Supporting Information

Graphene with Atomic-level In-plane Decoration of *h*-BN Domains for Efficient Photocatalysis

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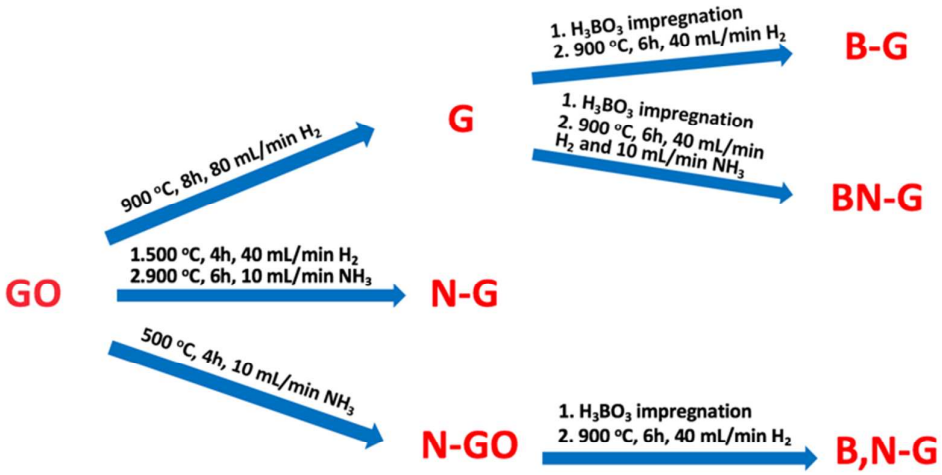

Figure S1. synthetic processes of G, N-GO, B-G, N-G, B,N-G, and BN-G.

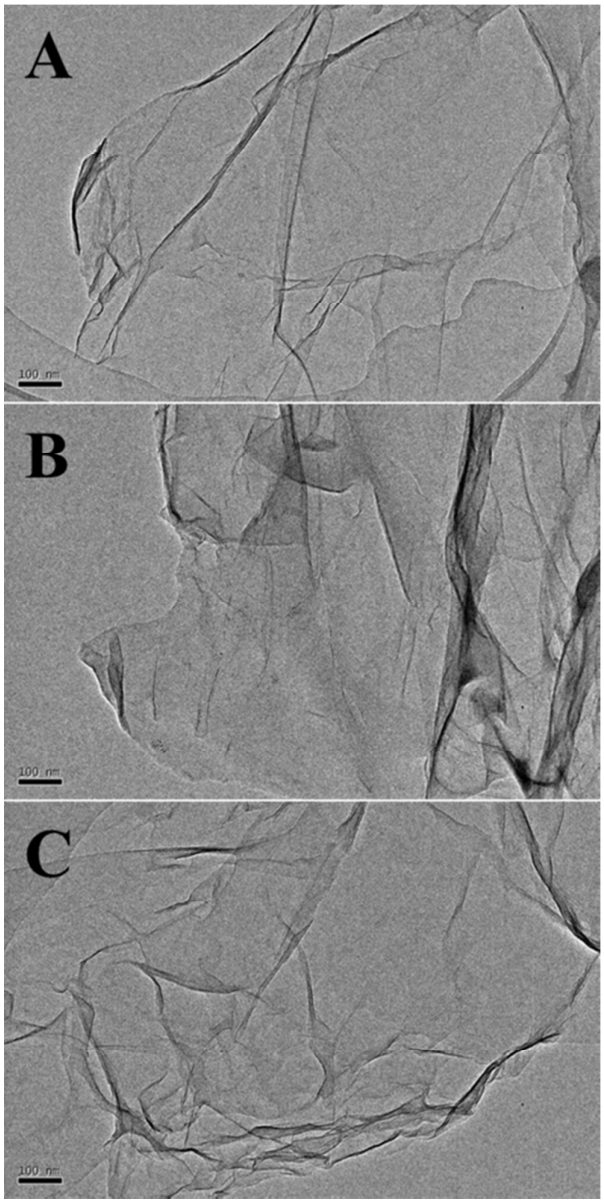

Figure S2. Typical TEM images of (A) G, (B) B-G, (C) N-G.

