

Synthesis, characterization and catalytic activity of sulphonated multi-walled carbon nanotubes as heterogeneous, robust and reusable catalysts for the synthesis of bisphenolic antioxidants under solvent-free conditions

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Abstract. In this study, a simple and green method has been developed for the synthesis of bisphenolic antioxidants by the reaction of 2-*tert*-butyl-4-methylphenol and aldehydes in the presence of sulphonated multi-walled carbon nanotubes (MWCNTs–SO₃H) as heterogeneous, robust and reusable catalysts under solvent-free conditions. MWCNTs–SO₃H was prepared and characterized by some microscopic and spectroscopic techniques including scanning electron microscopy, transmission electron microscopy, FT-IR spectroscopy and Raman spectroscopy. Acidity of the catalyst was measured by acid–base titration. The catalyst was reused several times without efficient loss of its activity for the preparation of bisphenolic antioxidants. In addition, high yields of the products, relatively short reaction times, being solvent-free and non-toxicity of the catalyst are other worthwhile advantages of the present method.

Keywords. Sulphonated carbon nanotubes; acidic catalyst; bisphenolic antioxidant; solvent-free; reusable catalyst.

1. Introduction

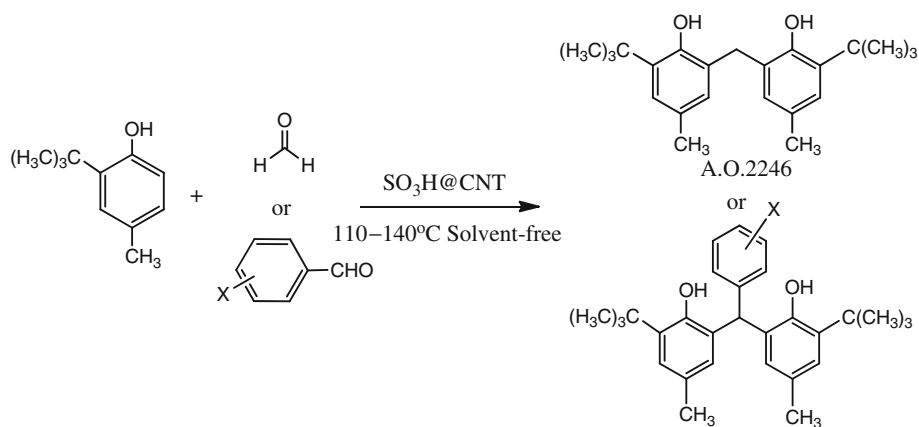
Diarylmethanes (DAMs) and triarylmethanes (TAMs) are very important materials in organic chemistry. Some DAMs and TAMs have been used as dyes,^{1,2} protecting groups for nucleosides, carbohydrates,^{3,4} anticancer drugs,⁵ epoxy resins,⁶ and antioxidants.^{7,8} Bisphenolic antioxidants are an important class of DAMs and TAMs. Bisphenolic antioxidants are substances that play important roles in dealing with oxidative damages caused by reactive oxygen species.⁹ Bisphenolic antioxidants neutralize these types of oxygen by intercepting and interacting with reactive radicals. This fact is still important in many research areas and considerable efforts are directed toward the synthesis of TAMs and DAMs.

DAMs and TAMs are usually manufactured by an acid catalysed condensation reaction of carbonyl and aromatic compounds. Several synthetic methods by using H₂SO₄,¹⁰ HCl,¹¹ trifluoroacetic acid,¹² heteropoly acids,¹³ zeolites,¹⁴ silica sulphuric acid,¹⁵ [Ir (COD)Cl]₂-SnCl₄,^{16a} AuCl₃ or AuCl₃/

AgOTf,^{16b} Cu(OTf)₂,^{16c} FeCl₃,^{16d} Yb(OTf)₃,^{16e} and AcBr/ZnBr₂/SiO₂^{16f} have been developed for the preparation of DAMs and TAMs. Using homogeneous acid catalysts has several disadvantages such as being corrosive, difficulty in recovery, high toxicity, safety and handling.¹³ However, in spite of their potential applications, many of the published papers report long reaction times^{12,14,16} and excess amount of catalyst^{10–14} for a successful reaction. In addition, the use of toxic organic solvent^{10–12,16} and non-reusable catalyst^{10–16} confine the usefulness of some reported studies. Therefore, considerable attempts have been made for the development of suitable solid acid catalysts in a wide range of organic transformations.¹⁷

The superior properties of carbon nanotubes (CNTs)¹⁸ and their wide ranges of potential applications in medicine,¹⁹ electronic instruments, optic devices²⁰ and catalytic applications,²¹ have made them an important material in science and technology. Due to the high specific surface area of CNTs; they are effective supports for the synthesis of solid acid catalysts. Sulphonated multi-walled carbon nanotubes (MWCNTs–SO₃H) are useful as solid acid catalyst in organic transformations. In recent years,

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Scheme 1. Synthesis of bisphenolic antioxidants catalysed by MWCNTs–SO₃H.

MWCNTs–SO₃H has been produced by some reported methods.^{22–25}

In continuation of our interest towards development of acidic nanocatalysts,²⁶ in this study, we wish to report a facile and environmental-friendly method for the synthesis of bisphenolic antioxidants using MWCNTs–SO₃H as reusable solid acid catalyst under solvent-free conditions (scheme 1).

