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Confirmation of Ceria-polyaniline Core-shell Nanostructure: An Optical Approach

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Abstract: Nanostructured ceria/polyaniline core shell particles were synthesized via polymerization of aniline monomers with the cerium oxide nanoparticles. Cerium oxide nanoparticles were prepared by hydroxide-mediated treatment and the shell was formed by polymerization of aniline hydrochloride with ammonium peroxydisulphate. Structural and optical characteristics of the prepared nanocomposites were studied separately for cerium oxide, polyaniline and core-shell ceria-polyaniline. The UV-Vis absorption spectra of the CeO₂-PANI confirmed the formation of the core-shell nanostructure. The optical properties of nanocomposites obtained from this method were analyzed as a function of preparation condition and the same has been reported.

Key words: Polyaniline, cerium oxide, core-shell nanocomposites

INTRODUCTION

Core-shell particles have become one of the most interesting topics in the field of nanomaterials because of their wide range of optic and electronic properties (Kalele *et al.*, 2006). These core-shell particles form a special class of nanocomposite material. In particular, the preparation of these particles with the metal oxide and conducting polymer is of great interest and becomes a novel challenge because of its properties and potential applications in the technological fields. The main advantage of going for these core-shell particles is to combine the unique properties and characteristics of organic and inorganic constituents at the nanoscale. By tailoring the structure of these materials at nanometer scale, it is possible to change their properties at the larger scale. Tailoring the properties of the core-shell nanocomposites can be done by changing either the materials or their core-to-shell ratio (Oldenburg *et al.*, 1998).

Core is made of inorganic material e.g., cerium oxide because it possesses special properties like stability, insolubility and the capacity to store or release oxygen to the variation of oxidation states. These admirable properties make them to find its application in catalysis (Kitiwang and Phanichphant, 2009), gas detectors and ultraviolet ray detectors (Dao *et al.*, 2011). The shell is made up of conducting polymer which can be used in various electronic devices such as rechargeable battery (Chuang and Yang, 2008), display and chemical

sensor. Among the conducting polymer, polyaniline is used most common because of its high processability (Camargo *et al.*, 2009), stability and controllable charge-transfer (Ansari and Keivani, 2006). Polyaniline is combined with Cerium oxide to form the nanocomposites in order to provide improved physical and electrical properties such as conductivity, solubility (Chujo, 2007) etc.

Variety of significantly different preparation methods has been involved in the core-shell formation like sol-gel method, layer-by-layer adsorption technique (Sounderya and Zhang, 2008), reverse micelle, micro emulsion and incorporation of inorganic constituent into an organic constituent. One of the new emerging techniques is the physical adsorption of inorganic component onto the organic component which is the most simple and efficient technique. This technique is used to overcome the difficulties possessed by the other methods like time consuming, inability to maintain the homogeneity and thickness of core-shell particles.

MATERIALS AND METHODS

Cerium nitrate hexahydrate was purchased from Aldrich chemicals with the molecular weight of 434.25. Polyacrylic acid with the molecular weight of 1800 was purchased from Aldrich chemicals.

Preparation of ceria: Ceria has been prepared by using simple hydroxide mediated method. 0.1 M cerium nitrate

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hexahydrate is dissolved in 50 mL of distilled water. Then 50 mL of 0.3 M NaOH solution is added rapidly under constant stirring. The obtained pale yellowish white precipitate is then centrifuged at 8000 rpm for 20 min. The pellets are dried at 150 and heated at 250°C for 3 h to obtain the powdered cerium oxide nanoparticles.

Preparation of polyaniline (PANI): Polyaniline has been obtained by the polymerization of aniline hydrochloride with ammonium peroxydisulphate. 0.2 M of aniline hydrochloride and 0.25 M of ammonium peroxybisulphate is mixed under constant stirring for about 12 h. This mixed solution has been maintained at 2-5°C. A colour change from light green to dark green is observed which confirms the formation of polyaniline.

Formation of core-shell particles: The formation of core-shell involves two steps. In the first step, before the absorption of inorganic component into the organic component the synthesis of polyaniline: polyacrylic acid complex is necessary because the organic component is an inter-polymer complex of conducting polymer. This polymer complex consists of two polymers of which polyaniline serves as the first strand and the polymeric dopant as the second strand i.e., Polyacrylic acid (PAA). These two strands were non-covalently bonded in a side-by-side arrangement (Tang *et al.*, 2003). The polymeric ionic dopant, polyacrylic acid not only enables the PAA: PANI complex to be dispersible in water but also provides good adsorption of inorganic nanoparticles. The synthesis of polymeric complex and the formation of core-shell nanocomposites are as follows.

