RESEARCH ARTICLE

Polyethylene Glycol (PEG) Assisted Tungsten Oxide (WO_3) Nanoparticles by Microwave Irradiation Method

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ABSTRACT: The present work presents the synthesis and characterizations of Polyethylene glycol (PEG) assisted tungsten oxide (WO_3) nanoparticles as surfactant by simple household microwave irradiation (2.45 GHz) method. The samples were characterized using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), UV–visible diffusion reflectance spectroscopy (UV–VIS-DRS) and Fourier Transform Infrared Spectroscopy (FT-IR). Powder XRD results revealed that both the samples prepared with and without surfactant crystallize in the orthorhombic structure corresponding to $WO_3 \cdot H_2O$ phase. Subsequent annealing under identical conditions (600°C/air/6 h) led to significantly different products i.e. monoclinic $W_{17}O_{47}$ from surfactant free sample and orthorhombic WO_3 from PEG assisted sample. Blue emission was observed through UV–VIS-DRS with band gap energy around 2.7 and 3.28 eV for PEG assisted as prepared ($WO_3 \cdot H_2O$) and annealed samples (WO_3) respectively. These results will be helpful in knowing the suitability of the material for sensor applications.

KEYWORDS: Surfactant, WO_3, Polymer, Oxygen deficient, TEM

1.INTRODUCTION

Nanotechnology has become the most influential force in the world today almost it determines all the future technology around the world [1]. It combines sciences like physics, chemistry, biology and engineering which complement each other. In general it is understood that the nano dimension should have the range between 1 to 100 nm [2]. Moreover, Nanotechnology will provide the capacity to create affordable products with dramatically improved performances for various fields of technology [3].

Industrial points of view the production and application of physical, chemical, and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems [4]. In addition with the above features the fabrication of nanomachines, nanoelectronics and other nanodevices will undoubtedly solve an enormous amount of the problems faced by mankind today [5]. Abraham Wolcott et al [6] reported the synthesis of ultrathin WO_3 nanodisks using a wet chemical route with polyethylene glycol (PEG) as a surface modulator. The reported nanodisk structure was based on the interaction of the non ionic 10000 g/mol PEG molecules with tungsten oxoanion precursors. The large flat surface area and high aspect ratio of the WO_3 nanodisks were potentially useful in PEC cells. It was reported that using PEG-10000 as a surface modulator that adsorbs preferentially to the (010) crystal face and thereby inhibits crystal growth and the nanodisk formation is critically influenced by the interaction between PEG and the $WO_3.2H_2O$ precursors as compared to other studies resulting in spherical nanoparticles.

The present paper completely describes the synthesis and characterizations of PEG assisted Tungsten Oxide (WO_3) nano dimensional materials for the suitability of sensor applications.

2. EXPERIMENTAL PROCEDURE

The precursor solution was prepared by dissolving 2.49g of tungstic acid (H_2WO_4) in 10 ml of sodium hydroxide (NaOH). This resulted in yellow colored hydrated sodium tungstate solution due to proton exchange protocol process. Subsequently 0.5g (~20% of tungstic acid) of PEG was added to the precursor solution to act as a surfactant and several drops of HCl were introduced into the solution to attain the pH value of 1. HCl can act as a precipitating agent and also medium for the product to have desired morphology. Double distilled water (~50% of the total volume) was added with the above solution in order to respond microwave quickly. Final solution was transformed into microwave oven under the power of 180W for 10min (Choice was random manner). After irradiation a very small amount of surrounding water present in the product was removed by drying process at 60°C in air for 1 hr. The above process was repeated without adding PEG under the identical conditions. Both products resulted in yellow colored powder which was annealed at 600°C in air for 6 hrs to attain crystalline anhydrous tungsten oxide. The horizontal tubular furnace with two zones and temperature controllers is shown in Fig.3. The maximum temperature of the furnace is 1400°C and the operating temperature is around 1300°C.