2. Experimental

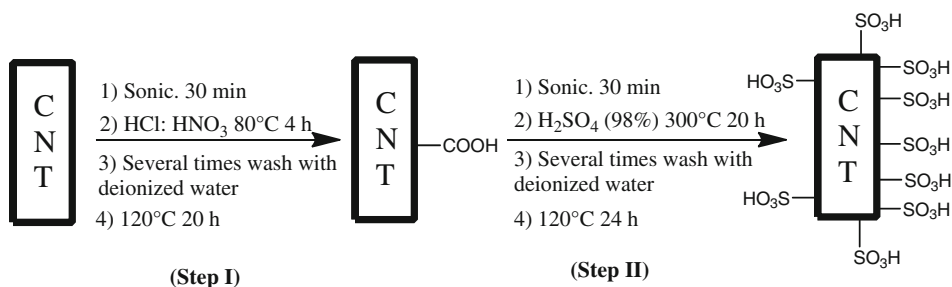
2.1 Materials and apparatus

MWCNTs–SO₃H was prepared by modification of the method reported by Peng *et al.*²⁴ as shown in scheme 2. The chemicals used in this study were purchased from Fluka and Merck chemical companies. MWCNTs (purity >96%) were purchased from Research Institute of Petroleum Industry (RIPI-Iran). The specifications of CNTs, used in this study, are listed in table 1. Melting points were determined using melting point IA 8103 apparatus. FT-IR spectra were obtained with KBr pellets in the range of 400–4000 cm^{−1} with a Nicolet-860 spectrometer. ¹H NMR spectra were recorded in DMSO-(d₆) solvent on a Bruker-Avance 500 MHz

spectrometer using TMS as an internal standard. Raman spectra were recorded with an Almega Thermo Nicolet Dispersive Raman spectrometer excited at 532 nm. Scanning electron micrographs of CNTs were taken on a Philips XL30 SEM instrument. Transmission electron micrographs were recorded with a JEOL-JEM 2010 microscope.

2.2 General procedure for synthesis of bisphenolic antioxidants in the presence of MWCNTs–SO₃H under solvent-free conditions

In a 25 ml flask equipped with a condenser and magnetic stirring bar, a mixture of 2-*tert*-butyl-4-methylphenol (9 mmol), aldehyde (3 mmol) and MWCNTs–SO₃H (35 mg) was heated at 140°C under solvent-free conditions for appropriate time according to table 2. Progress of the reaction was monitored by TLC (n-hexane/ethyl acetate 10:3). After completion of the reaction, the mixture was cooled to room temperature and 15 ml acetone (3 × 5 ml) was added. The catalyst was filtered by simple filtration. The liquid was recovered by evaporation on a rotary evaporator. Then, the solid materials were washed with n-hexane (5 ml) and deionized water, successively, to afford pure



Scheme 2. Preparation of MWCNTs–SO₃H.

Table 1. Specification of MWCNTs used in this study.

MWCNTs		
Diameter (nm)	Length (μm)	Specific surface area (m^2/g)
10–15	30	>500

products. The pure products were kept in an oven at 80°C for 24 h. All the products were identified by FT-IR, ¹H NMR and melting points.

2.3 Acidity of MWCNTs-SO₃H

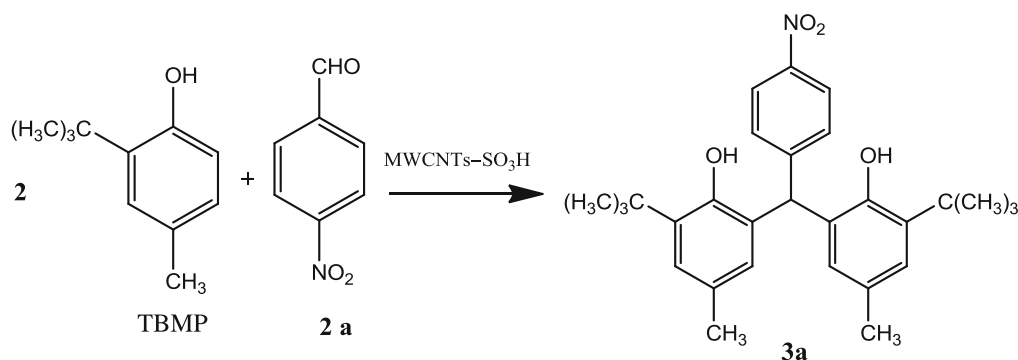
Density of SO₃H groups in the MWCNTs was determined by acid–base titration. Acid–base titration showed that the amount of SO₃H attached to MWCNTs is 1.80 mmol. g⁻¹.

2.4 Reusability of the catalyst

Recovery and reusability of the MWCNTs-SO₃H is very important factor in practice and also from an economical viewpoint. Reusability of the MWCNTs-SO₃H was investigated in the reaction of 2-*tert*-butyl-4-methylphenol and 4-chloro-3-nitrobenzaldehyde. At the end of each reaction, the catalyst was isolated by filtration, washed exhaustively with chloroform and ethanol, and dried at 120°C for 24 h before being used with fresh 2-*tert*-butyl-4-methylphenol and aldehyde. The catalyst can be reused 10 times without any reduction in its catalytic activity.

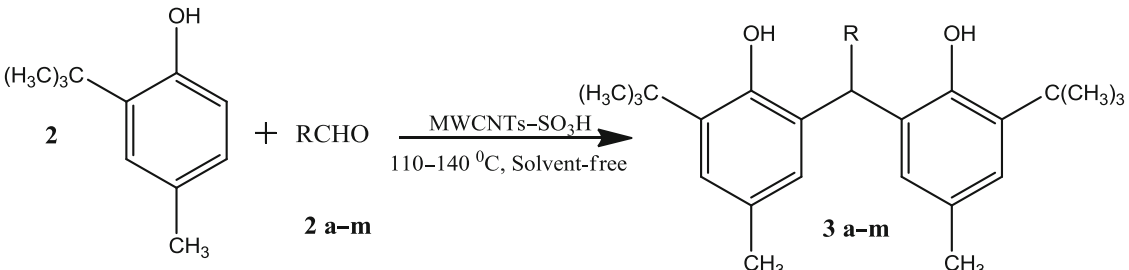
2.5 Spectroscopic and physical data

2.5a 6,6'-((4-Nitrophenyl)methylene)bis(2-(*tert*-butyl)4-methylphenol) (table 3, Compound **3a**): Mp 217–219°C; IR (KBr) ν (cm^{-1}) 3608, 3507, 2955, 1600,

Table 2. Optimization of reaction conditions for MWCNTs-SO₃H catalysed reaction of TBMP with 4-nitrobenzaldehyde (**2a**).

