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DEFECTIVE VOPCPHO NANOTUBES FOR IMPROVED OPTICAL PROPERTIES

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ABSTRACT

In this study, the synthesis of defect-free and defective vanadyl 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine (VOPcPhO) nanotubes via templating method is reported. VOPcPhO nanotubes are successfully grown by immersing the porous alumina template into 5 and 15 mg/ml of solution concentration for 24 hours and annealed at 150 °C. Changes in morphological and optical properties are observed as the solution concentration is varied. Interestingly, defective VOPcPhO nanotubes that obtained from the higher solution concentration of 15 mg/ml recorded enhancement in optical properties. Defects by means of voids and circular-shaped holes along the nanotubes have caused to the reduction of nanotubes' diameter. Defective nanotubes that contribute to improve optical properties have been postulated to have low band-gap energy and enhanced photoluminescence quenching.

Keywords: defect; nanotubes; optical properties

INTRODUCTION

The growth of small molecules organic nanostructures such as nanotube, nanowire, nanoflower, nanorod and nanocomposite via the versatile fabrication techniques have been commenced to appraise their unique morphological, optical and electronic properties [1-4]. These nanostructures can be synthesised via template-assisted method of different approaches such as spin coating, immersion, drop-casting, vapour deposition and pressure-filter techniques [1, 5-8]. Synthesis of nanostructures via porous alumina template has been known as one of the promising methods due to its reasonably low cost and permanence architecture. In addition, a porous alumina template provides a hexagonal pore structures which enable the generation of one-dimensional nanostructured materials.

Nanostructured small molecules organic materials of vanadyl 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine (VOPcPhO) have significantly improved in structural, morphological and optical properties [1, 9, 10]. However, these have been reported from the defect-free VOPcPhO nanostructures and the defective VOPcPhO nanostructures have not been considered in such analysis. Structural defect, length distributions and the presence of impurities establish intricacies in the performance of nanotubes' optical properties [11, 12]. Defective inorganic nanotubes have shown alterations in electronic properties which are due to the vacancies defects [13-15]. It is noteworthy to investigate the performance of defective organic nanotubes in maximising their utilisation for optoelectronic and photovoltaic applications. In this paper, we report the optical properties of defective VOPcPhO nanotubes which notable than the defect-free VOPcPhO nanotubes.

EXPERIMENTAL

VOPcPhO was purchased from Sigma Aldrich and used without further purification. 5 and 15 mg/ml of VOPcPhO solution concentration were prepared in chloroform. Commercial porous alumina template with nominal pore diameters of 200 nm and a thickness of 60 micron was used and cleaned as in literature [1]. Template was immersed in VOPcPhO solution for 24 hours prior to the annealing at 150 °C (1 minute). In order to obtain the nanostructures, template that has been immersed in VOPcPhO solution needs to be dissolved in 4 M sodium hydroxide for 24 hours. The characterisation of nanostructures was carried out using field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), UV-vis, photoluminescence (PL) and Raman spectroscopy.

RESULTS AND DISCUSSION

Figure 1 shows the morphological characteristics of defect-free VOPcPhO nanotubes and defective VOPcPhO nanotubes. From the FESEM images (Figure 1(a) & (b)), the defect-free nanotubes exhibit an aligned arrays with free from the morphological defects such as voids, pits and breakage. Defect-free nanotubes are closely-packed with their tubes obviously exhibit the inner- and outer walls. The diameter of nanotube and wall thickness of defect-free VOPcPhO nanotube is about ~ 200 nm and ~ 20 nm, respectively. By increasing the VOPcPhO solution concentration from 5 mg/ml to 15 mg/ml, discernible nanotubes' morphologies of circular-shaped defects are yielded (Figure 1(c-e)). In comparison to defect-free nanotubes, the defective nanotubes are collapsed with the formation of voids along the tubes. Disregard with the imperfection morphologies, defective nanotubes comprise a comparable nanotube's diameter and wall thickness with the defect-free nanotubes. It thus implies that, high solution concentration of VOPcPhO is able to infiltrate into the porous template and allowed the replication. However, due to the low viscosity properties of high solution concentration (15 mg/ml), the flowing of solution may have been perturbed. One can imagine that defective nanotubes have experienced the localised stress during the infiltration process. When a solution of low viscosity and high viscosity is flowing into the porous template, the different localised stress between the solution (VOPcPhO) and surface (template) is generated (Figure 2(a) & (b)). Formation of voids along the nanotubes represents the localised stress concentration that occurred along the porous, in which, uniform distributions of voids are revealed.