2.1 MICROWAVE IRRADIATION MECHANISM

Intercalation chemistry and interfacial polarization phenomenon play a major role in the synthesis of oxide

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Received: 10.10.2016 **Accepted:** 24.11.2016 **Published on**: 30.11.2016

based metal nanoparticles. Interfacial polarization is an effect which is very difficult to treat in a simple manner, and is most easily viewed as a combination of the conduction and dipolar polarization effects. During the intercalation process the strong absorbing nature of tungstic acid and water at2.45GHz may be responsible for the heating and initiating the reaction.

$$H_2WO_4 + 2\ NaOH \longrightarrow Na_2WO_4.2H_2O \quad (1)$$

According to reaction (1), high concentrations of hydrated sodium tungstate would shift the reaction to the right side (Formation of sodium tungstate $Na_2WO_4.2H_2O$) ensuring the formation of WO_3, although many intermediate steps and compounds with various phases may exist during the reaction time. It is thus the formation of WO_3 should have dependence on the acid medium. To convert WO_4^- to neutral WO_3, excess divalent oxygen must be removed by microwave irradiation method.

The thermal analysis was performed on SDT Q600 V8.3 Build 101. The X-ray powder diffraction (XRD) patterns of all the samples were measured on a Bruker AXS D8 advanced diffractometer with monochromatic CuKα – radiation (λ = 1.5406Å). The TEM images and a selected-area electron diffraction (SAED) were recorded on a Technai G20-stwin High resolution electron microscope (HRTEM) using an accelerating voltage of 200 kV. The optical properties were analyzed by UV-VIS diffusion reflectance spectroscopy using CARY 5E UV-VIS-NIR spectrophotometer (200–800 nm).

3. RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION ANALYSIS

Hydrated tungsten oxide ($WO_3.H_2O$) was successfully synthesized by microwave irradiation method with and without using PEG as surfactant. The reaction time required in both cases was about 10min only. Fig. 5 shows the XRD pattern of prepared sample ($WO_3.H_2O$) synthesized with and without PEG could be indexed as orthorhombic structure (JCPDS: 43-0679) with high crystallinity. After annealing, both samples showed variation in oxygen content which was clearly observed in XRD pattern (Fig.6). Fig. 6a shows the XRD pattern of annealed sample at 600°C prepared without PEG formed oxygen deficient tungsten oxide ($WO_{2.76}$) matches with monoclinic structure (JCPDS: 79-0171)[7]. Interestingly, the XRD pattern (Fig. 6b) of the annealed sample under the identical conditions using PEG attained stoichiometric tungsten oxide (WO_3) matches with the orthorhombic structure (JCPDS 89-4480) [8]. The oxygen content of the PEG assisted annealed sample is more than that of the surfactant free sample. The PEG enhances the crystallinity and increases the oxygen content of the end product.

In general, tungsten oxides easily lose and are represented as $WO_{3-\delta}$. The oxidation state of tungsten in $W_{18}O_{47}$ lies between +4 (WO_2) and +6 (WO_3). With larger non-stoichiometry the defects preferentially accumulate at so called crystallographic shear planes along *(l, m,* 0*)* with the formation of edge-shared WO_6 octahedra [9].

The addition of lower molecular weight PEG-6000 complex into the solution results in crystalline $WO_3.H_2O$ directly due to adsorption process.

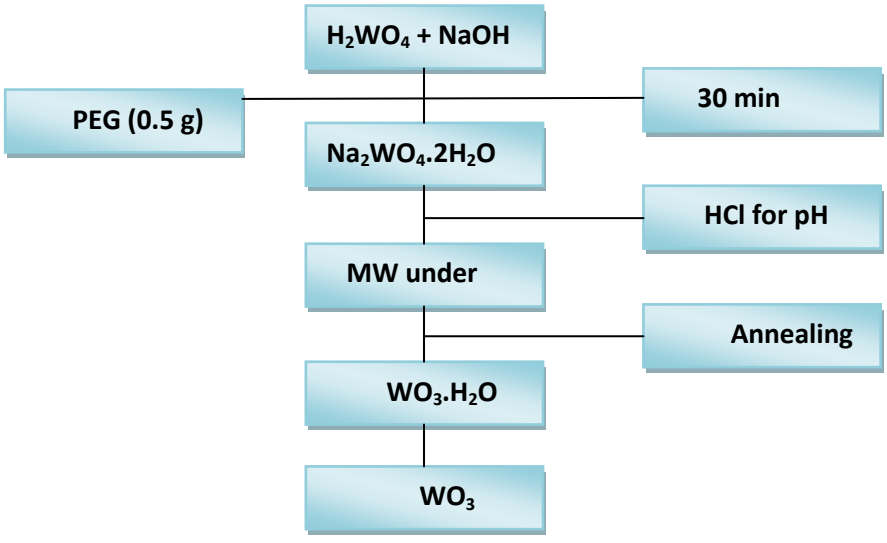

Figure 1. Schematic representation of experimental procedure

(a) (b)