Entry	MWCNTs-SO ₃ H (mg)	TBMP (mmol)	Aldehyde (mmol)	Solvent	<i>T</i> (°C)	Time (min)	Yield (%) ^a
1	35	6	3	n-hexane	Reflux	120	10
2	35	6	3	CH ₃ CN	Reflux	120	45
3	35	6	3	H ₂ O	Reflux	120	40
4	35	6	3	CH ₃ CN/H ₂ O	Reflux	120	35
5	35	6	3	CH ₃ NO ₂	Reflux	120	50
6	35	6	3	Solvent-free	60	120	55
7	35	6	3	Solvent-free	80	90	55
8	35	6	3	Solvent-free	100	75	60
9	35	6	3	Solvent-free	120	45	65
10	35	6	3	Solvent-free	140	25	65
11	35	7.5	3	Solvent-free	140	25	85
12	35	9	3	Solvent-free	140	25	95
13	35	10.5	3	Solvent-free	140	25	95
14	0	9	3	Solvent-free	140	180	5
15	20	9	3	Solvent-free	140	90	50
16	30	9	3	Solvent-free	140	60	80
17	35	9	3	Solvent-free	140	25	95
18	40	9	3	Solvent-free	140	25	95

^a isolated yield

Table 3. Synthesis of bisphenolic antioxidants in the presence of MWCNTs-SO₃H.


Entry	Aldehyde	Product	Yield (%) ^b	Time (min)
1	4-Nitrobenzaldehyde (2a)	3a	95	25
2	3-Nitrobenzaldehyde (2b)	3b	95	30
3	4-Chloro-3-nitrobenzaldehyde (2c)	3c	100 (100) ^c	15 (12) ^c
4	4-Chlorobenzaldehyde (2d)	3d	95	25
5	2-Chlorobenzaldehyde (2e)	3e	95	20
6	4-Bromobenzaldehyde (2f)	3f	92	25
7	Benzaldehyde (2g)	3g	90	35
8	4-Methylbenzaldehyde (2h)	3h	87	40
9	3-Methylbenzaldehyde (2i)	3i	88	30
10	3-Hydroxybenzaldehyde (2j)	3j	88	25
11 ^c	4-Hydroxybenzaldehyde (2k)	3k	Trace	100
12 ^c	2-Hydroxy-4-methoxybenzaldehyde (2l)	3l	Trace	100
13 ^d	CH ₂ O (2m)	3m	100	20

^aReaction conditions: 2-tert-butyl-4-methylphenol (9 mmol), aldehyde (3 mmol), solvent-free, $T = 140^{\circ}\text{C}$, catalyst (35 mg)

^bIsolated yield

^cStarting material was recovered from reaction mixture

^dReaction conditions: 2-tert-butyl-4-methylphenol (6 mmol), formaline (3 mmol), solvent-free, $T = 110^{\circ}\text{C}$, catalyst (30 mg)

^eThis result was obtained by SWCNTs-SO₃H.

1515, 1447, 1347, 1230, 1118, 884. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): 1.39 (18H, s, *tert*-butyl), 2.08 (6H, s, CH₃), 6.24 (1H, s, Ar₃CH), 6.30 (2H, s, OH), 6.93 (2H, s, 3-H TBMP), 7.16 (2H, d, $J = 8$ Hz, 2,6-H aldehyde), 7.64 (2H, s, 5-H TBMP), 8.12 (2H, d, $J = 8$ Hz, 3, 5-H aldehyde). Anal. Calcd for C₂₉H₃₅NO₄: C, 75.46; H, 7.64; N, 3.03%. Found: C, 75.62; H, 7.39; N, 2.95%.

2.5b 6,6'-((3-Nitrophenyl)methylene)bis(2-(*tert*-butyl)4-methylphenol) (table 3, Compound **3b**): Mp 174–176°C; IR (KBr) ν (cm⁻¹) 3542, 3477, 3004, 2956, 2915, 1530, 1441, 1344, 1175, 696. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): 1.39 (18H, s, *tert*-butyl), 2.14 (6H, s, CH₃), 6.25 (1H, s, Ar₃CH), 6.30 (2H, s, OH), 6.94 (2H, s, 3-H TBMP), 7.35 (1H, d, $J = 7.3$ Hz, 5-H aldehyde), 7.55 (1H, t, $J = 7.3$ Hz, 6-H aldehyde), 7.65 (2H, s, 5-H TBMP), 7.72 (1H, s, 2-H aldehyde), 8.06 (1H, d, $J = 7.3$ Hz, 4-H aldehyde). Anal. Calcd for C₂₉H₃₅NO₄: C, 75.46; H, 7.64; N, 3.03%. Found: C, 75.55; H, 7.69; N, 3.00%.

2.5c 6,6'-((4-Chloro-3-nitrophenyl)methylene)bis(2-(*tert*-butyl)4-methylphenol) (table 3, Compound **3c**): Mp 201–203°C; IR (KBr) ν (cm⁻¹) 3564, 3522, 3000, 2951, 2914, 1530, 1470, 1364, 1185, 1155, 1051, 842, 766, 664, 482. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): 1.34 (18H, s, *tert*-butyl), 2.09 (6H, s, CH₃), 6.20 (1H, s, Ar₃CH), 6.30 (2H, s, OH), 6.94 (2H, s, 3-H TBMP), 7.17 (1H, d, $J = 7.9$ Hz, 6-H aldehyde), 7.52 (1H, s, 5-H aldehyde), 7.63 (1H, d, $J = 1.3$ Hz, 2-H aldehyde), 7.64 (2H, s, 5-H TBMP). Anal. Calcd for C₂₉H₃₄ClNO₄: C, 70.22; H, 6.91; N, 2.82%. Found: C, 70.55; H, 7.09; N, 2.85%.

2.5d 6,6'-((4-Chlorophenyl)methylene)bis(2-(*tert*-butyl)4-methylphenol) (table 3, Compound **3d**): Mp 203–205°C; IR (KBr) ν (cm⁻¹) 3564, 3517, 2993, 2913, 2861, 1441, 1410, 1174, 1090, 1015, 873, 762. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): 1.38 (18H, s, *tert*-butyl), 2.08 (6H, s, CH₃), 6.06 (1H, s, Ar₃CH), 6.30 (2H, s, OH), 6.90 (2H, s, 3-H TBMP), 6.92 (2H, d, $J = 7.4$ Hz, 2,6-H aldehyde), 7.29 (2H, d, $J = 7.4$ Hz,

3,5-H aldehyde), 7.54 (2H, s, 5-H TBMP), Anal. Calcd for C₂₉H₃₅ClO₂: C, 77.22; H, 7.82%. Found: C, 77.55; H, 7.59%.

