Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Formation of onion-like fullerene and chemically converted graphene-like nano-sheets from low-quality coals: application in photocatalytic degradation of 2-nitrophenol

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Electron beam analyses (SEM)

For scanning electron microscopic (SEM) analysis, the samples were critical point dried, fixed to metal stubs with carbon conducting double sided adhesive tape. The samples were coated with platinum with the aid of a spot size 36 mm by Auto Fine Coater (JFC-1600; JEOL, Tokyo, Japan). and examined in a scanning electron microscope (Model No. JSM-6390LV; JEOL). Observations on the SEM images were made at 20 kV with a working distance of 11mm and spot size 36.

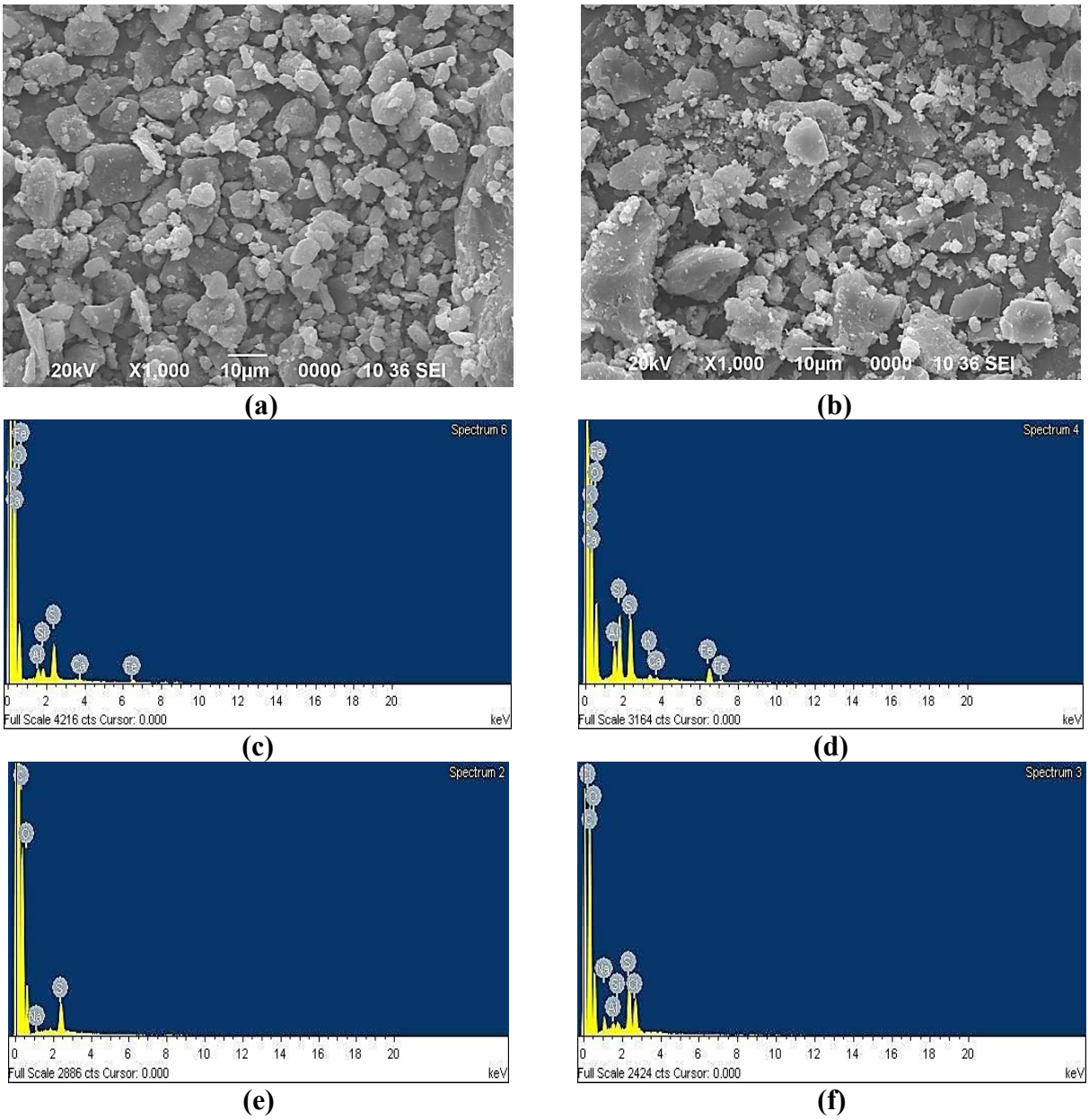


Figure S-1 SEM images of raw coals: **(a)** Coal-NG and **(b)** Coal-NK shows the presence of irregular size and shape distribution ranging from 1 to 50 micron in diameter; **(c)** EDX spectra of Coal-NG, **(d)** EDX spectra of Coal-NK, **(e)** EDX spectra of Coal-NG-NP, and **(f)** EDX spectra of Coal-NK-NP.

