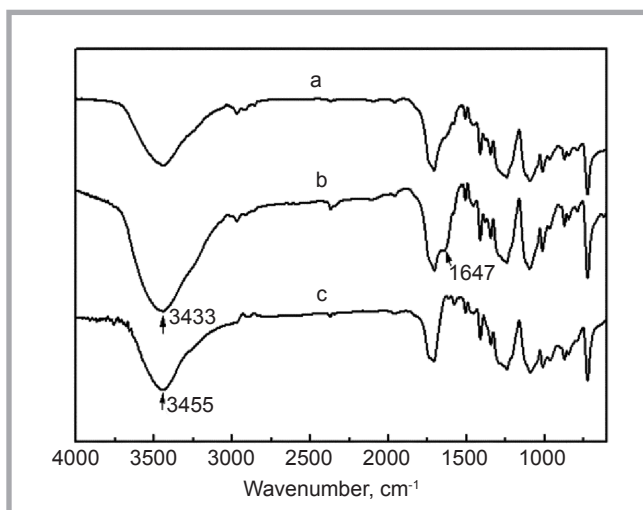
The morphology of the fibres was characterised by ZEISS-EVO18 (Germany) scanning electron microscopy (SEM). The samples were attached to sample supports and sputter-coated with a gold layer. A Fourier transform infrared spectrophotometer (FT-IR) (Nicolet 560, USA) was used to characterise the infrared spectra of the samples within the 4000-400  $\text{cm}^{-1}$  range. The structure of the fibres was studied by X-ray diffraction (XRD), and the diffraction patterns were recorded in the 2 $\theta$  range of 10-80°. The conductivity of the conductive fibres was measured using a digital multimeter (IDEAL 61-340, Victor, China). A thermal property test was carried out by means of an STA449C thermogravimetric analyzer (TGA, Germany).

## Results and discussion

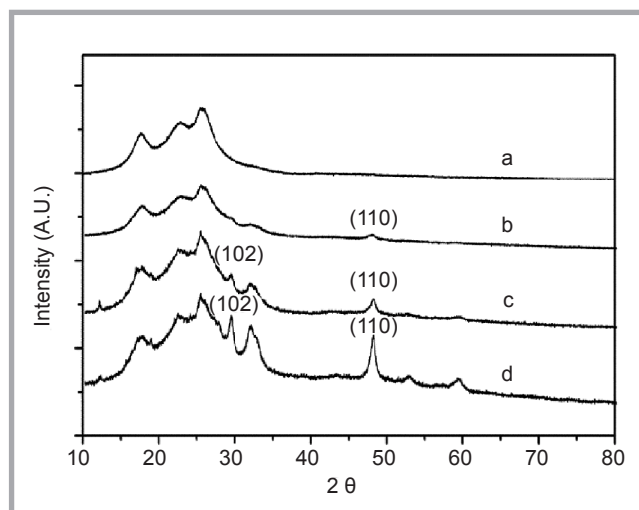
### Mechanical and conductive properties

To plate the PET fibres with CuS, as shown in **Figure 1**, the yarns were treated with CS to introduce amine groups on them in order to bond with CuS. The CS attached to the surface of PET fibres is reduced with sodium thiosulfate after complexing with copper ions and forms into CuS particles on the yarn surface. However, it is desirable for the amount of CS used to be as small as possible. Thus PET fibres were treated with five concentrations of 0%, 0.25%, 0.5%, 0.75%, 1.0% and 2.0% (w/v) CS to examine the effect of CS.

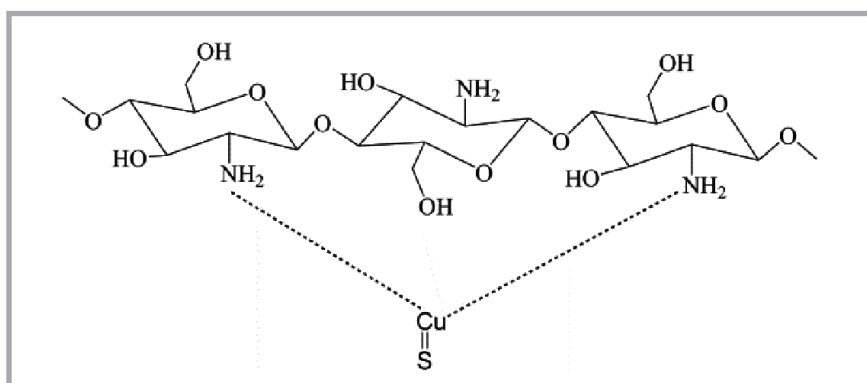
Mechanical and conductive properties of the CuS plated PET fibres are listed in **Table 1**. As can be seen in **Table 1**, the CS treated and CuS-plated PET yarns showed a decrease in the elongation at break and an increase in the strength