Synthesis of polyaniline: Polyacrylic acid complex: In the synthesizing methodology of polymeric complex the PAA: PANI is taken in the molar ratio of 2:1. This complex is then allowed to stir for 2 h in order to obtain the equilibrium adsorption. The obtained complex is acidified by adding 4 mL 3 M nitric acid. Sodium persulphate of 0.006 M is dissolved in 10 mL distilled water. These two solutions were mixed and stirred for about 24 h to obtain the homogeneous solution of the polymeric complex. The obtained sample is taken for the FTIR studies which reveal the formation of the polymeric complex.

Formation of PANI: PAA: CeO₂ complex: Nanocomposites can be formed by the physical adsorption of the cerium oxide onto the organic polymeric complex i.e., PANI: PAA. The mixed solution of cerium oxide and PANI: PAA complex are mechanically stirred for 24 h. The UV-Visible spectroscopy results confirm the formation of the core-shell nanocomposites.

RESULTS AND DISCUSSION

The X-ray diffraction pattern shows that the CeO₂ powder is crystalline with preferred (111) orientation. The experimental d-spacing values of cerium oxide powder are 3.12, 2.69, 1.91, 1.62 and 1.5 which are found to be slightly different from the standard values. This variation may be due to the difference in synthesis methodology or preparation temperatures. The size of the CeO₂ particles for (111), (200), (220) and (311) were found to be 14, 43, 9.66, 9.41 and 9.54 nm, respectively. It is observed from Fig. 1 that peaks of the x-ray diffraction patterns are very sharp for (111) and (311).

The infrared spectra of polyacrylic acid, polyaniline and PANI-PAA complex are shown in the Fig. 3a-c, respectively and the peak locations related to the corresponding chemical bonds are described as follows. The characteristic IR peak of polyaniline at 1557 and 1482 cm⁻¹ are mainly due to the presence of quinoid ring-stretching vibrations and benzenoid ring. These two states give the clear indication of the polymer chain. The bond stretch like 1374, 1040, 1610 cm⁻¹ indicates the C-N bonds, sulfonate groups, C = C rings in the polyaniline compound.

The IR peak of polyacrylic acid at 1420.68 and 1714.61 cm⁻¹ indicates the symmetric and bending stretching corresponding to carbonyl and COOH groups, respectively. The PANI-PAA complex contains the vibrational characteristics of both the polymers. Furthermore when we compare the IR spectrum of PANI-PAA complex with those of pure PAA and PANI, we observe that all bands are shifted from 5 to 30 cm⁻¹, which may be due to the environmental changes and the variation in preparation temperature. IR spectroscopy

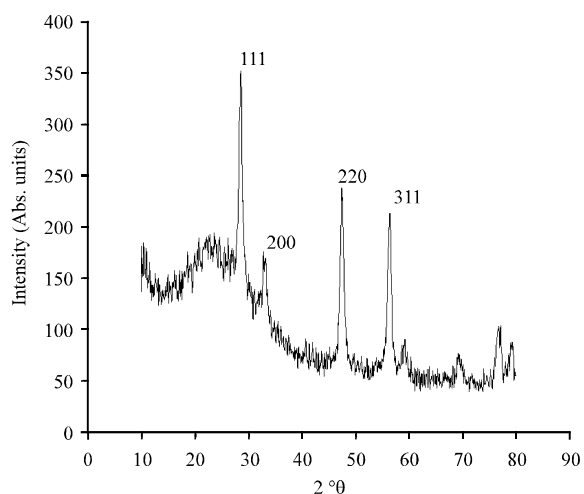


Fig. 1: XRD graph of CeO₂ nanoparticles

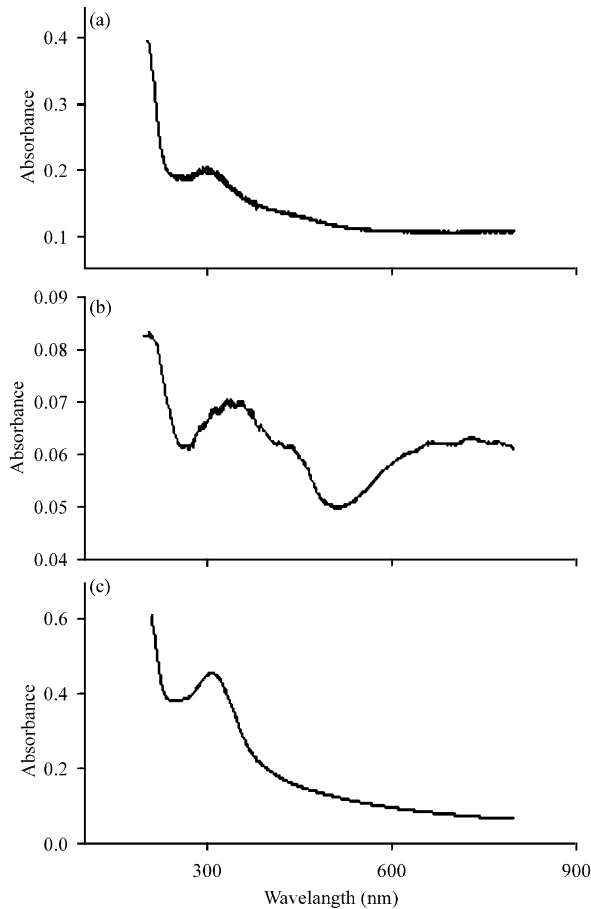


Fig. 2(a-c): UV visible absorption spectra; (a) Ceria-PANI, (b) PANI and (c) Ceria

provides evidence that the PANI-PAA complex is mixed at molecular level, thereby disrupting the bonds formed among PAA hydroxyl groups.