2.5e 6,6'-((2-Chlorophenyl)methylene)bis(2-(tert-butyl)4-methylphenol) (table 3, Compound 3e): Mp 193–195°C; IR (KBr): ν (cm⁻¹) 3577, 3515, 3000, 2962, 2914, 2866, 1440, 1360, 1182, 1045, 869, 757, 663. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): 1.32 (18H, s, *tert*-butyl), 2.16 (6H, s, CH₃), 6.23 (1H, s, Ar₃CH), 6.20 (2H, s, OH), 6.61 (1H, t, *J* = 6.9 Hz, 4-H aldehyde), 6.92 (2H, s, 3-H TBMP), 7.20 (2H, m, 5,6-H aldehyde), 7.39 (1H, d, *J* = 7.08 Hz, 3-H aldehyde), 7.46 (2H, s, 5-H TBMP). Anal. Calcd for C₂₉H₃₅ClO₂: C, 77.22; H, 7.82%. Found: C, 77.15; H, 7.80%.

2.5f 6,6'-((4-Bromophenyl)methylene)bis(2-(tert-butyl)4-methylphenol) (table 3, Compound 3f): Mp 210–212°C; IR (KBr): ν (cm⁻¹) 3560, 3517, 3026, 2944, 2862, 1441, 1251, 1216, 1175, 1010, 873, 825, 424. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): 1.33 (18H, s, *tert*-butyl), 2.08 (6H, s, CH₃), 6.04 (1H, s, Ar₃CH), 6.30 (2H, s, OH), 6.85 (2H, d, *J* = 8.34 Hz, 2,6-H aldehyde), 6.90 (2H, s, 3-H TBMP), 7.42 (2H, d, *J* = 8.32 Hz, 3,5-H aldehyde), 7.55 (2H, s, 5-H TBMP). Anal. Calcd for C₂₉H₃₅BrO₂: C, 70.30; H, 7.12%. Found: C, 70.15; H, 7.30%.

2.5g 6,6'-(Phenylmethylene)bis(2-(tert-butyl)4-methylphenol) (table 3, Compound 3g): Mp 176–178°C; IR (KBr): ν (cm⁻¹) 3562, 3495, 3001, 2930, 1870, 1443, 1215, 873, 645. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): 1.33 (18H, s, *tert*-butyl), 2.07 (6H, s, CH₃), 6.06 (1H, s, Ar₃CH), 6.33 (2H, s, OH), 6.89 (2H, s, 3-H TBMP), 6.92 (2H, d, *J* = 6.2 Hz, 3,5-H aldehyde), 7.17 (1H, t, *J* = 7.00 Hz, 4-H aldehyde), 7.24 (2H, d, 3,5-H aldehyde), 7.53 (2H, s, 5-H TBMP). Anal. Calcd for C₂₉H₃₆O₂: C, 83.61; H, 8.71%. Found: C, 83.44; H, 8.66%.

2.5h 6,6'-(*p*-Tolylmethylene)bis(2-(tert-butyl)4-methylphenol) (table 3, Compound 3h): Mp 195–197°C; IR (KBr): ν (cm⁻¹) 3542, 3514, 2948, 2916, 1470, 1141, 1320, 1178, 847, 760, 666. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): 1.33 (18H, s, *tert*-butyl), 2.07 (6H, s, CH₃), 2.25 (3H, s, CH₃-aldehyde), 5.99 (1H, s, Ar₃CH), 6.33 (2H, s, OH), 6.80 (2H, d, *J* = 7.82 Hz, 3,5-H aldehyde), 6.88 (2H, s, 3-H TBMP), 7.04 (2H, d, *J* = 7.82 Hz, 2,6-H aldehyde), 7.48 (2H, s, 5-H TBMP). Anal. Calcd for C₃₀H₃₈O₂: C, 83.67; H, 8.89%. Found: C, 83.64; H, 8.96%.

2.5i 6,6'-(*m*-Tolylmethylene)bis(2-(tert-butyl)4-methylphenol) (table 3, Compound 3i): Mp 166–168°C; IR (KBr): ν (cm⁻¹) 3552, 3524, 2948, 2906, 1466, 1141, 1318, 1168, 847, 760, 656. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): 1.33 (18H, s, *tert*-butyl), 2.07 (6H, s, CH₃), 2.16 (3H, s, CH₃-aldehyde), 6.01 (1H, s, Ar₃CH), 6.34 (2H, s, OH), 6.65 (1H, d, *J* = 7.95 Hz, 6-H aldehyde), 6.90 (2H, s, 3-H TBMP), 6.98 (1H, t, *J* = 7.60 Hz, 5-H aldehyde), 7.48 (2H, s, 5-H TBMP). Anal. Calcd for C₃₀H₃₈O₂: C, 83.67; H, 8.89%. Found: C, 83.74; H, 8.86%.

2.5j 6,6'-((3-Hydroxyphenyl)methylene)bis(2-(tert-butyl)4-methylphenol) (table 3, Compound 3j): Mp 196–198°C; IR (KBr): ν (cm⁻¹) 3544, 3497, 3001, 2957, 2914, 1599, 1444, 1254, 1176, 868, 766, 466. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): 1.28 (18H, s, *tert*-butyl), 2.09 (6H, s, CH₃), 5.91 (1H, s, Ar₃CH), 6.35 (2H, s, OH), 6.35 (2H, d, *J* = 7.65 Hz, 2,6-H aldehyde), 6.56 (1H, d, *J* = 7.25 Hz, 6-H aldehyde), 6.89 (2H, s, 3-H TBMP), 7.03 (1H, t, *J* = 7.76 Hz, 5-H aldehyde), 7.49 (2H, s, 5-H TBMP), 9.16 (1H, s, OH aldehyde). Anal. Calcd for C₂₉H₃₆O₃: C, 80.52; H, 8.39%. Found: C, 80.74; H, 8.26%.