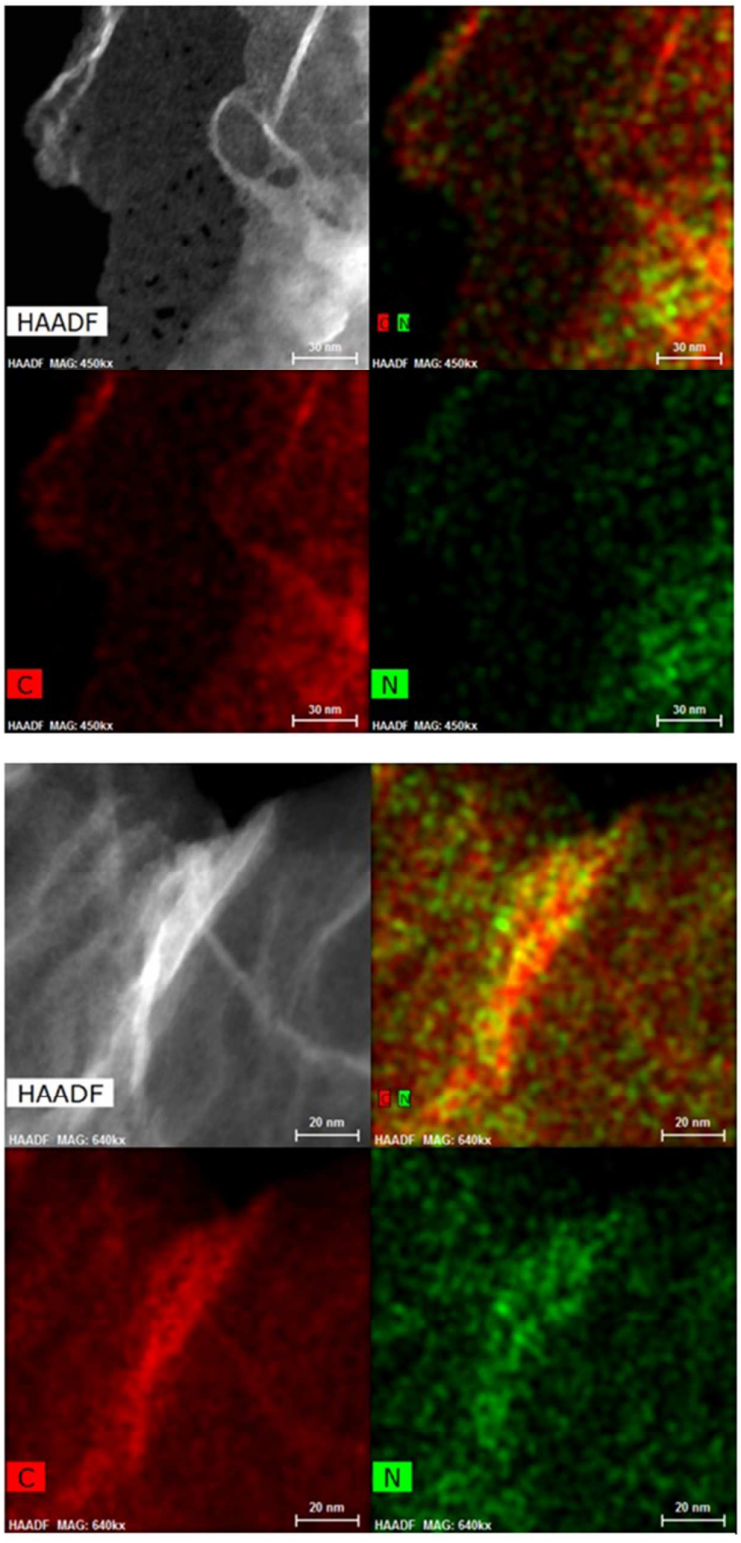

Figure S3. The HAADF-STEM images and corresponding EDX mapping images for C elements and N elements of BN-G in different area.

Table S1. Surface compositions of C, O, B, and N for heteroatom-doped graphene materials.