**Figure 3.** FTIR spectra of a) raw PET, b) PET 1% CS and c) PET 1% CS + CuS.



**Figure 5.** X-ray diffraction patterns of a) raw PET, b) PET 0% CS + CuS, c) PET 0.5% CS + CuS and d) PET 1% CS + CuS.



**Figure 4.** Schematic illustration of complexes of CS and Cu.

when the CS concentration was less than 1.0%. These changes are generally observed in polymer composites and are usually attributed to the effective stress transfer between the fillers and polymer matrix. In the same way, CS and CuS in the PET fibres are designed to make the transfer of stress effective by increasing the friction between PET fibres. The elongation-at-break of the plated PET yarns was reduced, but no problem was observed with respect to their use as yarns for textile. Conductivity was measured for plated PET yarns treated at different CS concentrations. **Table 1** plots the resistance of five types of PET yarns, including raw fibres. The resistance of PET fibres decreased with the increasing of CS concentration when the CS concentration was less than 1.0%. The average resistance of CuS plated PET fibre was 42  $\Omega$ /cm when the CS concentration was 1.0%, indicating good conductivity was imparted by this treatment.

#### SEM analysis

The effect of CS concentration on the deposited CuS layer was investigated by SEM. **Figure 2** shows the morphology of CuS-coated CS-PET fibres treated with different CS concentrations. It can be seen from **Figures 2.a, 2.b** and **2.c** that CuS particles on the surface of the PET fibres are sparse and discontinuous. Moreover most of the surface area of the PET fibres is not covered by CuS particles when the CS concentration is less than 0.5%. With an increase in concentration to 1.0% (**Figures 2.d, 2.e**), the CuS particle size increases, resulting in the formation of a continuous, uniform and compact CuS layer on the CS-PET fibre surface. When the CS concentration was 2.0% (**Figure 2.f**), the CuS layer was observed to have a lack of uniformity, with flaws. This non-uniformity causes a strong influence on the electrical resistance, because the flaws and metallic sulfide behave as a phase separated structure.

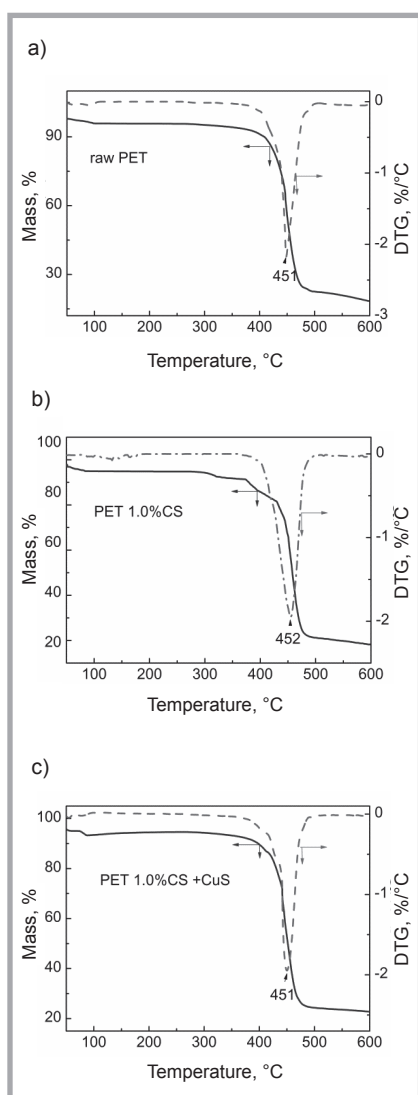
#### FTIR spectra

FTIR spectra of PET, CS 1.0%-PET and CuS-coated CS 1.0%-PET fibres are shown in **Figure 3**. As shown in **Figure 3.a**, a very intensive band was found at 1709  $\text{cm}^{-1}$ , which could be assigned to the stretching vibration of the C=O group in polyester. Some of the characteristics groups of polyester were also observed, such as the absorption peak at 1,412  $\text{cm}^{-1}$ , corresponding to the benzene ring skeleton structure, and at 1,242  $\text{cm}^{-1}$  and 1094  $\text{cm}^{-1}$ , attributed to symmetric and antisymmetric stretching vibration of the C-O-C bond, respectively. Comparing the spectra of **Figure 3.a** and **3.b**, the intensities of the absorbance at 1,647 and 3,433  $\text{cm}^{-1}$  correspond to C=O stretching (amide I) and NH bending (amide II), respectively. In the spectrum of CuS-coated CS 0.1%-PET fibres (**Figure 3.c**), the peak at 1,647  $\text{cm}^{-1}$  was significantly decreased, while the peak at 3,455  $\text{cm}^{-1}$ , which corresponds to the amino groups, substantially broadened and shifted to higher wavenumbers. These changes suggest that  $\text{Cu}^{2+}$  ions were complexed in the chitosan amino groups (illustrated in **Figure 4**).