2.5k 6,6'-Methylenebis(2-(tert-butyl)4-methylphenol) (table 3, Compound 3m): Mp 129–131°C; IR (KBr): ν (cm⁻¹) 3533, 3490, 3004, 2957, 2904, 1599, 1444, 1214, 1176, 868, 766, 466. ¹H-NMR (500 MHz, DMSO-*d*₆) δ (ppm): 1.30 (18H, s, *tert*-butyl), 2.11 (6H, s, CH₃), 5.84 (2H, s, Ar₂CH₂), 6.33 (2H, s, OH), 6.89 (2H, s, 3-H TBMP), 7.49 (2H, s, 5-H TBMP), Anal. Calcd for C₂₃H₃₂O₂: C, 81.13; H, 9.47%. Found: C, 81.64; H, 9.54%.

3. Result and discussion

3.1 Preparation of the catalyst

Scheme 2 shows the synthetic route for the preparation of MWCNTs-SO₃H catalysts. In order to increase the reactivity and purity of MWCNTs and to remove the catalyst particles such as Fe, Co and Ni, the mixture of HCl (37%) and HNO₃ (63%) were added to the set-up. This step also introduced oxygen containing groups, mainly carboxyl groups, on the CNTs.^{27,28} Then, sulphuric acid (98%) was reacted with MWCNTs-COOH to afford MWCNTs-SO₃H. The schematic of MWCNTs-SO₃H is shown in figure 1.

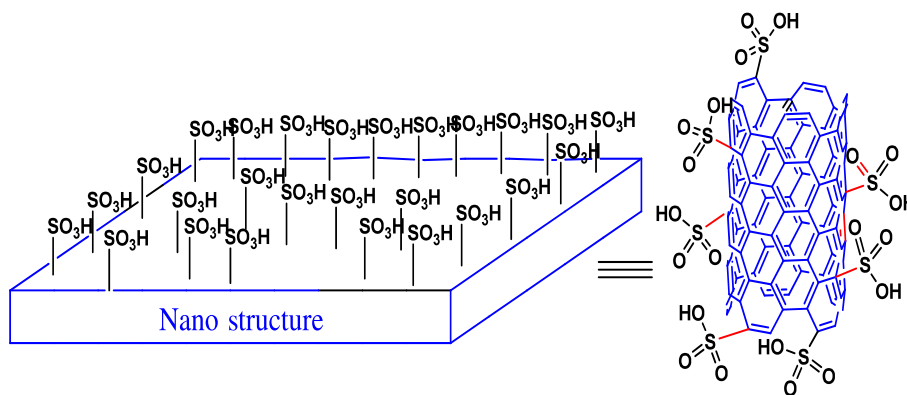


Figure 1. Schematic representation of MWCNTs-SO₃H.

3.2 Characterization of MWCNTs-SO₃H

The prepared catalyst was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), FT-IR spectroscopy, Raman spectroscopy, dispersibility test in various organic solvents and acid-base titration.

3.2a Microscopic characterizations: The SEM and TEM images of MWCNTs before and after H₂SO₄ treatment are shown in figure 2. SEM images (figure 2a, b) clearly indicate that functional groups such as sulphonic acid are attached to MWCNTs. Compared with the pristine MWCNTs, MWCNTs-SO₃H is

covered by a layer of foreign matter, resulting in thickened MWCNT bundles and a denser network of nanotubes. TEM images (figure 2c, d) also show that SO₃H group is supported on the CNTs. Foreign matter consists of groups of sulphonic acids and is marked by white arrows.

3.2b Spectroscopic characterizations: Spectroscopic data confirmed that functionalization of CNTs with sulphonic acids has occurred. Figure 3, shows the FT-IR spectra of pristine MWCNTs, MWCNTs-COOH and MWCNTs-SO₃H. FT-IR is mainly used to identify the presence or absence of functional groups in organic

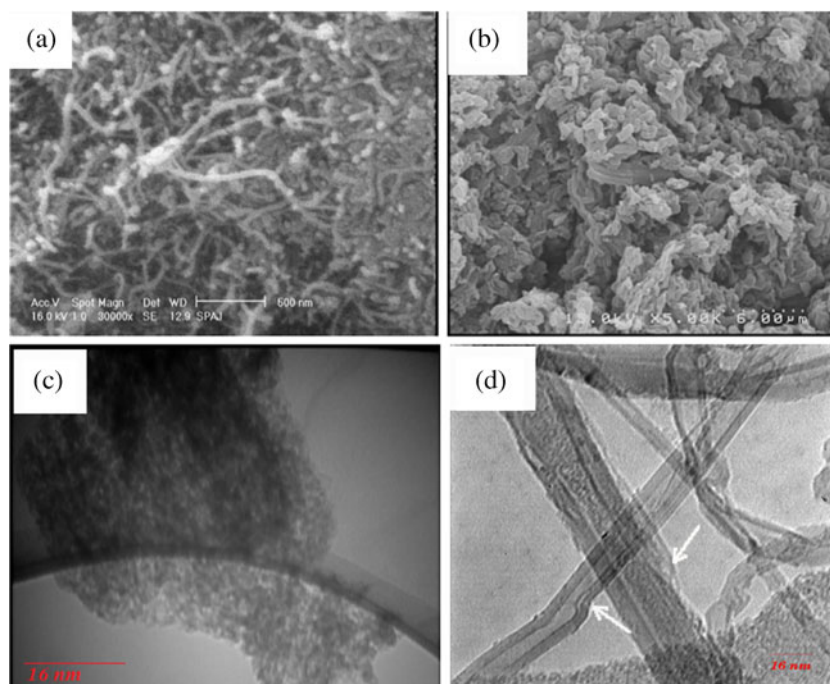


Figure 2. SEM images: (a) MWCNTs and (b) MWCNTs-SO₃H; TEM images; (c) MWCNTs and (d) MWCNTs-SO₃H.

