

Electronic Supplementary Information

The Influence of Source Molecule Structure on Low Temperature Growth of Nitrogen-doped Graphene

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- 1 Density functional theory calculations
- 2 XPS study of the film synthesized from a Ketone form molecule

1. Density functional theory calculations

To investigate the structure of the source molecules and N-doped graphene, we have performed DFT calculations with Gaussian 09 program package. All the calculations were done with Fujitsu PRIMERGY CX250S1 in Research Center for Computational Science

1.1 Structures of methyl-form and ketone-form molecules

Figure S1 shows the optimized structures of methyl-form and ketone-form molecules. The molecular structures were optimized at restricted B3LYP levels with 6-31G(d,p) basis set. The Cartesian coordinates for the two molecules are summarized in Tables S1 and S2. It should be noted that the nitrogen atom and the three benzene rings are in the same plane for both molecules.

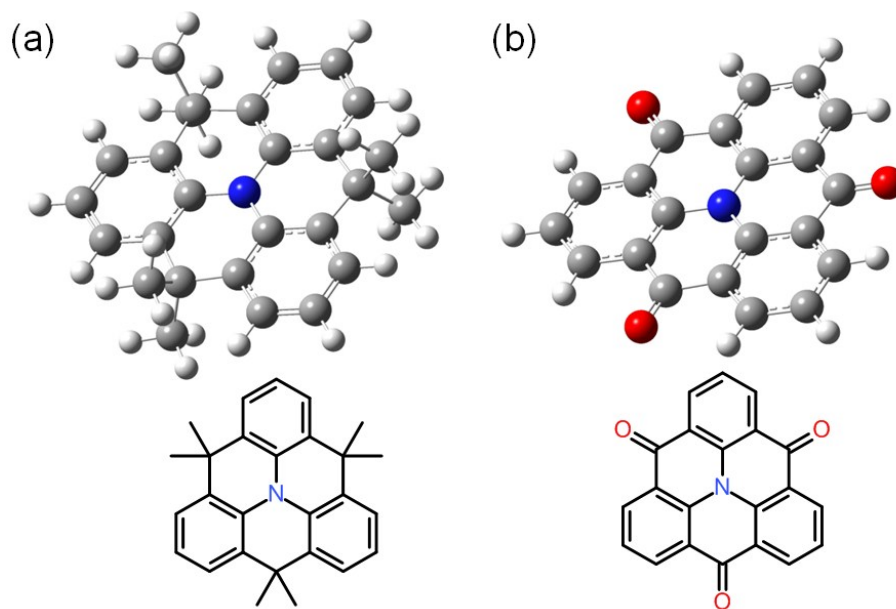


Fig.S1. Optimized structures of (a) a methyl-form and (b) a ketone-form molecules.

Table S1. Cartesian coordinates for the optimized structure of methyl-form (in Å).

atom	x	y	z	atom	x	y	z
C	2.981298	-0.211146	-0.000083	H	2.995313	4.431619	-0.001301
C	2.211164	1.101879	-0.000336	H	0.528942	4.579002	-0.000683
C	0.797843	1.180614	-0.000208	N	-0.000016	0.000022	0.000011
C	0.623499	-1.281271	0.000197	C	-1.699663	3.493272	1.271619
C	2.033784	-1.402516	0.000538	C	-1.700963	3.494661	-1.269265
C	0.197695	2.462624	-0.000288	C	3.87631	-0.274004	1.270122
C	-1.421437	0.100634	-0.000051	C	3.875506	-0.274957	-1.270807
C	-2.059951	1.364059	0.000181	C	-2.176026	-3.2197	1.26967
C	-1.307845	2.687542	0.000503	C	-2.174897	-3.218979	-1.271427
C	-3.456258	1.434002	0.00023	H	-1.189445	4.459744	1.30183
H	-3.929491	2.409592	0.00053	H	-1.429107	2.939122	2.174994
C	-4.253186	0.301099	-0.000118	H	-2.775249	3.686769	1.302701
C	-3.624008	-0.932833	-0.000404	H	-2.776518	3.688541	-1.298861
C	-2.231736	-1.06012	-0.000305	H	-1.431669	2.94137	-2.173546
C	-1.673561	-2.476296	-0.000479	H	-1.190573	4.461041	-1.299134
C	-0.151415	-2.465793	0.000173	H	4.582402	0.560164	1.299591
H	-5.335734	0.377816	-0.000158	H	4.457425	-1.199581	1.30079
H	-4.229994	-1.832051	-0.000741	H	3.262211	-0.229757	2.174157
C	0.486078	-3.710038	0.000615	H	3.260855	-0.231202	-2.174489
C	2.619636	-2.671844	0.001108	H	4.456414	-1.200682	-1.301207
C	2.970255	2.275856	-0.000717	H	4.581707	0.559094	-1.301238
C	1.004398	3.604489	-0.000681	H	-1.831004	-2.709583	2.173607
C	1.865635	-3.833735	0.001156	H	-1.806754	-4.248314	1.299743
C	2.387625	3.532447	-0.00096	H	-3.268135	-3.260258	1.299877
H	-0.122134	-4.60776	0.000492	H	-3.266997	-3.259448	-1.302588
H	2.340469	-4.809603	0.001554	H	-1.805594	-4.247592	-1.301693
H	3.701353	-2.74704	0.001442	H	-1.829081	-2.708408	-2.174811
H	4.05182	2.197564	-0.000839				