The diameter of voids and circular-shaped defect can vary between 10 to 50 nm, suggests that the formation of voids and localised stress may occur at various phases. Movement of solution within the cavity has undergone various rates at certain point and uniform coating has not fully achieved. Apparently, the stability of defective nanotubes is not as parity as defect-free nanotubes. Most of the defective nanotubes are seems to collapse and portray less dense distribution. Instable nanotubes could be due to the emergence of voids and circular-shaped defect along the defective tube in which resilience properties of tubes will be hard to attain. Unlike the defect-free nanotubes, standing nanotubes with closely-packed and dense distribution are realised. Without any appearance or influence of tubes' imperfection, the stability and permanency of VOPcPhO nanotubes can be reached.

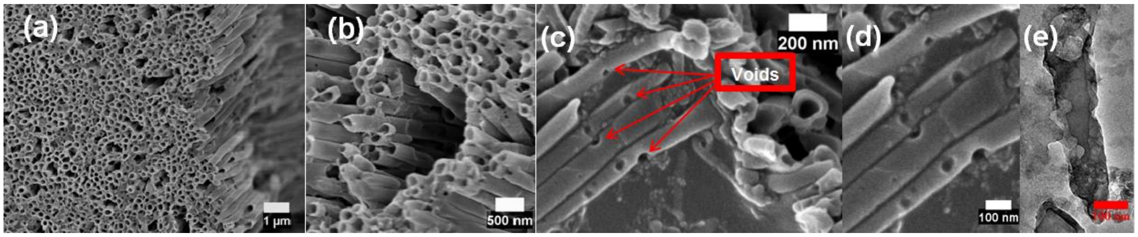

Figure 1: (a) and (b) FESEM images of defect-free VOPcPhO nanotubes, (c) and (d) FESEM images of defective VOPcPhO nanotubes (e) HRTEM image of defective VOPcPhO nanotube

The structural and optical properties of defect-free (smooth) and defective VOPcPhO nanotubes are shown in Figure 3. In the UV region, no changes of peak absorption at B-band (350 nm) are observed (Figure 3(a)) between the defect-free and defective nanotubes. It is notable that the defect-free VOPcPhO nanotubes have strong absorption intensity at their B-band than the Q-band. However, the B-band of defective VOPcPhO nanotubes displays similar absorption intensity with their Q-band. If the comparison is made between the absorption intensity (both B-band and Q-band) of defect-free and defective nanotubes, the latter has ability to absorb more light although no changes of peak absorption at B-band is observed. B-band is corresponding to the transition of electron from highest occupied molecular orbital to lowest unoccupied molecular orbital. Intense peak absorption at B-band and Q-band of defective nanotubes may be attributed to the better organization of phthalocyanine molecules due to morphological defects. Changes of morphologies from defect-free to defected nanotubes have led to the red-shift at the second peak of Q-band. The second molecular electronic transition (Q-band) is occurred when the electrons in molecules are excited from the π-bonding orbital to the antibonding π orbital*. Defective VOPcPhO nanotubes have the lower band-gap energy (E_g) of 1.29 eV if compared with the defect-free nanotubes (Figure 3 (b)). Defect-free nanotubes have increased the band-gap energy by 0.12 eV. A significant marginal change in the absorbance that occurs from the defective nanotubes could be due to the modification of molecular structure. Raman spectra of both defect-free and defective nanotubes show no differences at their molecular structure apart for the pyrrole stretch at 1529 cm^{-1} (Figure 3 (c)). Pyrrole stretch is corresponded to the adaptation of metal ion to phthalocyanine molecule [16]. Occurrence of voids and circular-shaped defects along the VOPcPhO nanotubes suggested that the attachment of vanadyl ion to the phthalocyanine molecules has been distorted. Enlargement or reduction in the diameter of VOPcPhO's cavity could be the main contribution to the pyrrole stretching, which has been supported by the morphological images. VOPcPhO nanotubes show emission in green regions with enhanced photoluminescence (PL) quenching effect is exhibited by the defective nanotubes (Figure 3(d)). Enhancement in PL quenching is correlated to the red-shift observed in the optical absorption and distortion in molecular structure. As the band-gap energy is reduced, more electrons are be able to transfer from the lower ground state to the upper excited state once the electrons in molecules react with photon. When the VOPcPhO nanotubes are illuminated, photons are absorbed and electron-hole pairs are created. The PL quenching occurred due solely to the defect shown that it is absorption that dominates over the light emission.