#### XRD characterisation

The X-ray diffraction patterns of PET and CuS-coated CS-PET fibres treated with different CS concentrations are shown in **Figure 5**. The diffraction pattern of the copper sulfide obtained is characteristic of a crystalline material [25], which was subsequently identified as covellite porcelain [26]. According to the literature, the  $2\theta$  signals at ca. 29 and 48° are assigned to crystallographic planes (1 0 2)





**Figure 6.** TGA and DTGA curves of raw: a) PET, b) PET 1% CS and c) PET 1% CS + CuS.

and (1 1 0), respectively [27]. An increasing intensity of the peaks concerning the CuS structure according to the concentration of CS treatment is observed, which suggests a continuous deposition of CuS on the PET surface.

### Thermal property

The effects of CuS and CS on PET fibres were also reflected in the fabric thermal behavior, which was analysed by means of thermogravimetric analysis (TGA). **Figure 6** shows degradation profiles of raw PET, PET 1.0% CS and PET 1.0% CS + CuS fibres. It was clear that all TGA curves display a slower initial and then rapid degradation process. The three changes in the samples' mass loss were speeded up in the range of 380-470 °C, which indicated that the main chains of the polymer degraded seriously. From

**Figure 6**, it can be seen that the CS and CuS coat did not considerably affect the onset of the degradation temperature of PET fibres. The maximum decomposition temperature ( $T_{max}$ ) of the polymer can be determined precisely in the DTG curves, corresponding to the temperature peak in the DTG curve. It can be found that for untreated PET, PET 1.0% CS and PET 1.0% CS + CuS fibre, there was also not a significant difference for the  $T_{max}$  value, which was presumably due to the CS and CuS being attached to the surface of the fibres, and did not affect the internal structure and crystallinity of PET.

### Conclusions

In conclusion, this study aimed to enhance the electrical conductivity of PET fibres by introducing CuS – a stable compound with high electrical conductivity attached to PET fibres. We investigated how CuS plating changed the surface morphologies as well as mechanical, thermal, and electrical properties of the PET fibres. Three different concentrations of CS were used to determine the optimal concentration of CS required to plate PET fibres with CuS. The study's findings revealed that the PET fibres had the highest electrical conductivity when they were treated with 1.0% CS concentration. FTIR, SEM and XRD studies confirmed the presence of CuS on the CS modified PET fibre surface. TG analysis showed that CS-copper ion complex activation and the chemical deposition method did not affect the thermal properties of PET.

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### References

- Xiao-Sai H, Yong S, Li-Hui X, Li-Ming W, Li-Sha L, Ya-Ting Z. Preparation of flower-like CuS by solvothermal method for photocatalytic, UV protection and EMI shielding applications. *Applied Surface Science* 2016; 385: 162-170.
- Kemmler M, Lazell M, O'Brien P, Otway DJ, Park JH, Walsh JR. The growth of thin films of copper chalcogenide films by MOCVD and AACVD using novel single-molecule precursors. *Journal of Materials Science: Materials in Electronics* 2002; 13(9): 531-535.