Sample	C (at%)	O (at%)	B (at%)	N (at%)
GO	82	18	-	-
G	98.5	1.5	-	-
B-G	94.3	3.5	2.2	-
N-G	93.3	3.3	-	3.4
N-GO	90.9	5.1	-	4.0
B,N-G	83.7	6.6	5.3	2.4
BN-G	87.2	3.5	4.8	4.3

Table S2. I_D/I_G Ratio for heteroatom-doped graphene materials obtained from Raman Spectra

Sample	G	N-GO	B-G	N-G	B,N-G	BN-G
I_D/I_G	1.20	0.91	1.28	1.16	0.99	1.53

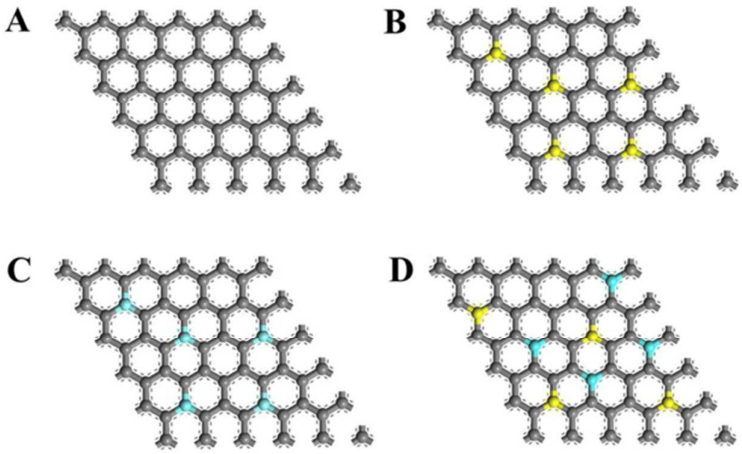

Figure S4. The supercell model of (A) G, (B) B-G, (C) N-G, (D) B,N-G.