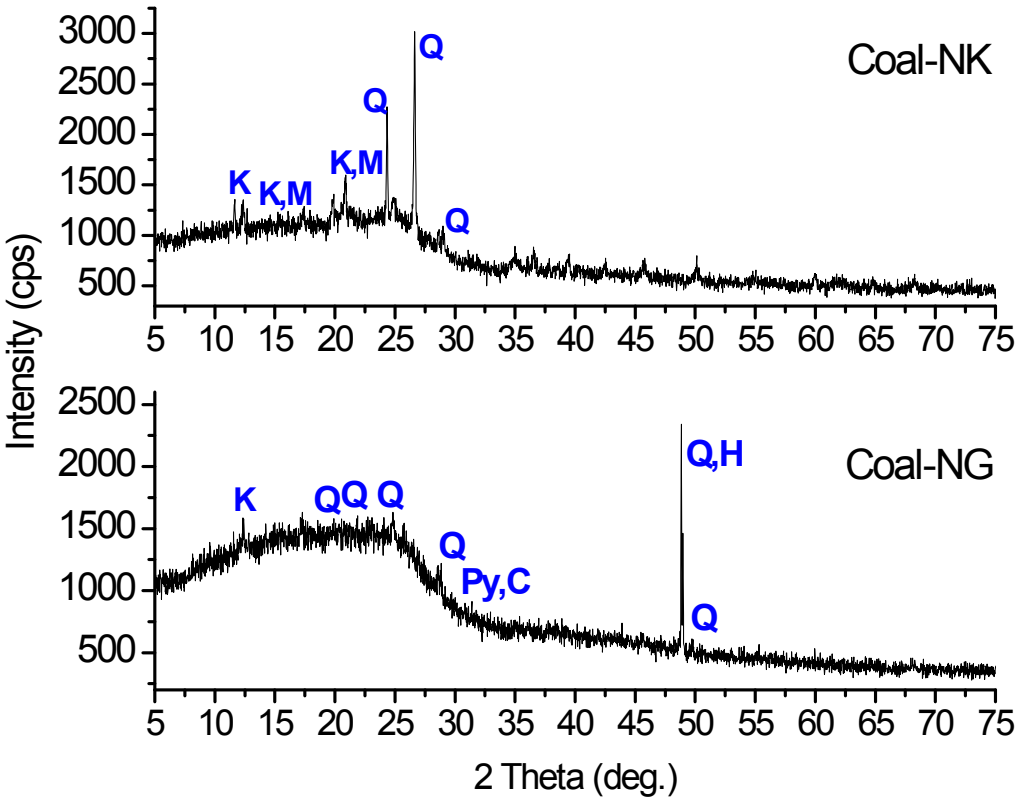


Figure S-2 XRD spectra of raw coal samples

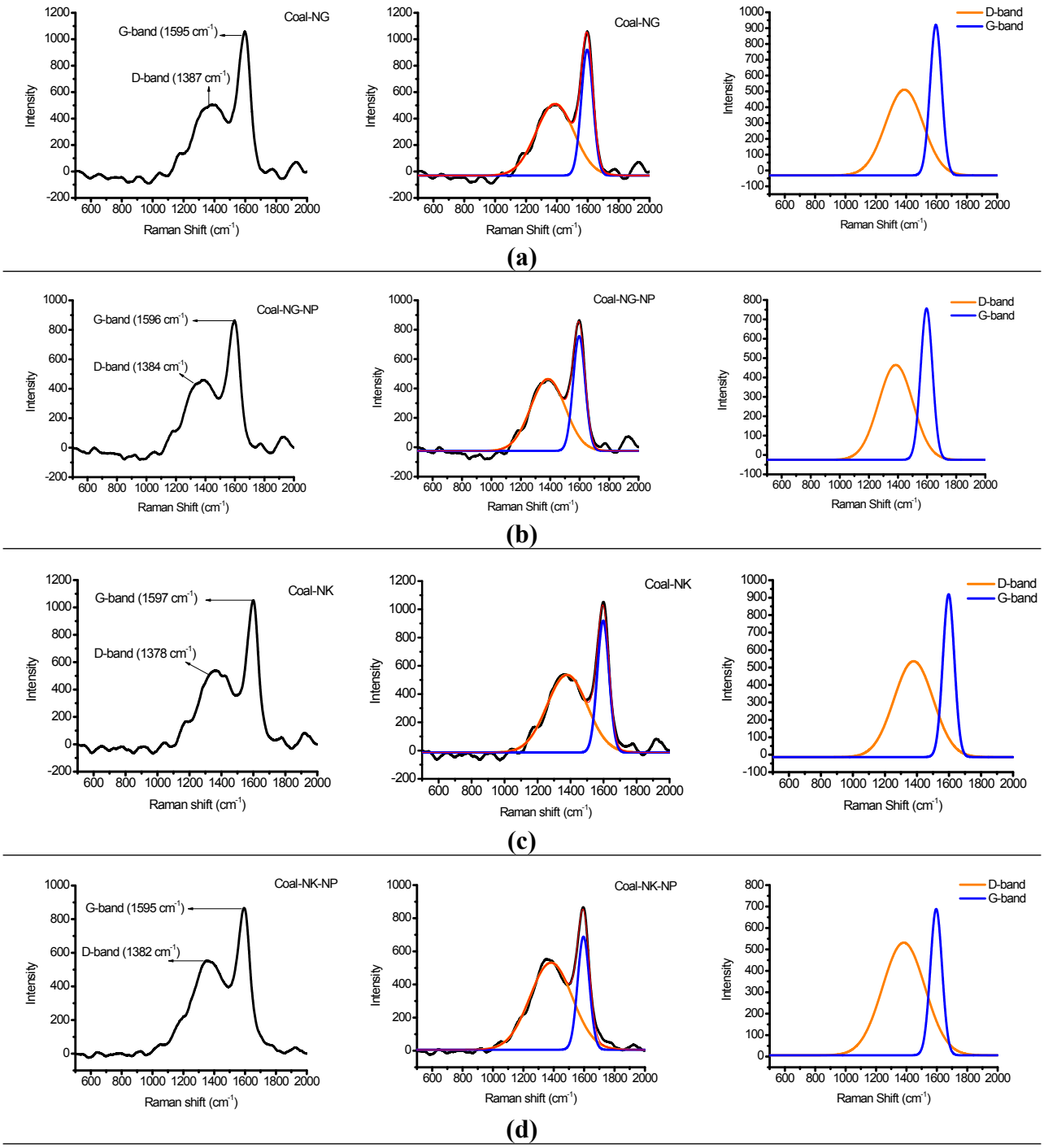


Figure S-3 Raman multi peak fitting spectra of **(a)** Coal-NG, **(b)** Coal-NG-NP, **(c)** Coal-NK, and **(d)** Coal-NK-NP.