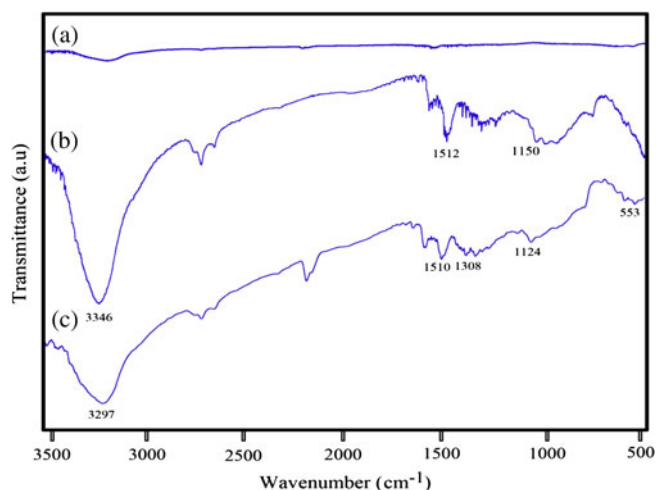


Figure 3. FT-IR spectra. (a) MWCNTs, (b) MWCNTs-COOH and (c) MWCNTs-SO₃H.

chemistry. The high symmetry presented on pristine MWCNTs generates very weak infrared signals, due to weak difference in charge states and very small induced electric dipole. The peak related to C=C double bond at approximately 1500 cm⁻¹ is not seen in the spectrum of pristine MWCNTs (figure 3a). Functionalization breaks the symmetry of CNTs, which enhances generation of induced electric dipoles and signs as detected. FT-IR spectrum of MWCNTs-COOH is shown in (figure 3b). This spectrum shows lines at about 1650–1700 cm⁻¹, which could be assigned to C=O stretching mode of the COOH group. The broad band centred at about 3300 cm⁻¹ is the contribution of the OH stretching mode of COOH groups.²⁷ The HNO₃: HCl oxidation process introduces not only carboxylic acid, but also alcohol or ketone species.²⁹ A weak line at approximately 1150 cm⁻¹ from the C-O stretching mode in alcohol species can be observed.²⁷ Sulphuric acid treatment also results in the appearance of peaks at about 1300 and 1120 cm⁻¹, which corresponds to SO₂ asymmetric and symmetric stretching modes, respectively. In addition, in the low frequency part of spectrum the line at 550 cm⁻¹ was assigned to C-S stretching mode, suggesting the existence of covalent sulphonic acid groups (figure 3c).

Raman spectroscopy is a technique frequently used to characterize CNTs.³⁰ In the region spectrum of 1300–1600 cm⁻¹; two bands are observed showing the characteristic of CNTs. These bands point out the graphite band (G-band) and disorder and defects of the structure, named D-band. The ratio between the intensity of the D-band and the G-band, noted $I_{D/G}$ value, corresponds to a higher proportion of sp³ carbon.³¹ In the low frequency part of the spectrum, there is a second region characteristic of CNTs; this region is named

radial breathing mode (RBM). The RBM Raman features (appearing between 150 and 250 cm⁻¹ for SWCNTs within $1 < d_t < 3$ nm) corresponds to atomic vibration of carbon atoms in radial directions, as if the tube was breathing.^{30,31} These features are very useful for characterizing nanotube diameter. Schematic pictures showing atomic vibrations for RBM and G-band modes of CNTs are shown in figure 4. Figure 5 shows the Raman spectra of MWCNTs, MWCNTs-COOH and MWCNTs-SO₃H. As shown in figure 5(a) the spectrum exhibits three peaks at about 1320, 1571 and 2660 cm⁻¹. The feature in 1571 cm⁻¹ is identified with the tangential mode (G-band). The origin of the line at 1320 cm⁻¹ is the D-band and its appearance has been tentatively assigned to a symmetry lowering effect, such as the presence of nanoparticles (synthesis of CNTs) and functional groups such as sulphonic acid on the side walls of MWCNTs. The line at 2660 cm⁻¹ has been attributed to the overtone of the D-band (G'-band). We can calculate that I_D/I_G values of MWCNTs, MWCNTs-COOH and MWCNTs-SO₃H are 0.24, 0.37 and 0.84, respectively. This increasing value implies that a strong damage to the side walls of CNTs is due to functionalization. Existence of RBM in figure 5(c) indicated that MWCNTs are still in their tubular structure after treatment with sulphuric acid and functionalization, although some MWCNTs were probably damaged by strong oxidation. Results obtained by Raman spectroscopy showed good agreement with results of FT-IR spectroscopy.

3.2c Dispersibility of MWCNTs-SO₃H: Dispersibility of MWCNTs was significantly enhanced by functionalization. Figure 6 shows dispersed states of MWCNTs, MWCNTs-COOH and MWCNTs-SO₃H

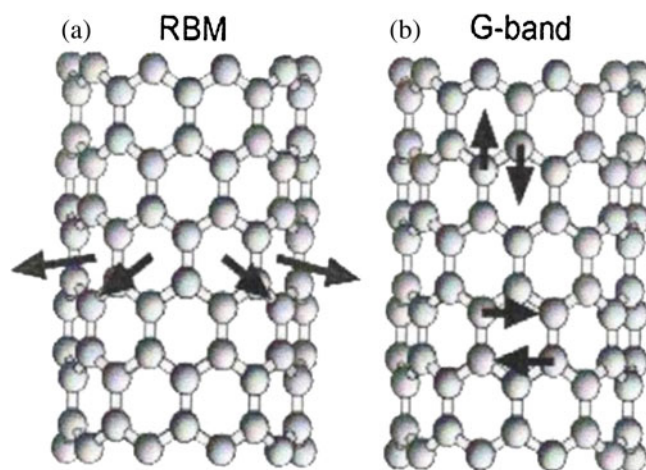


Figure 4. Two modes of stretching in CNTs.