- Bollero A, Grossberg M, Asenjo B, Gutierrez MT. CuS-based thin films for architectural glazing applications produced by co-evaporation: Morphology, optical and electrical properties. *Surface & Coatings Technology* 2009; 204(5): 593-600.
- Pathan HM, Desai JD, Lokhande CD. Modified chemical deposition and physico-chemical properties of copper sulphide (Cu<sub>2</sub>S) thin films. *Applied Surface Science* 2002; 202(1): 47-56.
- Podder J, Kobayashi R, Ichimura M. Photochemical deposition of Cu<sub>x</sub>S thin films from aqueous solutions. *Thin Solid Films* 2005; 472 (1-2): 71-75.
- Cordova R, Gomez H, Schrebler R, Cury P, Orellana M, Grez P, Leinen D, Ramos-Barrado JR, Del Rio R. Electro-synthesis and Electrochemical Characterization of a Thin Phase of Cu<sub>x</sub>S (x = 2) on ITO Electrode. *Langmuir* 2002; 18(22): 8647-8654.
- Shamraiz U, Hussain RA, Badshah A. Fabrication and applications of copper sulfide (CuS) nanostructures. *Journal of Solid State Chemistry* 2016; 238: 25-40.
- Bagul SV, Chavhan SD, Sharma R. Growth and characterization of Cu<sub>x</sub>S (x = 1.0, 1.76, and 2.0) thin films grown by solution growth technique (SGT). *Journal of Physics & Chemistry of Solids* 2007; 68(9): 1623-1629.
- Chaki SH, Deshpande MP, Tailor JP. Characterization of CuS nanocrystalline thin films synthesized by chemical bath deposition and dip coating techniques. *Thin Solid Films* 2014, 550: 291-297.
- Kim HJ, Kim JH, Kumar CHSS Pavan, Punnoose D, Kim SK, Gopi Chandu VVM, Rao SS. Facile chemical bath deposition of CuS nano peas like structure as a high efficient counter electrode for quantum-dot sensitized solar cells. *Journal of Electroanalytical Chemistry* 2015; 739: 20-27.
- Gouanve F, Marais S, Bessadok A, Langevin D, Metayer M. Kinetics of water sorption in flax and PET fibers. *European Polymer Journal* 2007; 43(2): 586-598.
- Korehei R; Kadla JF. Encapsulation of T4 bacteriophage in electrospun poly(ethylene oxide)/cellulose diacetate fibers. *Carbohydrate Polymers* 2014; 100(2): 150.
- Jinglong W, Rizwangul Y, Jinge L, Peilin L, Pengyi Z, Jeonghyun K. In situ synthesis of manganese oxides on polyester fiber for formaldehyde decomposition at room temperature. *Applied Surface Science* 2015; 357: 787-794.
- Karbownik I, Bucheńska J, Lipp-Sypmonowicz B, Wrzosek H. Studies on the Influence of Grafting PET Fibres with Acrylic Acid on Molecular Orientation. *FIBRES & TEXTILES in Eastern Europe* 2008, 16, 5(70): 108-111.
- Kardas I, Lipp-Symonowicz B, Sztajnowski S. Comparison of the Effect of PET Fibres' Surface Modification Using Enzymes and Chemical Substances with Respect to Changes in Mechanic

- cal Properties. *FIBRES & TEXTILES in Eastern Europe* 2009, 17, 4(75): 93-97.
16. Metosen ANSB, Pang SC, Chin SF. Nanostructured multilayer composite films of manganese dioxide/nickel/copper sulfide deposited on polyethylene terephthalate supporting substrate. *Journal of Nanomaterials* 2015; 16(1): 131.
  17. Yamamoto T, Tanaka K, Kubota E, Osakada K. Deposition of copper sulfide on the surface of poly(ethylene terephthalate) and poly(vinyl alcohol) films in aqueous solution to give electrically conductive films. *Chemistry of Material* 1993; 5(9): 1352-1357.
  18. Rui X, Shimao W, Weiwei D, Xiaodong F, Linhua H, Zhu J. A new probe into thin copper sulfide counter electrode with thickness below 100 nm for quantum dot-sensitized solar cells. *Electrochimica Acta* 2016; 205: 45-52.
  19. Xiaoyun A, Jingjing M, Kai W, Maosheng Z. Growth of silver nanowires on carbon fiber to produce hybrid/waterborne polyurethane composites with improved electrical properties. *Journal of Applied Polymer Science* 2016; 133(9): 43056.
  20. Karaca E, Omeroglu S, Akcam O. Investigation of the effects of perlite additive on some comfort and acoustical properties of polyester fabrics. *Journal of Applied Polymer Science* 2016; 133(16): 43128.
  21. Shen Y, Zhang HF; Wang LM, Xu LH, Ding Y. Fabrication of electromagnetic shielding polyester fabrics with carboxymethyl chitosan-palladium complexes activation. *Fibers and Polymers* 2014; 15(7): 1414-1421.
  22. Dagang L, Zehui L, Yi Z, Zhenxuan L, Rakesh K. Recycled chitosan nanofibril as an effective Cu(II), Pb(II) and Cd(II) ionic chelating agent: Adsorption and desorption performance. *Carbohydrate Polymers* 2014; 111(1): 469-476.
  23. Ramesh A, Hasegawa H, Sugimoto W, Maki T, Ueda K. Adsorption of gold(III), platinum(IV) and palladium(II) onto glycine. *Bioresource Technology* 2008; 99(9): 3801-3809.
  24. Kos L. Use of Chitosan for Textile Wastewater Decolourization. *FIBRES & TEXTILES in Eastern Europe* 2016; 24, 3(117): 130-135. DOI:10.5604/12303666.1196623.
  25. Grijalva H, Inoue M, Boggavarapu S, Calvert P. Amorphous and crystalline copper sulfides, CuS. *Journal of Materials Chemistry* 1996; 6(7): 1157-1160.
  26. Joint Committee on Powder Diffraction Standards (JCPDS) Card File 6-464.
  27. Lindroos S, Arnold A, Keskela M. Growth of CuS thin films by the successive ionic layer adsorption and reaction method. *Applied Surface Science* 2000, 158(1-2): 75-80.

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