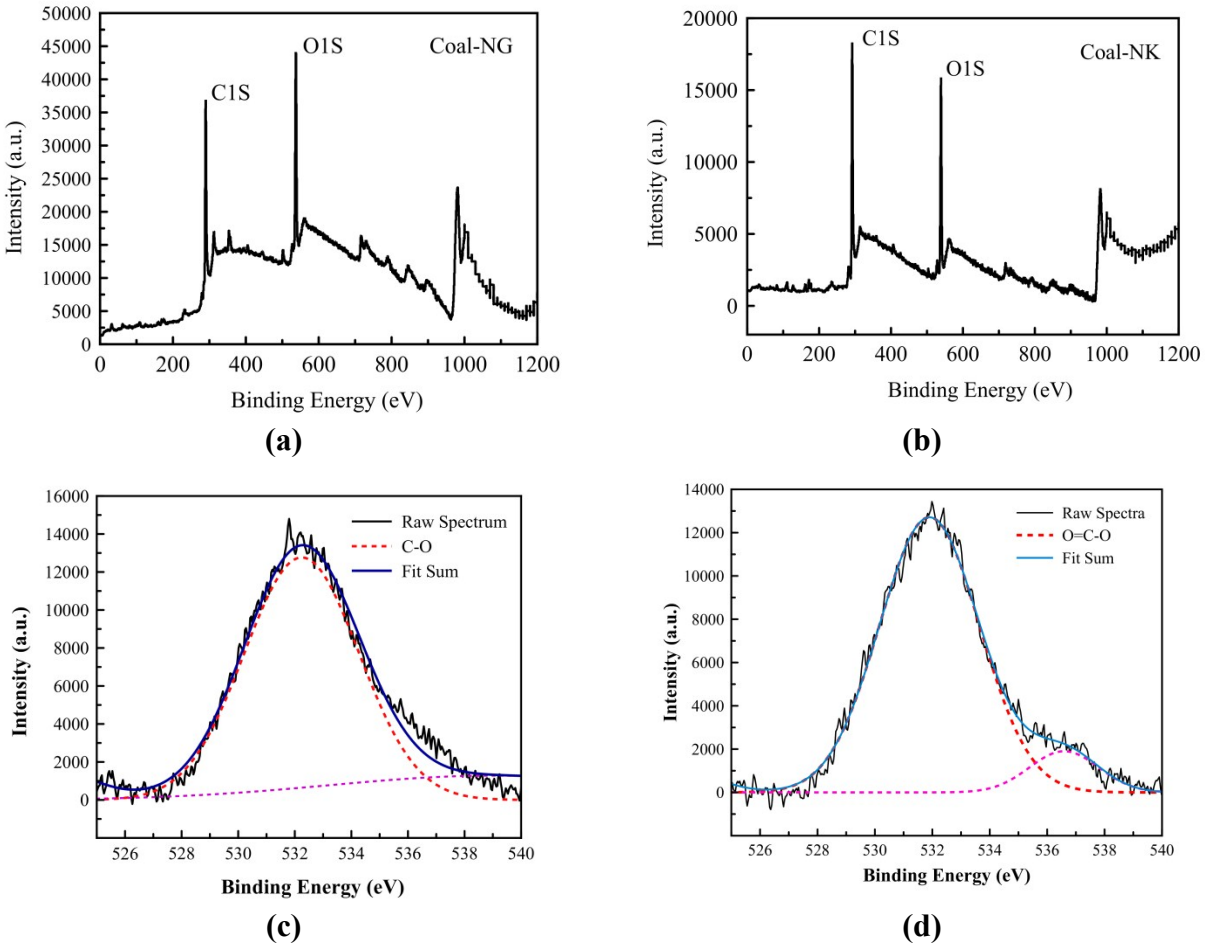


Figure S-4 XPS survey spectra of raw coals: **(a)** Coal-NG and **(b)** Coal-NK show C1S peak at around 290 eV due to Carboxyl (COO^-) and Carbonyl (C=O) group; High resolution XPS spectra of O1S spectra of **(c)** Coal-NG-NP and **(d)** Coal-NK-NP show the presence of Carboxyl (O=C-O) and C-O, which are located at 531.90 eV and 532.24 eV respectively.