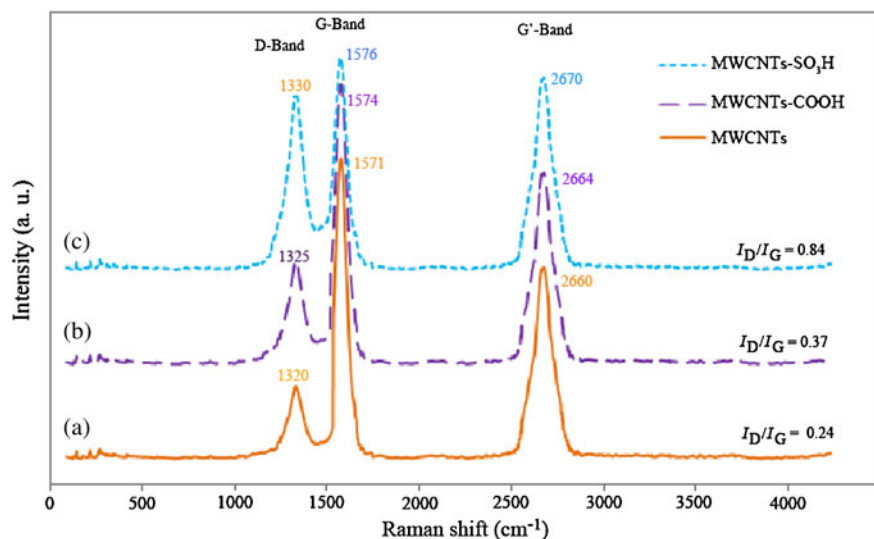


Figure 5. Raman spectra. (a) MWCNTs, (b) MWCNTs–COOH and (c) MWCNTs–SO₃H.

samples in various organic solvents used in this study. The MWCNTs–SO₃H (50 mg) dispersed well and formed uniform dispersion in 20 ml organic solvents. These dispersions were stable in nitromethane, acetonitrile and water, respectively after 100 days. Comparison of dispersion analysis images indicates that the suspension stability of the pristine MWCNTs was poor as they easily sediment. Sedimentation could be due to the agglomeration of nanotubes and lack of hydrogen bonding. Thus, the sulphonation process can be used as an effective method to obtain dispersive MWCNTs for variety of applications, for e.g., composites and catalysts. In addition, the highly sulphonated surfaces of MWCNTs act as proton carrier; therefore they can be used as solid acid catalysts in organic synthesis.

3.3 Catalytic test

The MWCNTs–SO₃H was used for the synthesis of bisphenolic antioxidants. First, the reaction parameters such as solvent, temperature, molar ratio of the reactants and catalyst amount were optimized in the reaction of 4-nitrobenzaldehyde with 2-*tert*-butyl-4-methylphenol in the presence of MWCNTs–SO₃H as a model reaction (table 2). In order to choose the reaction solvent, the reaction was performed in different solvents such as n-hexane, CH₃CN, H₂O, CH₃NO₂ and also under solvent-free conditions (table 2, entries 1–6). Entry 6 gave the best result. Solvent-free condition was chosen as the reaction medium, because of the higher catalytic activity of MWCNTs–SO₃H and

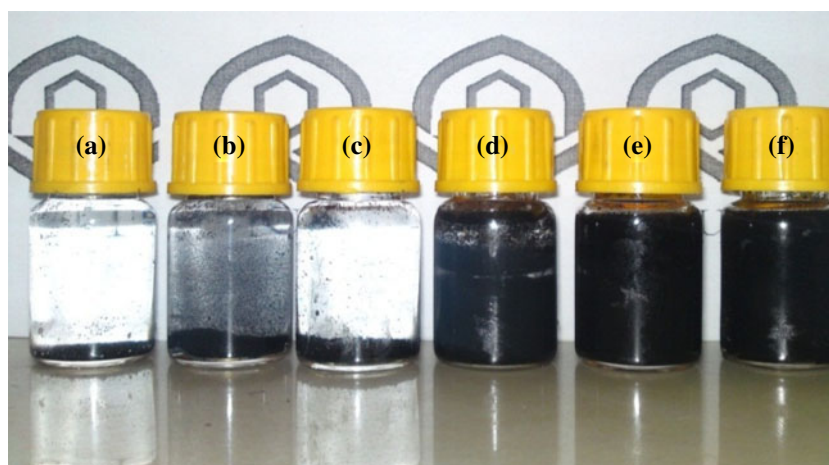


Figure 6. Dispersibility of CNTs in (solvent). (a) MWCNTs (CH₃NO₂), (b) MWCNTs–COOH (CH₃NO₂), (c) MWCNTs–SO₃H (n-hexane), (d) MWCNTs–SO₃H (H₂O), (e) MWCNTs–SO₃H (CH₃CN) and (f) MWCNTs–SO₃H (CH₃NO₂).