Table S2. Cartesian coordinates for the optimized structure of ketone-form (in Å).

atom	x	y	z	atom	x	y	z
C	2.520242	1.455062	0	C	1.195445	3.534289	0
C	1.213784	2.134544	0	C	0	4.242764	0
C	0	1.408884	0	C	-2.463061	-2.80243	0
N	0	0	0	C	-3.658507	-0.731859	0
C	1.220129	-0.704442	0	C	-3.674341	-2.121382	0
C	2.455461	-0.016104	0	O	0	-4.139345	0
C	-1.220129	-0.704442	0	O	3.584778	2.069673	0
C	-1.241677	-2.11844	0	O	-3.584778	2.069673	0

C	0	-2.910125	0	H	-2.413776	-3.886145	0
C	1.241677	-2.11844	0	H	-4.613821	-2.663791	0
C	-1.213784	2.134544	0	H	-4.572388	-0.147318	0
C	-2.520242	1.455062	0	H	-2.158613	4.033464	0
C	-2.455461	-0.016104	0	H	0	5.327582	0
C	3.658507	-0.731859	0	H	2.158613	4.033464	0
C	2.463061	-2.80243	0	H	4.572388	-0.147318	0
C	3.674341	-2.121382	0	H	4.613821	-2.663791	0
C	-1.195445	3.534289	0	H	2.413776	-3.886145	0

1.2 DFT Calculation on model clusters

In addition to the optimization of methyl-form (Figure S2a), we performed DFT calculations on two model clusters, which we named 3H (Figure S2b) and GN (Figure S2c). These clusters were optimized at B3LYP levels with 6-31G(d,p) basis set. The shifts in the binding energy of N 1s are also shown in Figure S2. Compared to the methyl-form, the N 1s is shifted by +0.209 eV and +1.29 eV for 3H and GN, respectively. The large N 1s shift for GN can be attributed to the expansion of the π -conjugated system surrounding the N atom. Since N 1s peak was shifted by +1.0 eV for the sample deposited at 400 °C (Figure 3c), this shift implies that the methyl-form molecule was decomposed at 400 °C and N atoms are incorporated into graphene.