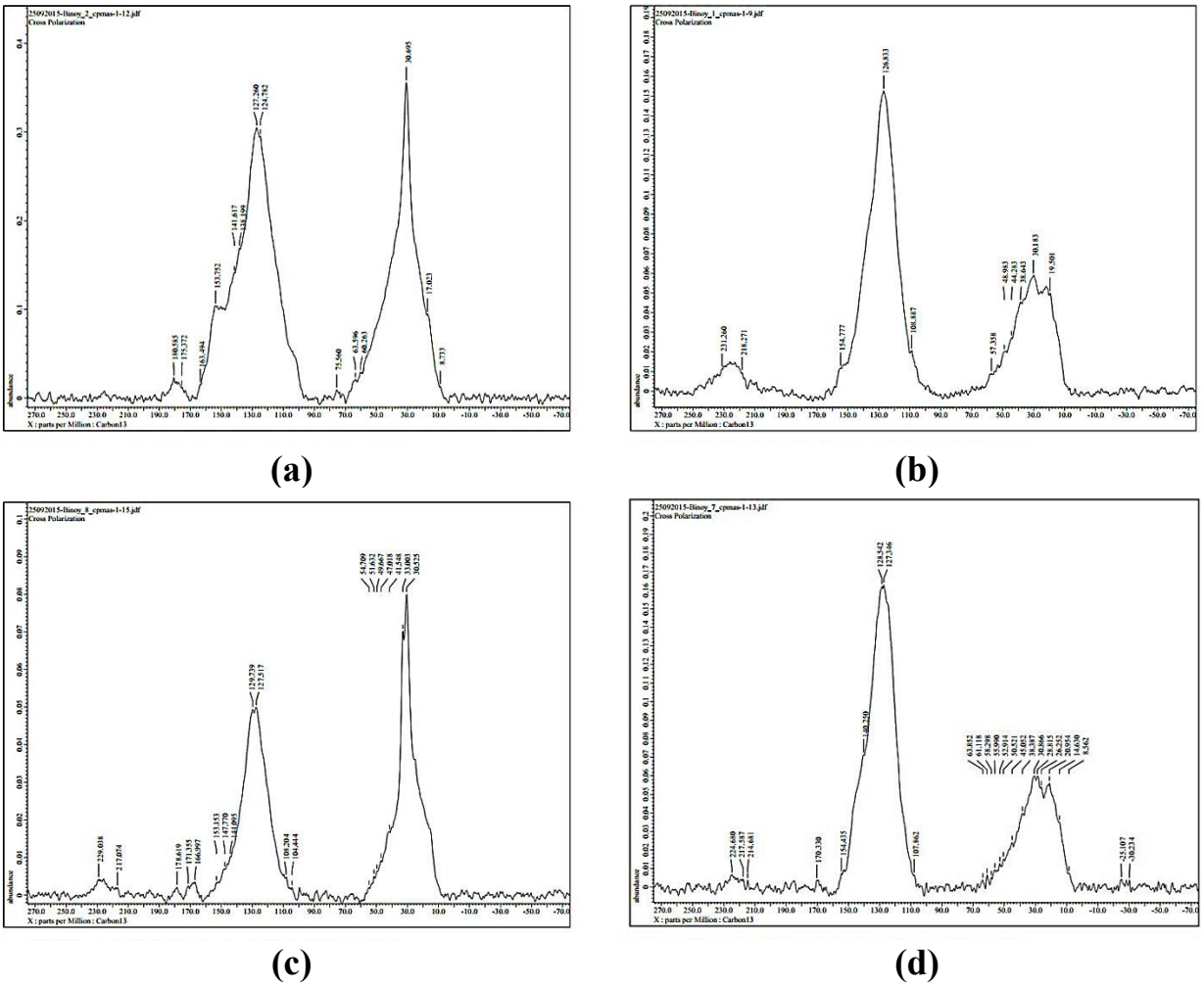


Figure S-5 Solid-state C^{13} NMR spectra of **(a)** Coal-NG. The prominent band at 30.69 ppm is for aliphatic carbon, 127.26 and 124.78 ppm for unsubstituted aromatic carbon, and 180.58 and 175.37 ppm for aromatic carbonyl group; **(b)** Coal-NK. The prominent band at 30.18 ppm is for aliphatic carbon, 126.83 ppm for unsubstituted aromatic carbon, 231.12 and 218.27 ppm for aromatic structural units; **(c)** Coal-NG-NP. The prominent band at 30.32 ppm is for aliphatic carbon, 36-50 ppm for protonated aromatic carbon, 129.73 and 127.51 ppm for unsubstituted aromatic carbon, 178.61, 171.35 and 166.99 ppm for the formation of carbonyl group in aromatic system, 229.03 and 217.07 ppm for aromatic structural units; **(d)** Coal-NK-NP. Small peak appearing in the range of 14-16 ppm are for the sp^3 hybridized carbon atoms attached to the aliphatic carbon atoms and small peak in the range of 22-36 ppm are for sp^2 and sp-hybridized carbon atoms attached to the aliphatic groups/or aliphatic carbon, 36-50 ppm for protonated aromatic carbon, 128.54 and 127.34 ppm for unsubstituted aromatic carbon, 170.33 ppm for the formation of carbonyl group in aromatic system, 224.68, 217.58 and 214.68 ppm for aromatic structural units.