The UV-Visible spectroscopy shows the optical property of absorbance of ceria in the UV region. This absorbance property makes ceria to be used as the UV absorbing semiconducting material. The sharp absorbance edge is found to be at 310 nm for ceria heated at 250°C. The absorbance spectra for polyaniline shows the maximum absorbance obtained at 340 nm. The UV studies of CeO₂-PANI confirm the formation of core-shell structure. Figure 2 shows the absorption spectra carried out by UV-visible spectroscopy on CeO₂/PANI nanocomposites measured in the range of 200-900 nm wavelengths. The absorption spectrum of CeO₂/PANI core-shell particles shows the absorption band at 290-320 nm. The shift in the peak formed in the core-shell particles from 340 to 310 nm indicates the doping effect of nano CeO₂ particles on conducting polyaniline. The formed absorption spectrum (Fig. 2) confirms the binding of the ceria nanoparticles with the polyaniline.

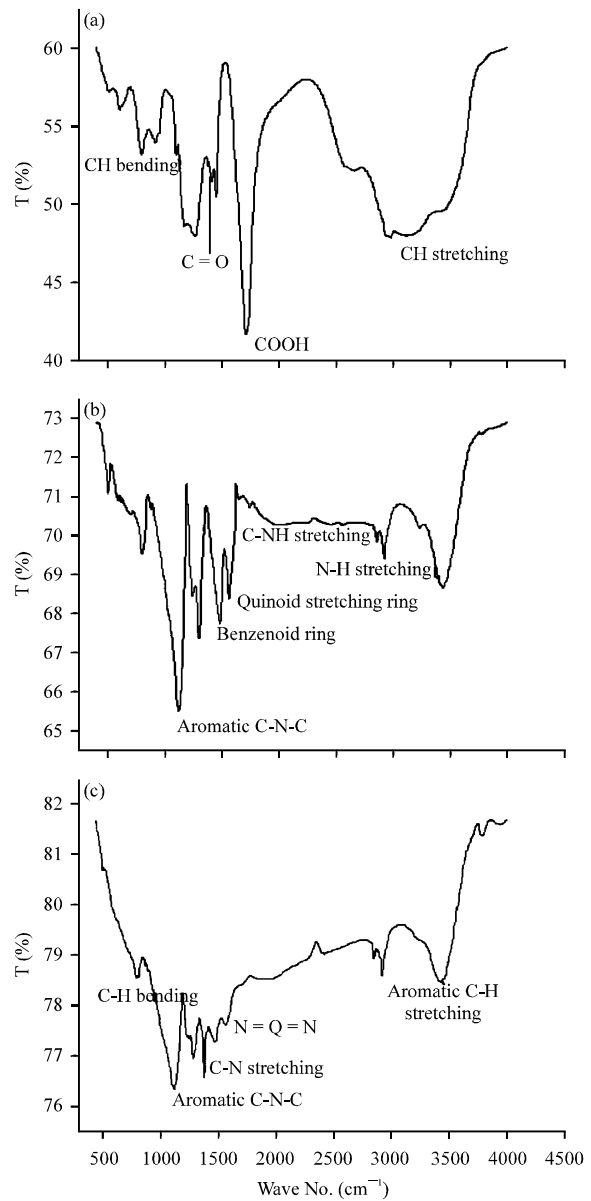


Fig. 3(a-c): FTIR spectra of (a) PAA, (b) PANI and (c) PAA-PANI complex

CONCLUSION

Core shell nanocomposites of CeO₂ and polyaniline were synthesized by simple hydroxide mediated method and polymerization of aniline hydrochloride with ammonium peroxydisulphate, respectively. The formation of cerium oxide particles were confirmed by the yellow coloration and UV-Visible absorption spectra. The PANI-PAA complex is confirmed by the FTIR spectroscopy results. The absorption peak in the UV-Vis spectra of CeO₂-polyaniline nanocomposites is found to

be shifted from its original position as compared to those observed in pure polyaniline. This result indicates the binding of the CeO₂ nanoparticles with the polyaniline forming a core-shell nanocomposite. Further studies are being conducted to study the exact morphology of the formed core-shell nanocomposites.

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