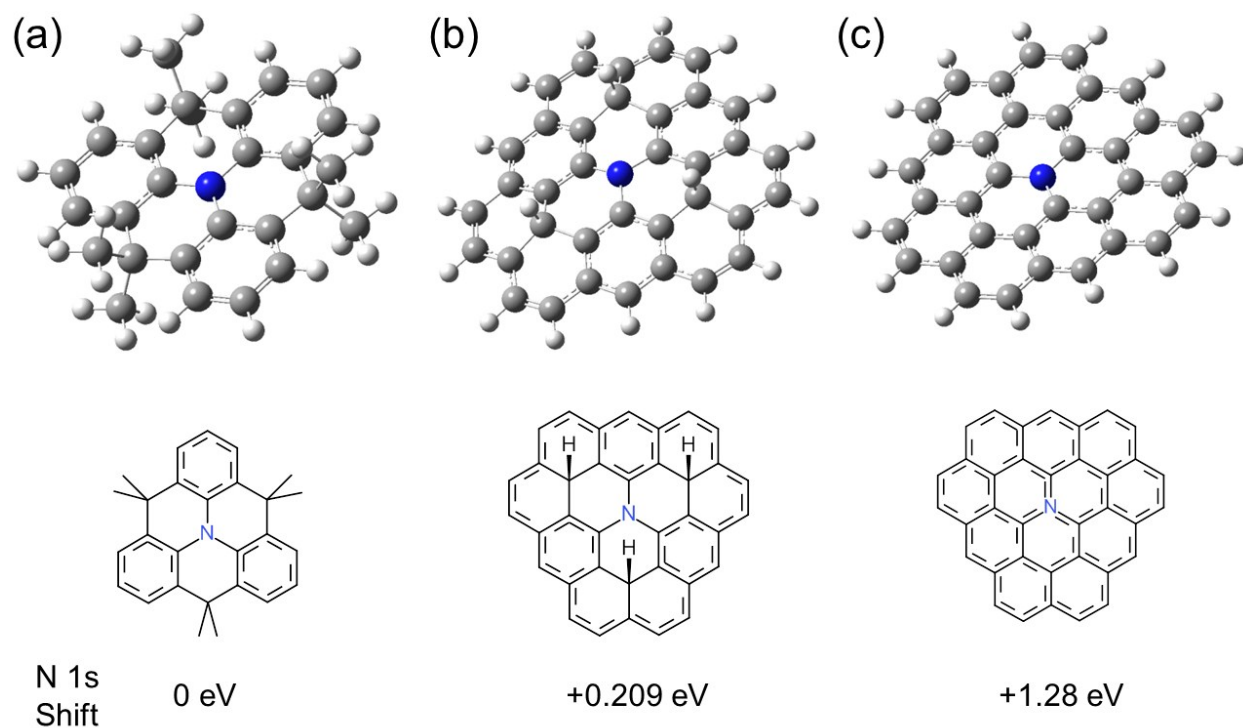


Fig.S2. Optimized structures of (a) methyl-form, (b) 3H and (c) GN. The value of N 1s shift from the methyl-form is shown below the chemical structures.

2. XPS study of film fabricated from Ketone form

Figure S3a shows the XPS C 1s region spectra of the films synthesized from a Ketone form molecule. The spectrum for RT consists of two peaks at 287.2 eV and 285.3 eV. The former comes from the C-O bonds. Only one peak was observed for the films deposited at elevated temperatures indicates that C-O bond was decomposed at 300 °C. Figure S3b shows XPS O 1s region spectra. The spectrum at 300 °C clearly shows no trace O in the film. From these results we could conclude that carbonyl group of Ketone form was decomposed at 300 °C.

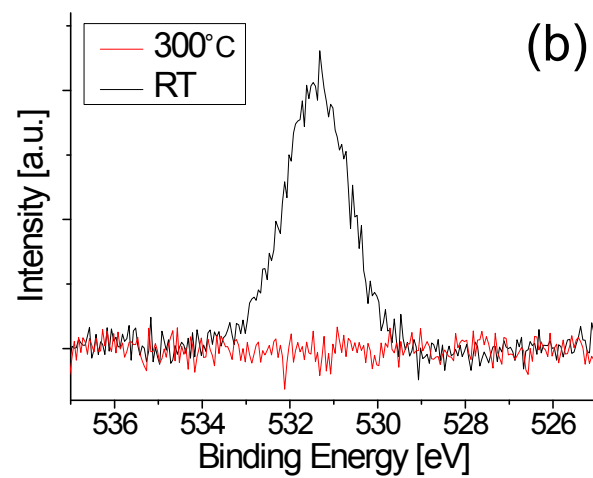
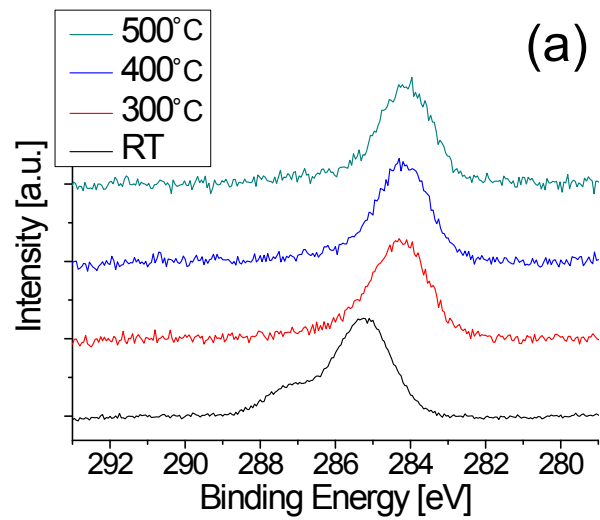


Fig.S3. (a) XPS spectra at C 1s region (b) O 1s region.