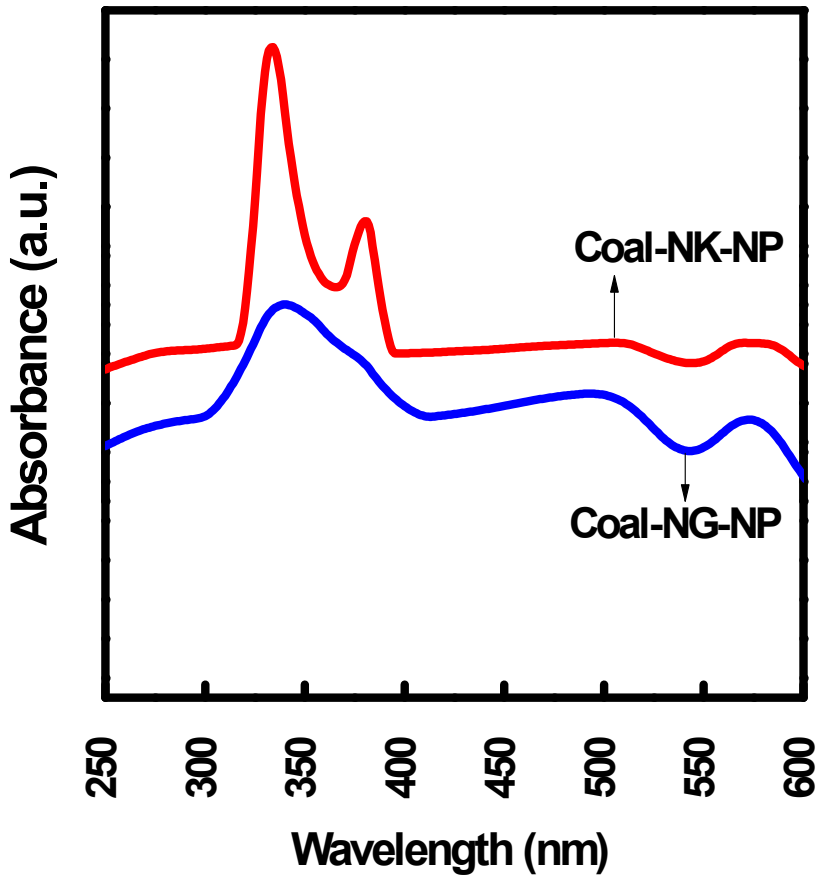


Figure S-6 UV-vis DRS spectra of the synthesized coal-derived CNMs

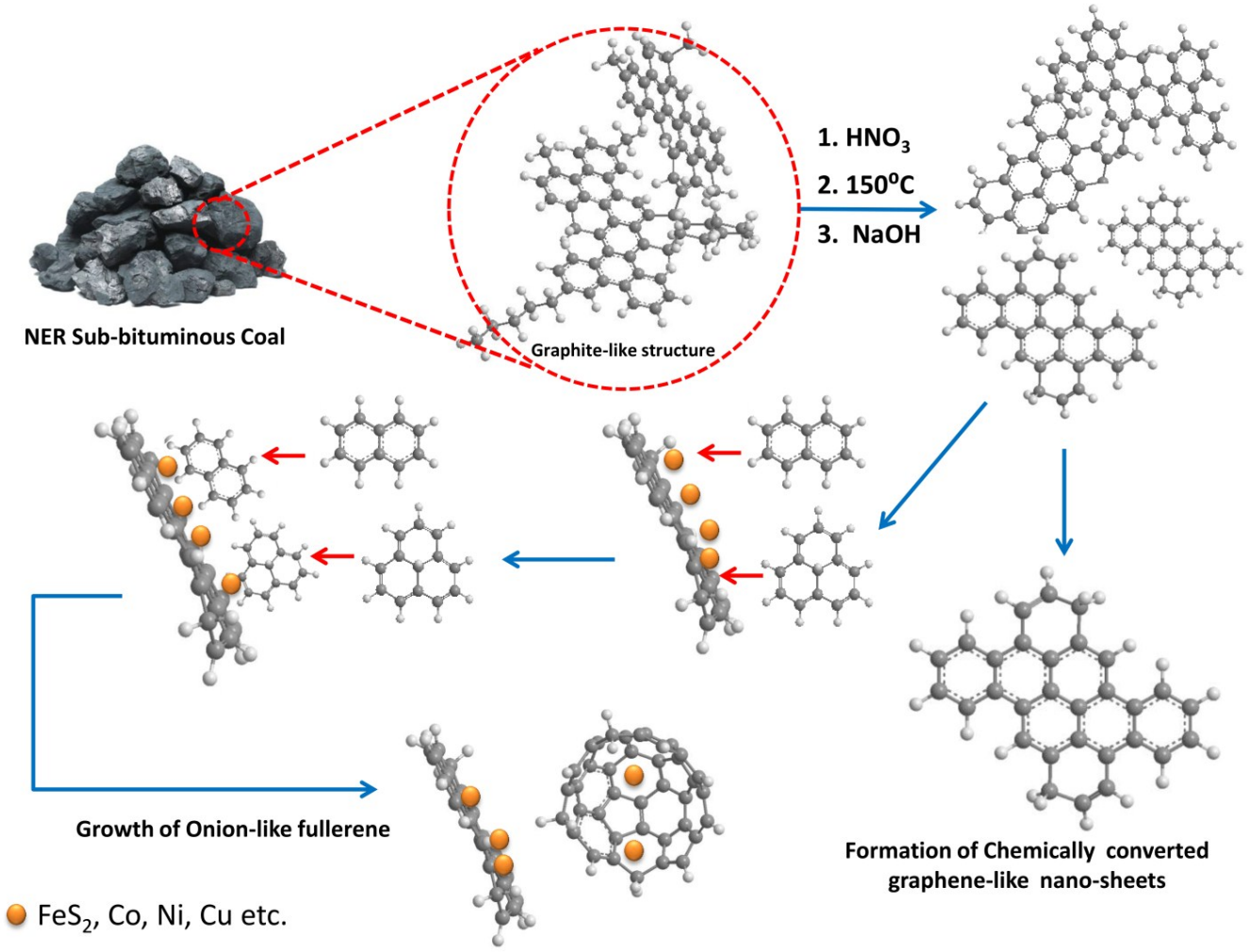


Figure S-7 Proposed mechanism for OCE process for preparing onion-like fullerene and chemically converted graphene-like nanosheets from low-quality coal.

Comparison of 2-NP adsorption performance of Coal-NG-NP and Coal-NK-NP under sunlight irradiation and in dark:

The adsorption of 2-NP onto Coal-NG-NP and Coal-NK-NP was investigated in dark to understand the adsorption behavior of these nanomaterials (at 0.1 mM concentration of 2-NP, catalyst loading $0.5gL^{-1}$ at pH 5). Due to the presence of pores and surface chemical group, adsorption efficiency of about 26.54% and 21.43% was observed for Coal-NG-NP and Coal-NK-NP, respectively at 40 min treatment in dark (Figure S-8a). However 99.34% and 92.49% 2-NP degradation efficiency was observed when Coal-NG-NP and Coal-NK-NP were used as a photocatalyst within 40 min under sunlight irradiation (Figure S-8a). Moreover, we also calculated the adsorption capacity (adsorption potential) of Coal-NG-NP and Coal-NK-NP nanomaterials for the 2-NP adsorption in dark. The adsorption capacity of Coal-NG-NP and Coal-NK-NP for 2-NP adsorption was found to be $0.0531mmol.g^{-1}$ and $0.0429mmol.g^{-1}$ respectively, in 40 min (Figure S-8b). Therefore, the adsorption potential for both these nanomaterials is found to be less as compared to their photocatalytic degradation efficiency.

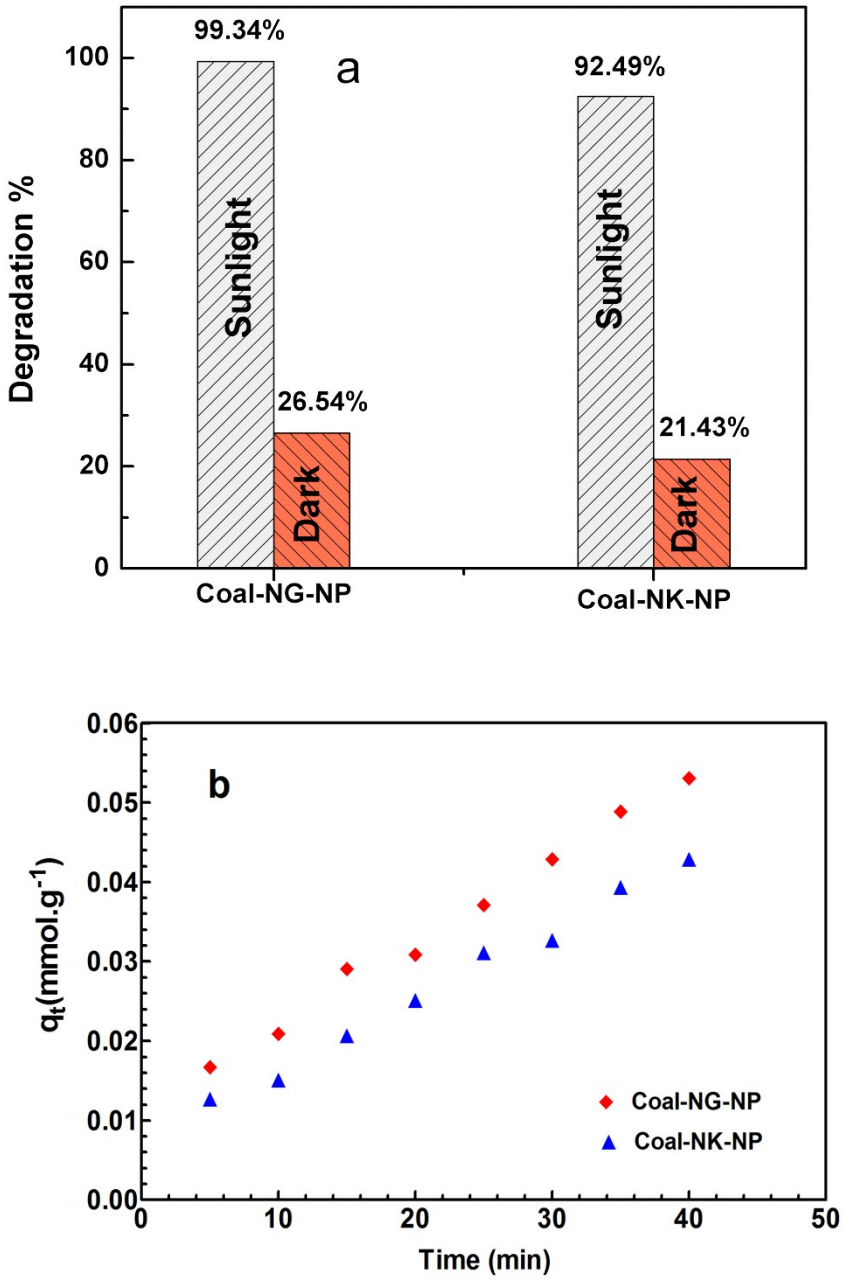
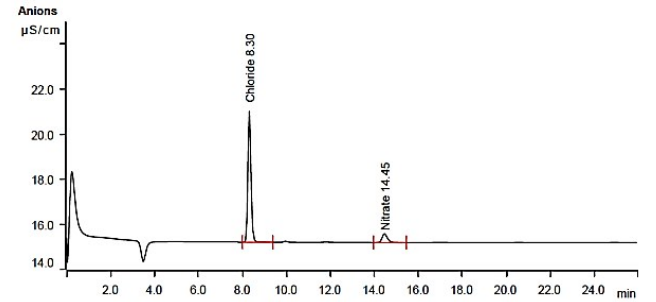
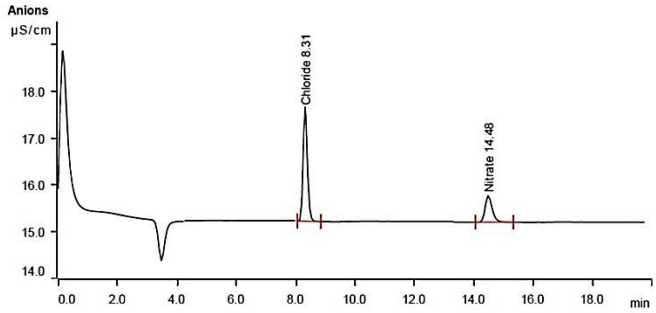