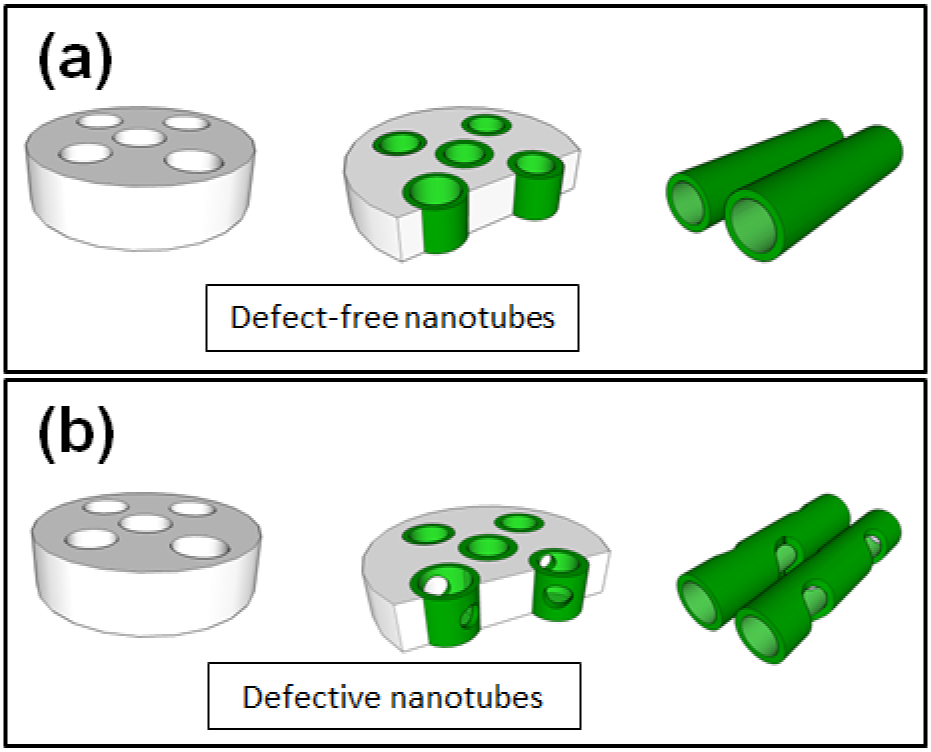

Figure 2: Schematic diagram of the proposed structure of defect-free and defective VOPcPhO nanotubes.