Figure 2. Microwave Oven used for synthesis (a) Outer view (b) Inner view

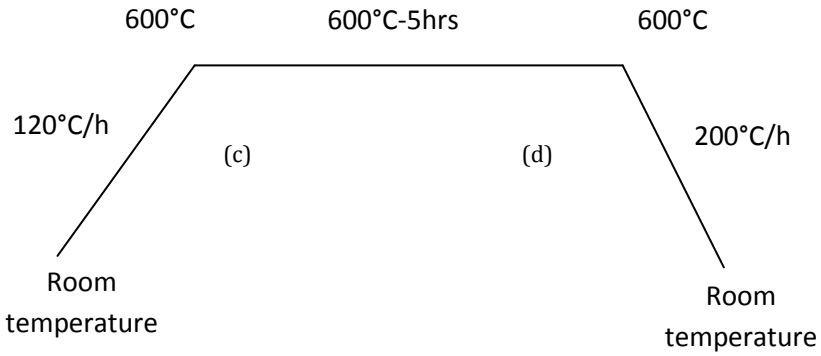

Figure 3. Temperature Profile of as prepared sample ($WO_3.H_2O$)

(a) ***(b)***

Figure 4. Synthesized samples (a) $WO_3.H_2O$ (b) WO_3

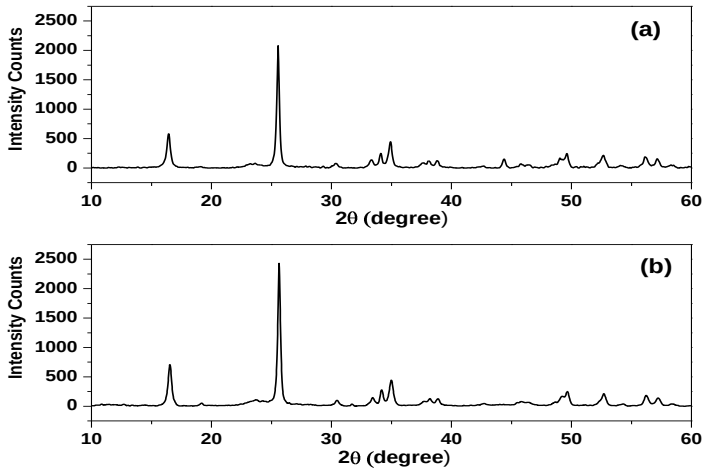

Figure 5. Powder X-ray diffraction pattern of $WO_3.H_2O$ prepared

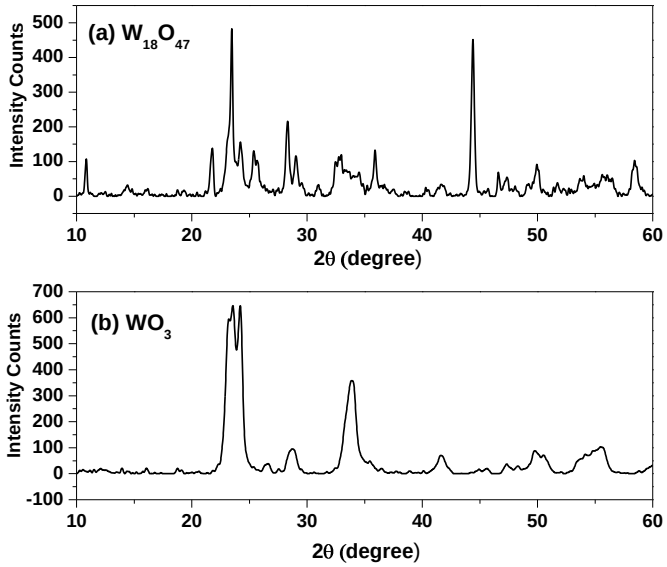

Figure 6. Powder X-ray diffraction pattern of annealed samples at 600 ℃
(a) W18O47 (b) WO3