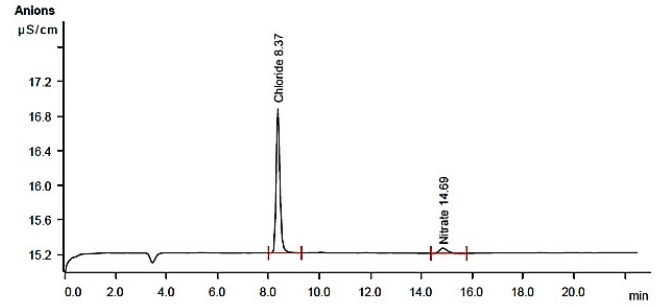
Figure S-8. (a) 2-NP removal performance of Coal-NG-NP and Coal-NK-NP under sunlight irradiation and in dark and (b) Adsorption potential vs time curve for the adsorption of 2-NP onto Coal-NG-NP and Coal-NK-NP in dark.



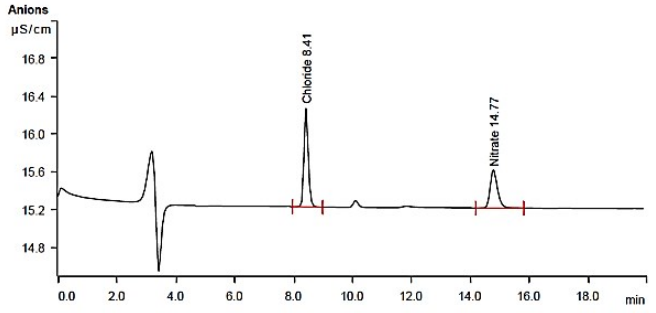
(a)



(b)

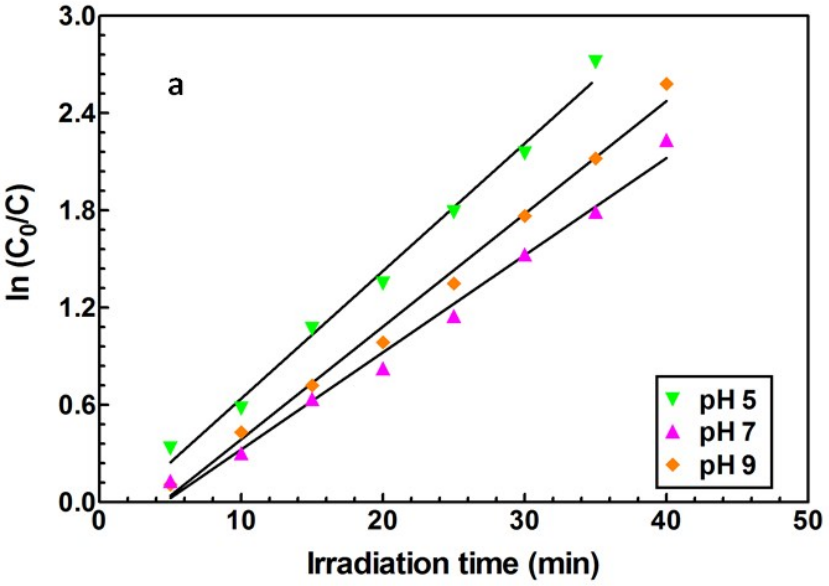


(c)

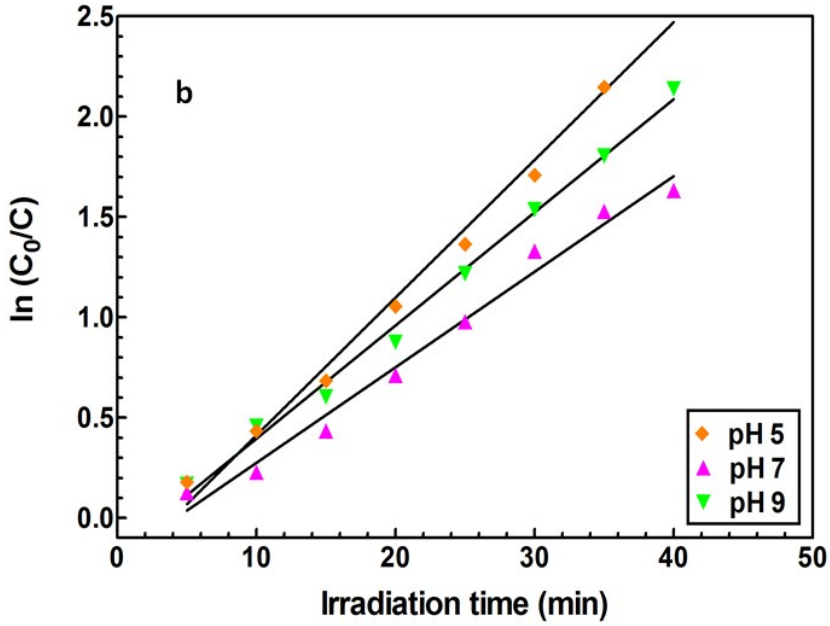


(d)

Figure S-9 IC-spectrum of Coal-NG-NP at pH 5 and reaction time of 10 minutes (a), 40 minutes (b); Coal-NK-NP at pH 5 and reaction time: 10 minutes (c), 40 minutes (d)



(a)



(b)

Figure S-10 Kinetic plot of ln (C_0/C) against time for 2-NP degradation using **(a)** Coal-NG-NP **(b)** Coal-NK-NP