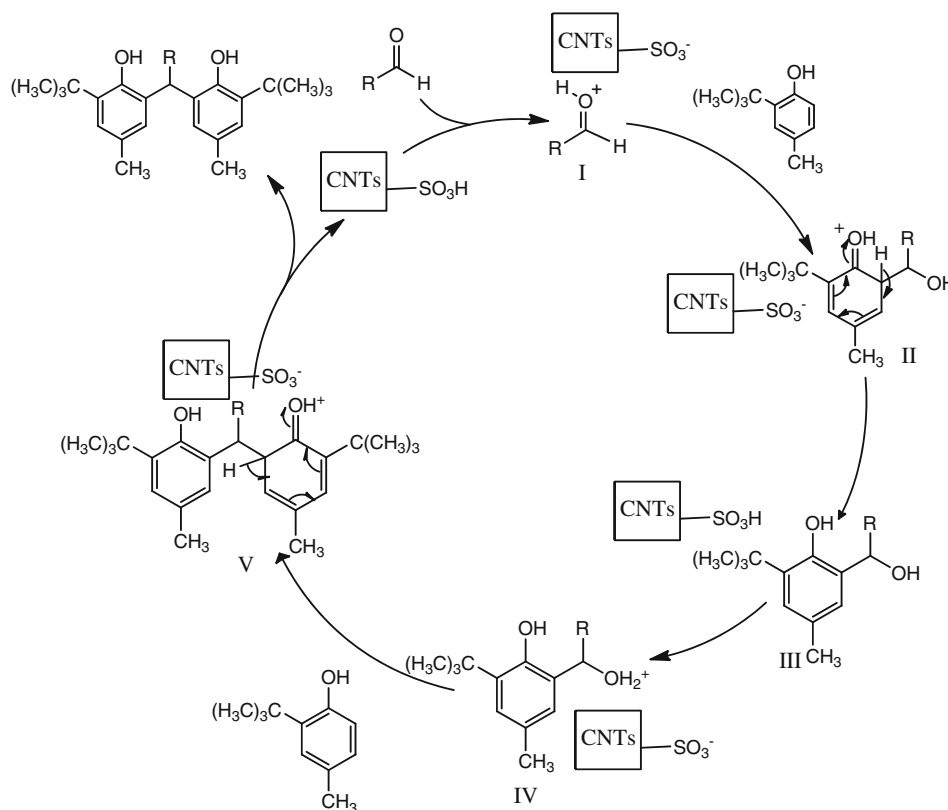
minimum time of the reaction. In solvent-free conditions, the reactants accomplish as solvent and increased number of collisions between reactants. Therefore, higher catalytic activity and minimum time of the reaction occurred. The reaction was studied at various temperatures ranging from 60° to 140°C (table 2, entries 6–10). At 60°C, the yield of reaction was 55% and it increased to 65% at 140°C. An increase in reaction temperature of more than 120°C, results in decreased reaction times and byproducts (O-alkylation). Therefore, 140°C was chosen as reaction temperature. To determine appropriate molar ratio of 2-*tert*-butyl-4-methylphenol to 4-nitrobenzaldehyde, the reaction was studied with different molar ratios of reactants and the best result was obtained with 3:1 molar ratio of 2-*tert*-butyl-4-methylphenol to 4-nitrobenzaldehyde (table 2, entry 12). Generally, 4-nitrobenzaldehyde conversion increased with an increase in amount of 2-*tert*-butyl-4-methylphenol. Using lower amount of 2-*tert*-butyl-4-methylphenol resulted in lower yields, while higher amount of 2-*tert*-butyl-4-methylphenol did not improve yield and reaction time. In order to optimize amount of catalyst, the model reaction was carried out in the presence of different amounts of catalyst (table 2, entries 14–18). Maximum yield was obtained by 35 mg of catalyst (table 2, entry 17). Further increase in amount of

MWCNTs-SO₃H, did not affect product yield, but a 100% amount of MWCNTs-SO₃H led to lower yield and higher time of reaction. Indeed in the absence of MWCNTs-SO₃H, the desired product was obtained in only 5% after 180 min.

3.4 Generality and versatility of initial studies

In this section, we investigated the generality and versatility of this method. A wide range of aromatic aldehydes were investigated for their reaction with 2-*tert*-butyl-4-methylphenol in the presence of MWCNTs-SO₃H under optimized reaction condition and results are shown in table 3. Electron-withdrawing substituents afforded the desired product in high yields within short reaction times (table 3, entries 1–6), while benzaldehyde with electron-donating groups failed to produce the desired products (table 3, entries 11–12).

The proposed reaction mechanism for MWCNTs-SO₃H catalysed synthesis of bisphenolic antioxidants using 2-*tert*-butyl-4-methylphenol and aldehyde is shown in scheme 3. The reaction proceeds via a series of protonic shifts from MWCNTs-SO₃H to the substrates. The aldehyde is first activated by protonation with MWCNTs-SO₃H to give I. Nucleophilic attack



Scheme 3. Proposed reaction pathway.

of 2-*tert*-butyl-4-methylphenol on **I** affords **II** and **III** which in turn is activated by MWCNTs–SO₃H to afford **IV**. Nucleophilic attack of second molecule of 2-*tert*-butyl-4-methylphenol to **IV**, gives **V** which is subsequently converted to the desired product and releases MWCNTs–SO₃H for the next catalytic cycle.

3.5 Reusability and stability of catalyst

Reusability of MWCNTs–SO₃H is of great importance from synthetic and economical points of view. Homogeneous acidic catalysts cannot be recovered even once; in contrast, the MWCNTs–SO₃H catalyst can be filtered and reused several times without significant loss of its activity. Reusability of MWCNTs–SO₃H was investigated in the multiple sequential reactions of 2-*tert*-butyl-4-methylphenol with 4-chloro-3-nitrobenzaldehyde. At the end of each reaction, MWCNTs–SO₃H was separated by simple filtration, washed with ethanol and chloroform and dried at 120°C for 24 h before using it in the next run. The MWCNTs–SO₃H was consecutively reused 10 times without significant loss of its activity (table 4). Initial experimental studies of SO₃H leaching were conducted by acid–base titration. In all these experiments, no density loss of SO₃H groups was observed. Nature of the reused catalyst was followed by FT-IR. Results showed no strong change in FT-IR spectra of MWCNTs–SO₃H after reusing several times.

3.6 Comparison study with SWCNTs–SO₃H as catalyst

Catalytic properties of multi-walled and single-walled CNTs were compared for the synthesis of bisphenolic

Table 4. Reusability of MWCNTs–SO₃H.

Run	Yield (%) ^b	Time (min)
1	100	15
2	100	15
3	98	15
4	95	15
5	95	15
6	92	15
7	94	15
8	92	15
9	90	15
10	90	15

^aReaction conditions: 2-*tert*-butyl-4-methylphenol (9 mmol), 4-chloro-3-nitrobenzaldehyde (3 mmol), solvent-free, *T* = 140°C, catalyst (35 mg)

^bIsolated yield

antioxidants. Results showed that there is no significant difference between these two types of catalyst. Single-walled CNTs were used for the reaction of acid 2-*tert*-butyl-4-methylphenol with 4-chloro-3-nitrobenzaldehyde. Observations showed no improvement in reaction efficiency. However, the reaction time was somewhat less.

4. Conclusion

In this study, a heterogeneous and stable MWCNTs–SO₃H was prepared and characterized by SEM, TEM, FT-IR spectroscopy and Raman spectroscopy. The total surface acidity of SO₃H groups on the MWCNTs was 1.80 mmol.g⁻¹. For the first time, we introduced a robust, eco-friendly, reusable and stable catalyst as an efficient catalyst for the synthesis of bisphenolic antioxidants under solvent-free conditions. In addition, relatively short reaction time, high yield of the products, solvent-free and non-toxicity of the catalyst are other worthwhile advantages of this study.

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