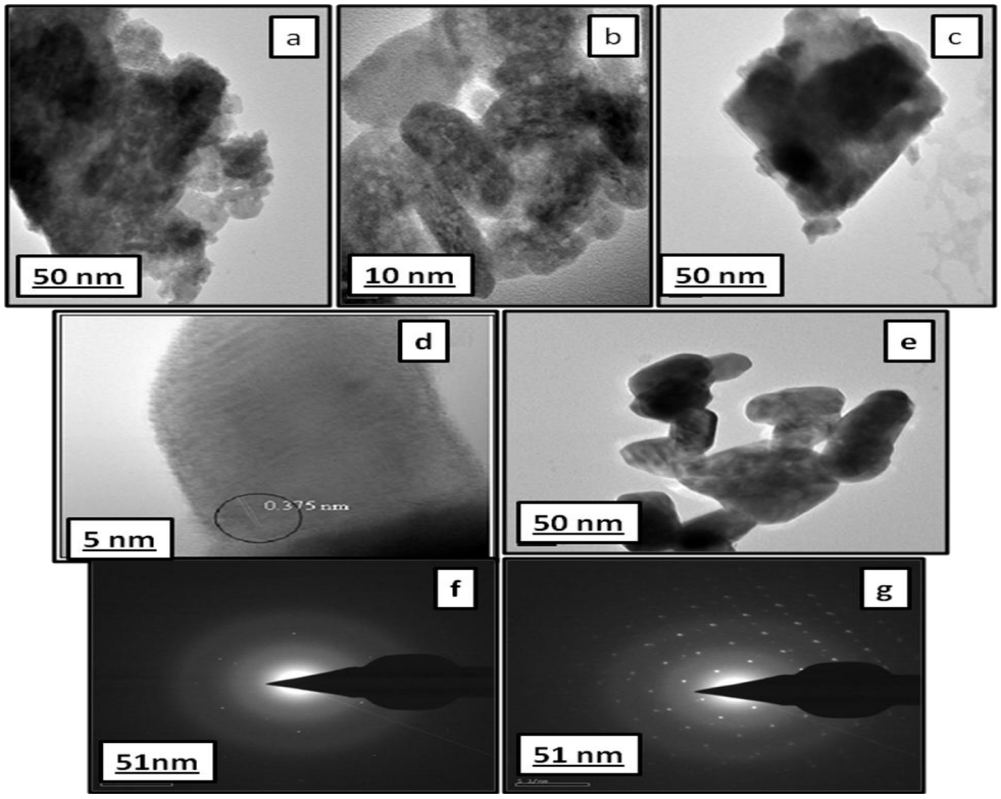

Figure 7. TEM image of $WO_3.H_2O$ (a-b) without PEG (c) $W_{18}O_{47}$ (d &e) WO_3 with PEG; SAED pattern of $WO_3.H_2O$ (f) without PEG (g) WO_3

Earlier it has been reported that the addition of PEG-600, PEG-1000 and PEG-2000 leads to the formation of spherical nanoparticles and globular/spheroid nanostructures respectively [10]. During annealing process there is no oxygen adsorbent element in PEG like carbon, but carbon forms carbon monoxide which can't be stable at this higher temperature. Hence, it is more reasonable to conclude that formation of stoichiometric tungsten oxide (WO_3) is possible, in spite of the presence of a small amount of sodium ion present in the reaction medium from hydrated sodium tungstate ($Na_2WO_4.2H_2O$).

On the other hand, without PEG there is possibility in the formation of sodium oxide (Na_2O) due to the presence of small amount of sodium present in the reaction medium from hydrated sodium tungstate which can be stable at this higher temperature (600°C) which leads to the formation of oxygen deficient tungsten oxide ($WO_{3-\delta}$). Similarly, we have prepared $WO_3.H_2O$ using EDTA as surfactant. Subsequent annealing under identical conditions resulted in non stoichiometric $WO_{3-\delta}$ which has been attributed to the presence of adsorbing oxygen element (Na^+ ion) in EDTA. This may be due to the formation of intermediate sodium oxide (Na_2O) during annealing process. Hence, it is reasonable to conclude that PEG-6000 is a driving force in producing such rod like structure as in the prepared sample. Subsequently $WO_3.H_2O$ was annealed at 600°C and 800°C to attain crystalline WO_3.