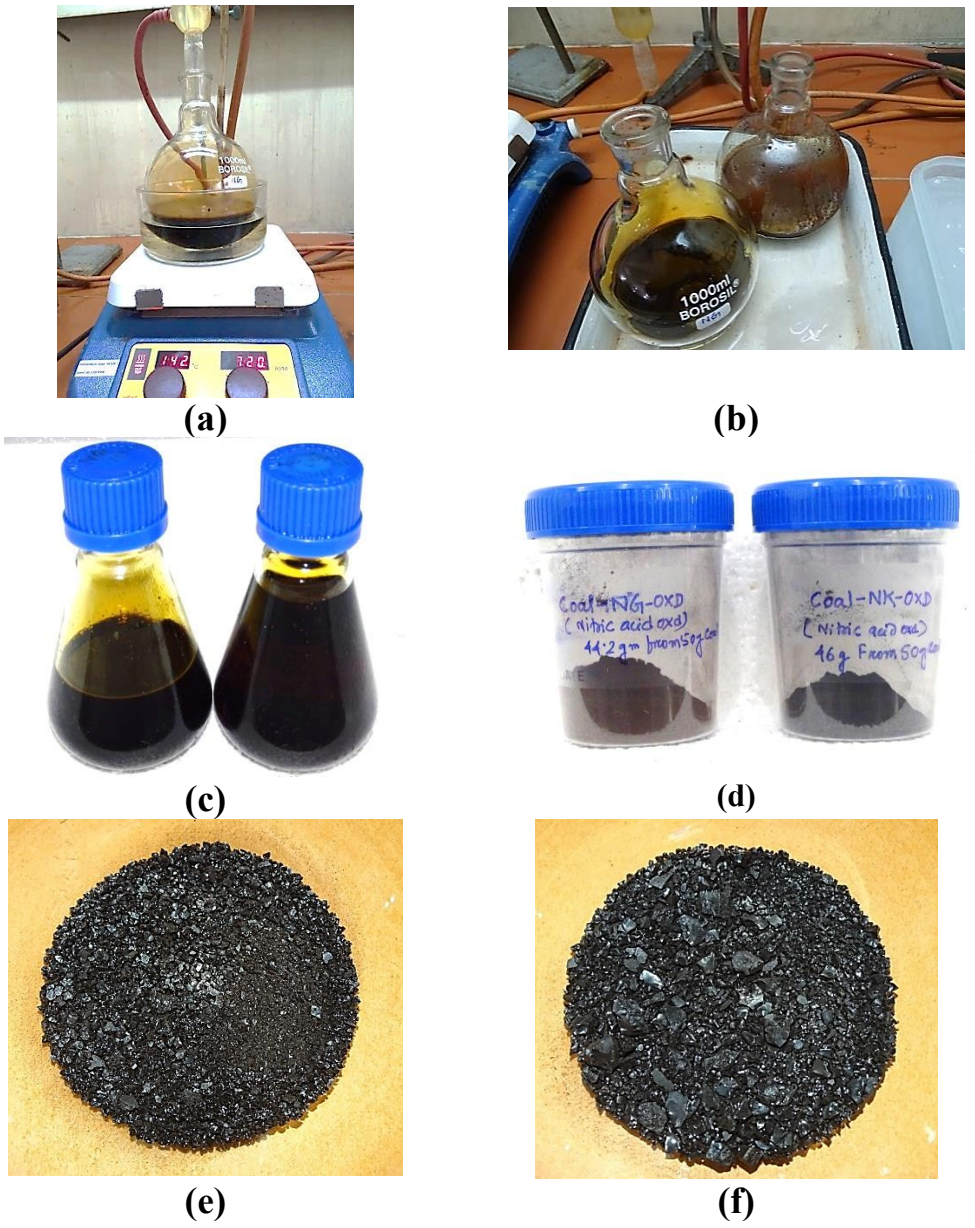
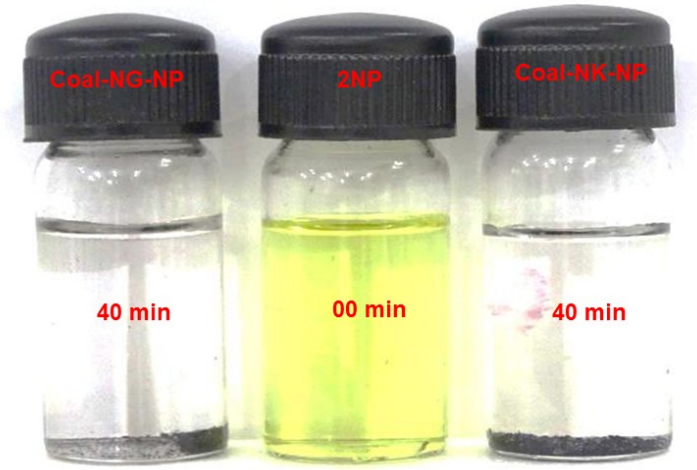


Figure S-11 (a) Coal and HNO_3 acid mixture heated in oil bath at 150ºC for 2 hours at atmospheric pressure; **(b)** Hot Coal and HNO_3 acid mixture was cooled in ice water bath; **(c)** recycled nitric acid were used in the oxidation process and molarity was adjusted by adding concentrated HNO_3 acid; **(d)** oxidized coal samples; **(e)** Final coal nano-products Coal-NG-NP (onion-like fullerene); **(f)** Final coal nano-product Coal-NK-NP (chemically converted graphene-like nano sheets).

(a)



(b)

Figure S-12 (a) photodegradation experiment of 2-nitrophenol by using the coal-derived carbon nanomaterials (photocatalyst) under sunlight; **(b)** 2-nitrophenol in aqueous phase (middle one in yellow colour) before treatment, treated with Coal-NG-NP (left one) become colourless, treated with Coal-NK-NP (right one) become colourless.