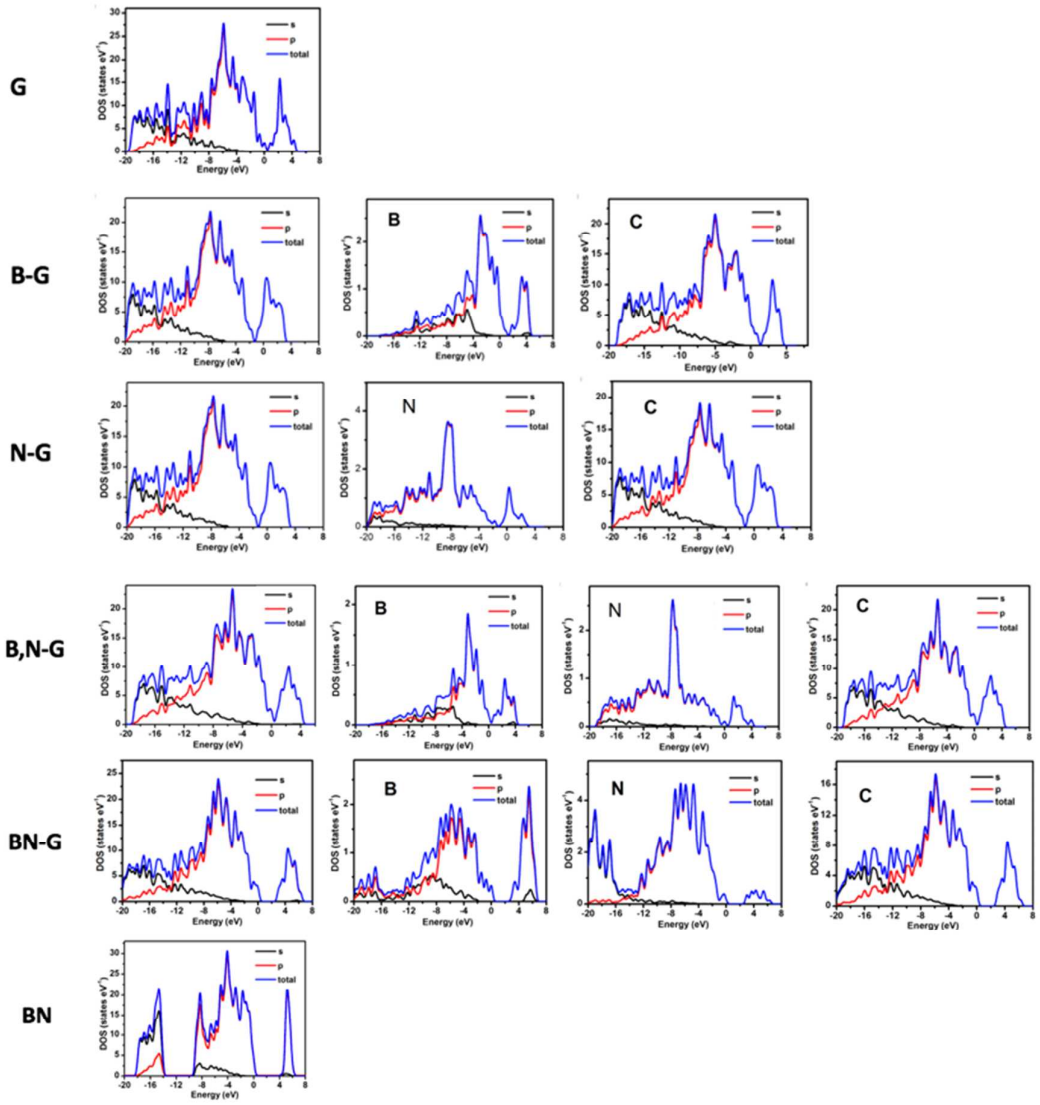

Figure S5. Total and partial electronic density of states (TDOS and PDOS) for G, B-G, N-G, B,N-G, BN-G, and BN and corresponding elements.

The band edge placement calculation.

In order to obtain the band edge placement (the conductive band minimum (CBM) and valance band maximum (VBM)) of the graphene-based catalysts, the work function (W) defined as the minimum thermodynamic energy that removing an electron from the surface to outside the solid surface in vacuum, as shown in Figure S6. W and the band gap energy (E_g) can also be directly obtained from the Accelrys Materials Studio software, and the position of Fermi level (E_F) can be calculated as $E_f = 4.5 - W$; $E_g = E_{CBM} - E_{VBM}$. By calculating the band gap of semiconductor, the relative Fermi level compared with VBM can be also calculated from the Accelrys Materials Studio software, and the energy difference (x) between E_F and VBM is obtained by the follows:[1]

$x = E_F - E_{VBM}$

Then, the band edge placement of the semiconductor can be obtained: [2,3]

$E_{VBM} = E_F - x$

$E_{CBM} = E_{VBM} + E_g$

Driving force (E_{df}) is assumed to be the difference between E_{VBM} and the O_2 evolution redox potential. Therefore, E_{df} can be calculated as follows:

$E_{df} = 0.82\text{eV} + 4.5\text{eV} - E_{VBM} = 5.32\text{eV} - E_{VBM}$

where 0.82 is the oxidation potential for O_2/H_2O *vs* SHE when pH = 7, and −4.5 V is the vacuum level. Since in our experiment, the H_2 evolution is more likely to occur, we pay more attention to the reduction potential (CBM).

Since the work functional is surface dependent,[4,5] the (001) face of graphene-based catalysts is the most preferably exposed surface. The (001) slabs of graphene catalysts with one layer are modeled. 15 angstroms of vacuum is built along the c to separate the periodic images. The detail calculation method is the same as above for the DOS calculation.