3.2 TEM STUDIES

Figs. 7a & 7b show the TEM micrographs surfactant free-$WO_3.H_2O$. Higher magnification picture reveals that the sample consists of nano sized tablets of different dimensions. Upon annealing at 600°C in air for 6 hrs, these tiny particles aggregated and resulted in platelet like morphology (see Fig.7c). Fig. 7d shows the micrograph of PEG assisted tungsten oxide at 800°C in air for 6 hrs, formed well separated elongated sphere like morphology that have dimensions of the order of 72 to 114 nm in length and 42 to 85 nm in widths due to the variation in oxygen content when compared to the surfactant free samples. The calculated'd' spacing from the HR-TEM of PEG assisted tungsten oxide found to be 0.375 nm matches with the (020) reflection. The corresponding selected area of electron diffraction (SAED) pattern as prepared (without PEG) and annealed sample (with PEG) are shown in Figs. 7f and g respectively. The occurrence of a very uniform electron diffraction spots in both the cases indicates single crystal nature of the samples.

3.3 FT-IR ANALYSIS

Fig. 8 shows the FT-IR spectra of pure and annealed WO_3 samples. The observed wave numbers, relative intensities obtained from the recorded spectra and the assignments proposed as prepared and annealed samples were listed in Table 3. In all the three samples, the frequency range between 900 and 600 cm^{-1} is clearly distinguished and attributed to stretching (O-W-O) modes of WO_3[11]. A slight shift towards higher wave number and sharpening of the main bands was observed in the annealed samples. This result is in agreement with the improvement in crystalline nature observed in XRD studies. The bands present in the region 3100-3550 cm^{-1} belong to O-H stretching vibrations (asymmetric and symmetric) of co-ordinated water. The bands observed at 1613 cm^{-1}, 1593 cm^{-1} and 1587 cm^{-1} prepared and annealed samples are assigned to the H-O-H bending of the co-ordinated water[12]. The additional peaks observed at 2905 cm^{-1}, 1345 cm^{-1} and 1107 cm^{-1} in the pure sample belongs to CH_2 stretching, CH wagging and CH_2 wagging and OH deformation vibration respectively[13]. The vibration at 943 cm^{-1} in pure sample may be due to the vibrations related to coordinated water in the W-OH_2 band [14].

3.4 UV-VIS DRS ANALYSIS

The diffuse reflectance spectroscopy was performed on all the samples (Fig. 9). The absorption from 550nm to 450 nm towards lower wavelengths in the entire spectrum (Blue-shift) corresponds to the absorption edge of the solids and it is due to transition from O2- to Mn+ [mainly transfer of 2p orbital of the oxygen anions to 5d orbital of the tungsten cation] which indicates the quantum confinement effect.

The band gap energies calculated using Kubelka – Munk (K-M) model are described below. The K-M model at any wavelength is given by

$$\frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \equiv F(R_\infty)$$

$F(R_\alpha)$ is the so called remission or Kubelka – Munk function, where

$$R_\alpha = R \text{ sample} / R \text{ standard}$$

A graph is plotted between $[F(R_\alpha)h\nu]^2$ Vs $h\nu$ and the intercept value is the band gap energy E_g [15] of the individual sample (See insert of Fig. 9). The band gap energies were thus estimated as 2.56, 3.10 and 3.16 eV in the prepared and annealed samples respectively. Similar process has been carried out for the samples prepared without PEG and the band gap energies were found to be 3.40 and 3.55 eV which showed that the surfactant free samples have less optical conductivity than the PEG assisted samples.