Proposed mechanism of photodegradation

The photoinduced charge separation and migration process under sunlight irradiations are involved in the photocatalytic degradation process of 2-NP. The 2-NP could act as a sensitizer under sunlight irradiation and excited electrons were injected to the coal-derived carbon nanomaterial surfaces (Coal-NK-NP and Coal-NG-NP). In addition, the Coal-NK-NP and Coal-NG-NP can act as an electron acceptor and electron transfer agent in the photodegradation process. Both the coal-derived carbon nanomaterials enhanced the continuous electron transfer from 2-NP to each surface. The surface adsorbed O_2 could trap the electrons and formation of $O^{\bullet}_2^-$ radicals (eq 1). In aqueous medium $O^{\bullet}_2^-$ radicals then reacts with H_2O and formation of highly active $H_2O^{\bullet}$ radicals **(**eq 2). Which are react with H^+ ions present in the aqueous medium and generates highly efficient $OH^{\bullet}$ radicals (eqs 3 and 4). $OH^{\bullet}$ radicals are responsible for the fragmentation of 2-NP (eq 5).

$$O_2 + e^- \rightarrow O^{\bullet}_2^- \quad (1)$$

$$e^- + O^{\bullet}_2^- + H_2O \rightarrow H_2O^{\bullet} + OH \quad (2)$$

$$e^- + H_2O^{\bullet} + H^+ \rightarrow H_2O_2 \quad (3)$$

$$e^- + H_2O_2 \rightarrow OH^{\bullet} + OH^- \quad (4)$$

$$OH^{\bullet} + \text{2-NP} \rightarrow \text{Degraded products} \quad (5)$$

Table S-1 EDX Characterization of the raw coal samples and coal-derived carbon nanomaterials (CNMs)

Samples	Element	Weight%	Atomic%
Coal-NG	C	68.15	75.09
	O	28.43	23.52
	Al	0.45	0.22
	Si	0.44	0.21
	S	1.99	0.82
	Ca	0.17	0.05
	Fe	0.37	0.09
Coal-NK	C	65.25	73.86
	O	26.96	22.91
	Al	1.10	0.56
	Si	2.35	1.14
	S	2.44	1.03
	K	0.25	0.09
	Ca	0.17	0.06
	Fe	1.48	0.36
Coal-NG-NP	C	59.86	67.24
	O	37.38	31.52
	Na	0.47	0.28
	S	2.29	0.96
Coal-NK-NP	C	64.74	72.73
	O	29.12	24.56
	Na	1.08	0.63
	Al	0.27	0.13
	Si	0.33	0.16

Table S-2 Assignments of the XRD d-values of raw coals (Coal-NG and Coal-NK)

Coals	d-values	Assignments
Coal-NK	10.16	Muscavite (M)
	7.19	Kaolinite (K)
	5.10	Kaolinite (K), Muscavite (M)
	4.27	Quartz (Q)
	3.93	Quartz (Q)
	3.35	Quartz (Q)
	3.25	Quartz (Q)
Coal-NG	7.26	Kaolinite (K)
	5.16	Quartz (Q)
	4.50	Quartz (Q)
	4.29	Quartz (Q)
	3.35	Quartz (Q)
	3.08	Pyrite, Calcite
	2.47	Hematite (H)
	2.19	Hematite (H), Quartz (Q)
	2.08	Quartz (Q)

Table S-3 Summary of D-band, G-band and I_D/I_G ratio of raw coal samples and coal-derived carbon nanomaterials

samples	**D-band (cm^{-1})**	**G-band (cm^{-1})**	**I_D/I_G**
Coal-NK	1378	1597	2.00
Coal-NK-NP	1382	1595	2.79
Coal-NG	1387	1595	1.83
Coal-NG-NP	1384	1596	1.81

Table S-4 FTIR Assignments of the raw coal samples and coal-derived carbon nanomaterials

Samples	Wave number (cm−1) (w: weak; m: medium; s: strong; b: broad)	Assignments
Coal-NG	3405 (b)	O-H and N-H stretching vibration
	2921 (s), 2850 (m)	CH_2 asymmetric vibration and CH_3 symmetric vibration bonded to aromatic groups
	1611 (s)	Aromatic C=C stretching vibrations, C=C vinyl or other containing functional group
	1444 (s)	Aliphatic CH_2 and CH_3 group
	1187 (b), 1007 (s)	Amorphous carbon or mineral matters
Coal-NK	3403 (b)	O-H and N-H stretching vibration
	2921 (s), 2854 (m)	CH_2 asymmetric vibration and CH_3 symmetric vibration bonded to aromatic groups
	1600 (s)	Aromatic C=C stretching vibrations, C=C vinyl or other containing functional group
	1442 (s)	Aliphatic CH_2 and CH_3 group
	1030 (s, b)	Amorphous carbon or mineral matters
Coal-NG-NP	3463, 3508 (b)	OH and N-H Stretching vibration
	2923 (s), 2851 (s)	CH_2 asymmetric vibration and CH_3 symmetric vibration bonded to aromatic groups
	2523 (b)	Intramolecular O-H stretching
	1711.90 (b,s)	C=O group
	1621.24 (b,s)	Aromatic C=C stretching
	1440 (s, w)	COO^- and CH_3 group
	1257.64 (b,s)	For C=O stretching of COOH
	1034.85 (w)	C-O stretching, Amorphous carbon or mineral matters
Coal-NK-NP	3639 (b)	OH and N-H Stretching vibration
	2912 (b), 2845 (b)	CH_2 asymmetric vibration and CH_3 symmetric vibration bonded to aromatic groups
	2541. 32 (b)	Intramolecular O-H stretching
	1720 (b)	C=O group
	1621(b,s)	Aromatic C=C stretching
	1440 (b)	COO^- and CH_3 group
	1250 (b)	For C=O stretching of COOH
	1042 (w)	C-O stretching, Amorphous carbon or mineral matters

Table S-5: Yield of different types of carbon nanomaterials produced from coal using different methods

Carbon product	Synthesis Technique	Carbon Sources	Yield	Reference
Graphene quantum dots, graphene oxide, carbon quantum dots, graphite nanocrystal	Chemical Oxidation methods	Six coal samples with different rank	14.66-56.30%	Dong et al. [4]
Multi-walled CNTs	DC arc discharge	Bituminous coals (Taiji, Fushun, Tonghua, Sanbao, Gujiao, Xiaoyi, Kailuan, Xiongtai, Pangzhuang, Xiangyuan), New Zealand)	Taiji: 62.60% Fushun: 58.20% Tonghua: 69.30% Sanbao: 81.90% Gujiao: 81.20% Xiaoyi: 76.40% Kailuan: 78.80% Xiongtai: 66.20% Pangzhuang: 75.70% Xiangyuan: 83.60% New Zealand: 71.40%	Qiu et al. [5]
Graphene quantum dots	Chemical oxidation methods	Anthracite, Bituminous, Coke	10-20%	Ye et al. [27]
Graphene quantum dots	Chemical oxidation methods	Anthracite coal	20%	Ye et al. [28]
Nanodiamonds	Laser ablation	Anthracite (Vietnam) Bitumite (Indonesia) Coke (China)	5-10%	Xiao et al. [51]
Onion-like Fullerenes and Chemically converted graphene-like nano-sheets	Oxidation-Cum-Extraction Process	Sub-bituminous coal (Northeastern coalfield, India)	76.25-82.00%	Present Study