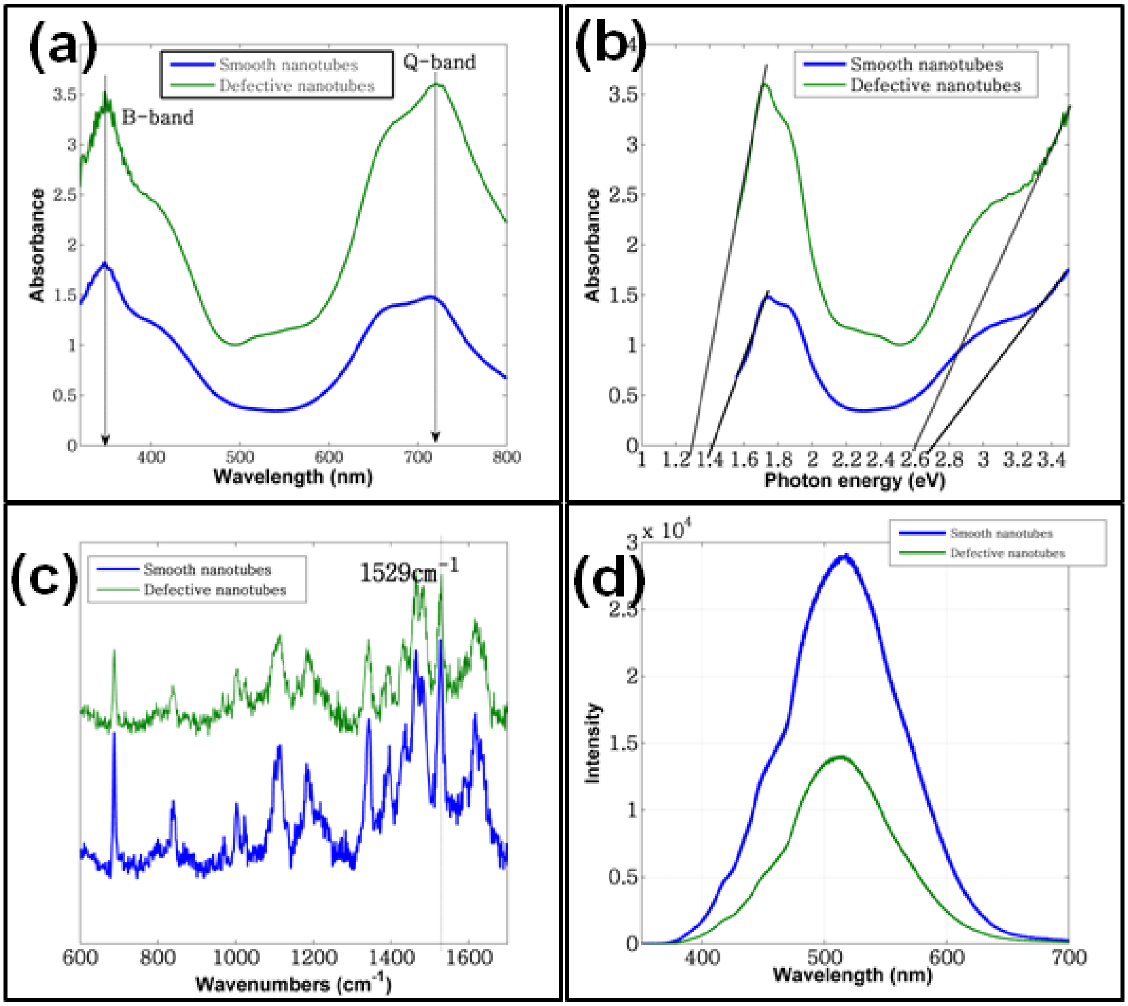

Figure 3: (a) UV-vis absorption spectra, (b) Variation of optical absorption as a function of photon energy, (c) Raman spectra and (d) PL spectra of VOPcPhO nanotubes

A possible contribution of structural defects in carbon nanotubes has been shown to exhibit an enhancement in quenching effect [11]. Complex interaction between two different species (vanadyl and phthalocyanine) is occurred by incorporating the defective nanotubes in the system. Decrease in PL intensity is likely to happen if adsorption of molecules on tubes' walls that due to electrostatic interaction is transpired. Morphological defects of VOPcPhO nanotubes can play an important role to improve the optical properties by allowing the efficient transfer of vanadyl ion through the macrocycle ring of VOPcPhO. Apparent red-shift of peaks absorption in visible region is probably due to the π-π* transition in macrocycle ring of VOPcPhO and excitonic transition [17]. Interaction of molecules with the defect sides has caused to the strong quenching behaviour of defective VOPcPhO nanotubes and hence the electronic absorption transition. Effect of electronic absorption transition from π-π* in phthalocyanine can lowered the photoluminescence intensity of defective VOPcPhO nanotubes. In addition, the energy transfer in the defective VOPcPhO nanotubes system has been completed due to the strong π-π* interaction.

CONCLUSION

Defect-free and defective VOPcPhO nanotubes can be realised from the immersion approach of templating method by varying the VOPcPhO solution concentration. Defective VOPcPhO nanotubes have shown the enhancement in optical properties although the morphological properties are better hold by the defect-free VOPcPhO nanotubes. Pyrrole stretch of defective nanotubes has been seen to change and alter the band-gap energy. Due to the low band-gap energy, photoluminescence quenching of VOPcPhO nanotubes is enhanced.

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