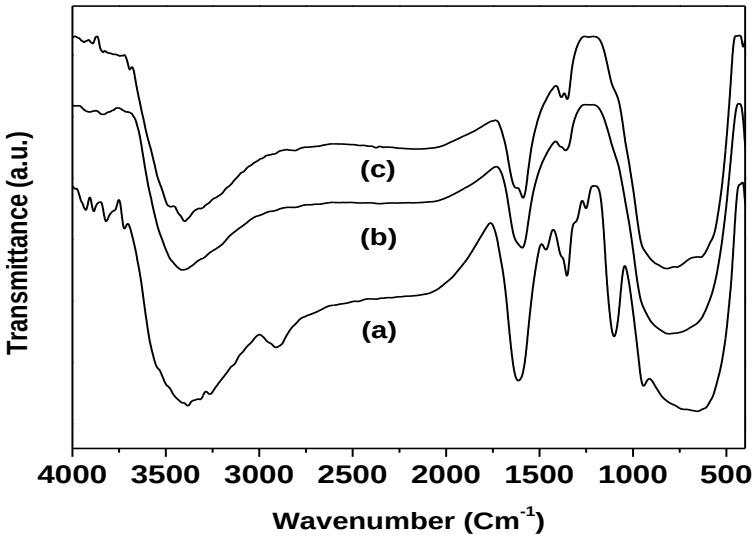

Figure 8. FT - IR spectrum of WO_3 powder (With PEG) (a) as prepared and annealed at (b) 600^0C and (c) 800^0C

Table 1
Observed FT - IR wave numbers (cm $^{-1}$) of as prepared and annealed WO_3 samples

$WO_3.H_2O$	Tentative assignment	WO_3 (600ºC)	Tentative assignment	WO_3 (800ºC)	Tentative assignment
3381 vs	H – OH stretching	3412 s	H-OH stretching	3399 s	H – OH stretching
3264 vs	H- Bonded OH	-	-	-	-
2910 s	Asymetric CH_2 Stretching	-	-	-	-
1613 vs	H-OH deformation vibration CH_2 wagging	1593 s	H-OH deformation vibration	1587 s	H-OH bending
1353 w	CH_2 twisting	1361vw	-	1351vw	-
1101.02 s	W-OH deformation Vibration	-	-	-	-
943 vs	W – O Stretching	-	-	-	-
655 vs		807vs	W – O Stretching	818 vs	W – O stretching

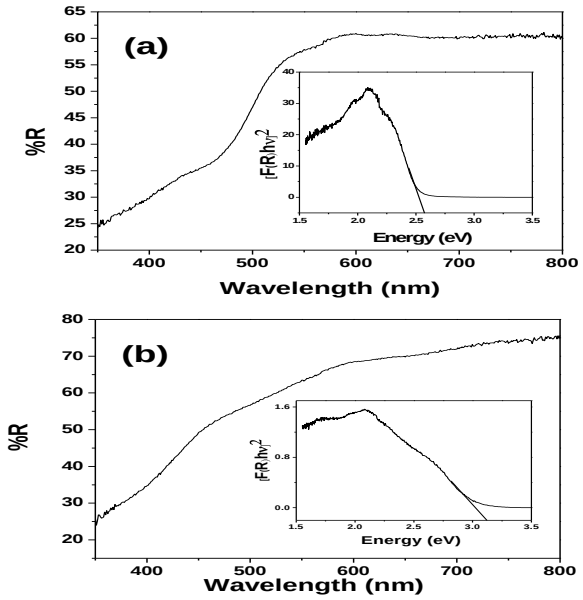

Figure 9. UV-VIS DRS spectra of WO_3 powder (With PEG) (a) as prepared and annealed at (b) 800 ℃

4. CONCLUSION

In this work, WO_3 nanoparticles were successfully synthesized by adopting a novel microwave irradiation method, using with and without PEG – 6000 as surface modulator. The XRD investigation confirmed that the samples ($WO_3.H_2O$) prepared using PEG have formed in the orthorhombic structure. Similarly the samples prepared without any surfactant also have the same structure. After annealing at 600˚C for 5 hours in ambient atmosphere, surfactant (PEG) free samples have turned out to be oxygen deficient ($W_{18}O_{47}$) in nature and PEG assisted samples turned out to be stoichiometric tungsten oxide (WO_3). FT-IR spectra confirmed the various functional groups present in the samples. TEM observation showed that the sample annealed at 800°C consisted of well separated elongated spheres composed of nanoparticles. Based on UV-VIS DRS analysis the band gap energies were estimated for all the samples indicating that surfactant free samples have less optical conductivity than the PEG assisted samples. These results suggest that the nanoparticles produced by this simple microwave irradiation method may be suitable for photo catalytic and for sensor applications.

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