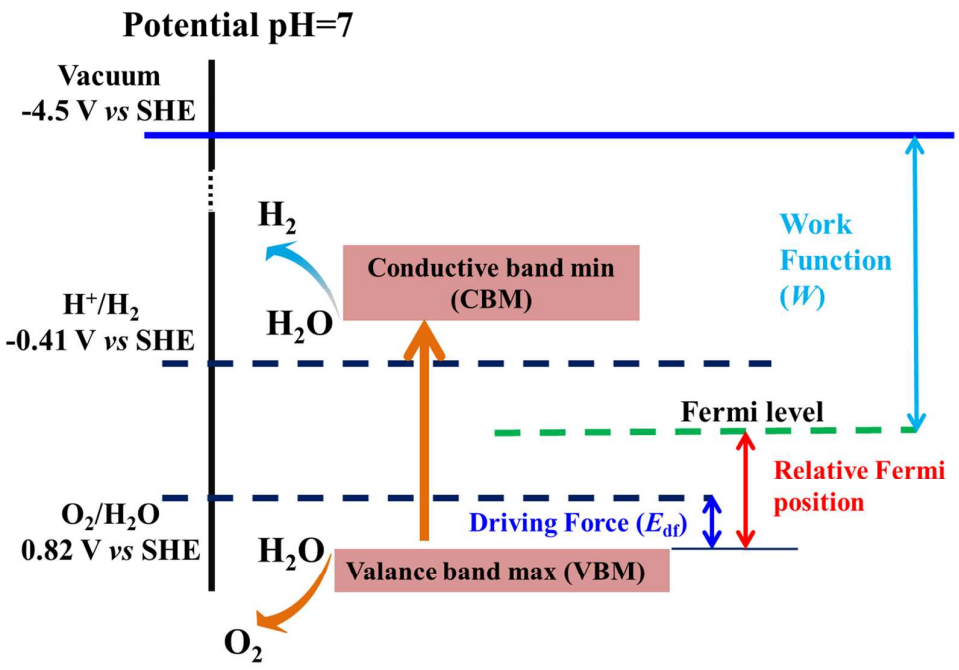

Figure S6. Schematic diagram of photocatalytic water splitting when pH is 7.

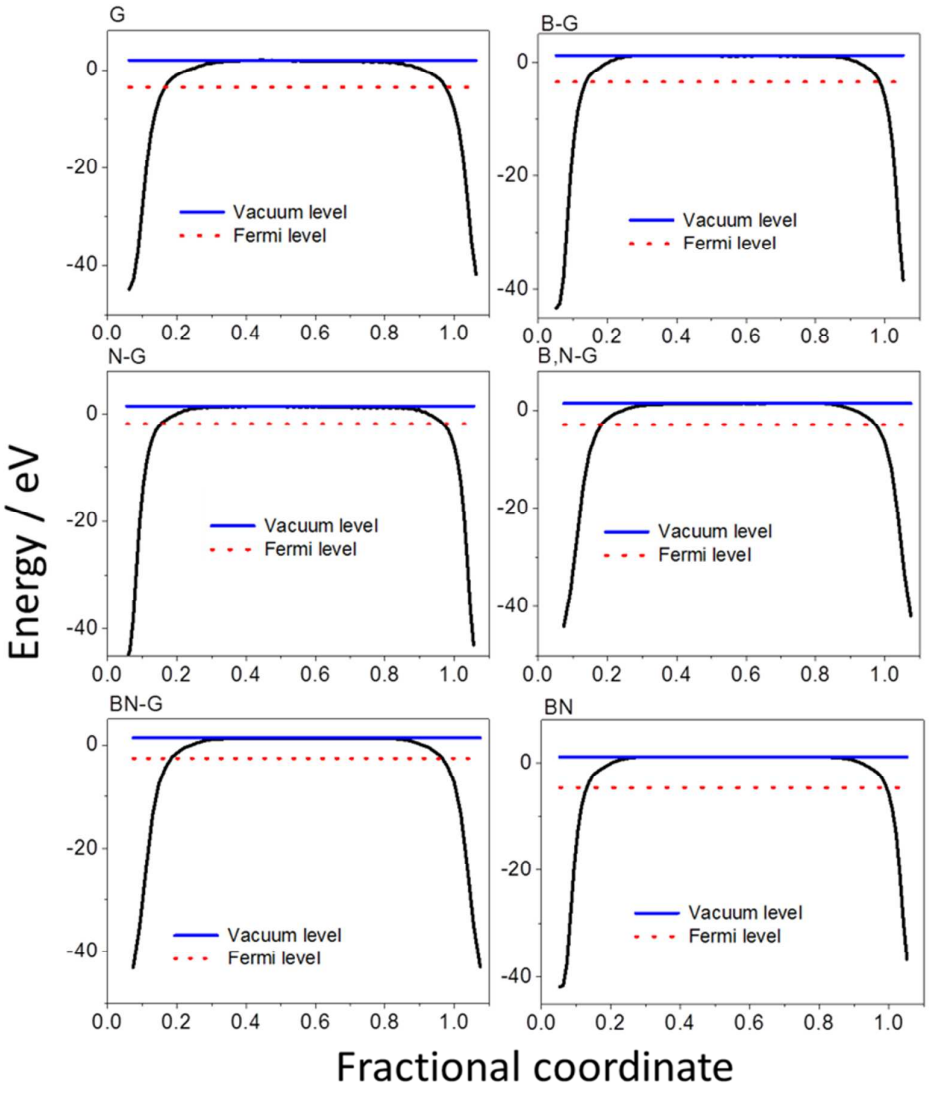

Figure S7. The work function of the (001) facet of graphene-based photocatalysts.

Table S3. Band Gap Energy (E_g), Work Function (W), Fermi level (eV) *vs* SHE, and relative Fermi level to VBM for graphene-based photocatalysts.

Photocatalysts	**Band gap energy (eV)**	**Work function (eV)**	**Fermi level (eV) *vs* SHE**	**Relative Fermi level to VBM (eV)**
G	0.01	5.03	0.53	-0.93
B-G	1.2	4.74	0.24	-0.41
N-G	1.3	3.39	-1.11	1.35
B,N-G	1.4	4.37	-0.13	-0.36
BN-G	2.8	3.89	-0.61	0.01
***h*-BN**	4.3	5.78	1.28	-1.74

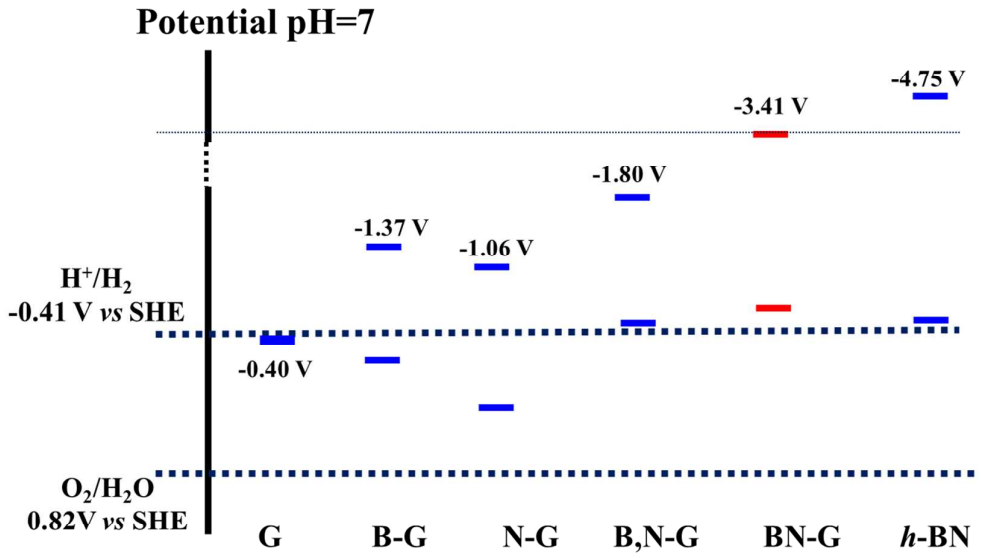

Figure S8. Band edge placements of graphene-based photocatalysts as calculated from Table S3. Two dashed red lines (-0.41 and 0.82 V *vs* SHE) represent the reduction and oxidation potential of H_2 and O_2 at pH 7, respectively.

The band structure for these graphene-based photocatalysts are listed as above without considering the solvent and the defect effect, which would give a underestimate for the calculated band structure. However, the CBM can give a relative comparison among these graphene-based photocatalysts.

Reference：

(1) Kanan, D. K.; Carter, E. A., Band Gap Engineering of MnO via ZnO Alloying: A Potential New Visible-Light Photocatalyst. *J. Phys. Chem. C*. **2012**, 116, 9876–9887.

(2) Xu, S. M.; Pan, T.; Dou, Y. B.; Yan, H.; Zhang, S. T.; Ning, F. Y.; Shi, W. Y.; Wei, M., Theoretical and Experimental Study on $M^{II}M^{III}$-Layered Double Hydroxides as Efficient Photocatalysts toward Oxygen Evolution. *J. Phys. Chem. C.* **2015**, 119, 18823−18834.

(3) Xu, S. M.; Yan, H.; Wei, M., Band Structure Engineering of Transition-Metal-Based Layered Double Hydroxides toward Photocatalytic Oxygen Evolution from Water: A Theoretical-Experimental Combination Study. *J. Phys. Chem. C.* **2017**, 121, 2683-2695.

(4) Nozik, A. J., Photoelectrochemistry: Applications to Solar Energy Conversion. *Annu. Rev. Phy. Chem.* **2003**, 29, 189-222.

(5) Charles, K., Introduction to Solid State Physics, 7th ed.; John Wiley & Sons Inc.: New York, **1996**.