Nitrogen-doped Graphene Stabilized Gold Nanoparticles for Aerobic Selective Oxidation of Benzylic Alcohols

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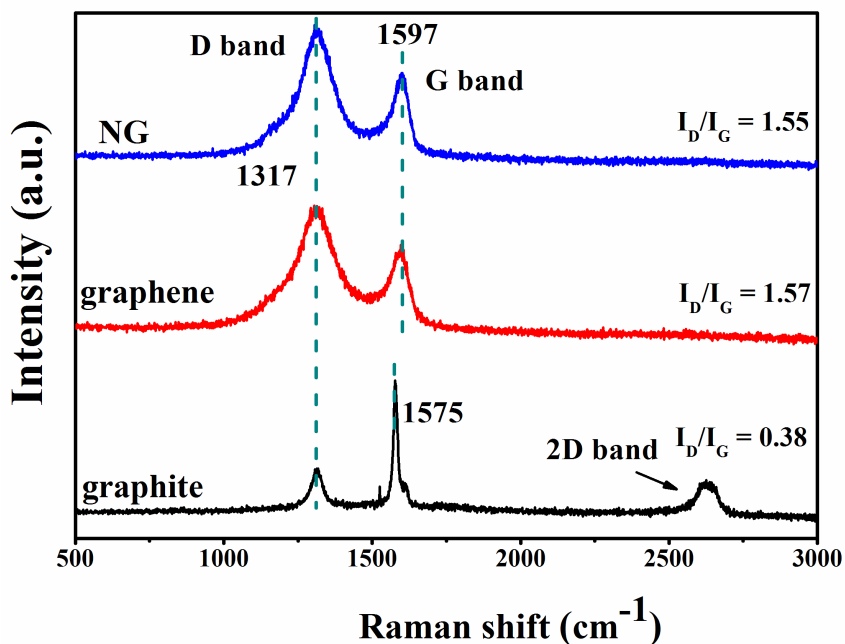
Fig. S1 Visible-Raman spectra of different samples.

Raman spectroscopy is widely used for evaluating the crystalline quality of carbon materials. Figure S1 shows the Raman spectra of different samples. Apparently, the D band (1317 cm^{-1}, defects induced absorption band) of NG is pronounced compared to the pristine graphite, which indicates partial restoration of the sp^2 hybridized graphene domains after the oxidation-reduction process. Careful comparation reveals that the G band of NG (1597 cm^{-1}) upshifts and broadens with respect to graphite. This is similar to the finding reported in the literature[1]. Generally, stiffening of the G band is due to the nonadiabatic removal of the Kohn anomaly at the Γ-point, and the broadening is attributed to the absence of blockage of the decay channels of the phonons into electron–hole pairs[2]. It is well known that 2D band (~2630 cm^{-1}) is very sensitive to the layer number of graphene. However, no 2D band appears in the Raman spectra of graphene and NG, probably resulting from structural disorder and damaging of lattice, which are also reflected by the high intensity of D band as mentioned above. On the other

hand, the intensity ratio of D band and G band (I_D/I_G) of NG and graphene, which is indicative of the structural defects amount and a quantitative measure of edge plane exposure, increases compared to graphite, indicating more defects are introduced. The ratio is determined by two aspects of effect. High temperature calcination leads to the corrosion of the sp^2 domains, thus the value increases; while the nitrogen heteroatom may be partially introduced to these defects, forming the "graphitic nitrogen", which results in the decrease of the ratio. Just as indicated in Figure S1, the I_D/I_G value of NG is almost same with that of graphene, which means the same amount of defects in graphene and NG. So we can exclude the effect of defects for the formation of the highly dispersed Au NPs.

Other research showed that the presence of oxygen functionalities at graphene surface provides reactive sites for the nucleation and growth of gold nanoparticles[3]. However, according to our XPS analysis, the oxygen percentage in NG is 2.0%; while the value is 2.9% in graphene. So the effect of residual oxygen is also excluded for the formation of the highly dispersed gold nanoparticles.
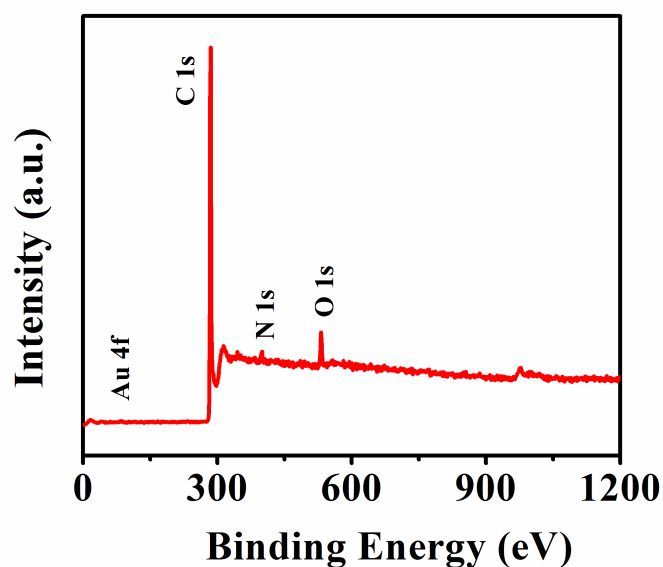

Fig. S2 XPS survey scan of Au/NG-4.0

Assuming that Au NPs on graphene and NG are both semispherical shaped, the number of external gold atoms (N_s) can be obtained by Equation (1):

$$N_s = \rho_{suf} \times 2\pi r^2 \times \frac{m}{\rho_{Au} \times 2/3\pi r^3} \qquad (1),$$

where ρ_{suf} is surface atomic density of Au, r is the radius of semispherical gold, ρ_{Au} is the mass density of Au, and m is the weight of gold nanoparticles loaded on graphene or NG.

TOF can be obtained from Equation (2):

$$TOF = \frac{r_0 \times N_A}{N_s} \qquad (2),$$

where r_0 refers to the initial reaction rate ($mol \cdot h^{-1}$) in the first 0.5 h, N_A is the Avogadro constant.

Thus, the ratio between TOF of Au/NG composite ($TOF_{Au/NG}$) and TOF of Au/G composite ($TOF_{Au/G}$) can be expressed as Equation (3):

$$\frac{TOF_{Au/NG}}{TOF_{Au/G}} = \frac{r_0(Au/NG)}{r_0(Au/G)} \times \frac{r_{Au/G}}{r_{Au/NG}} \qquad (3),$$

where $r_0(Au/NG)$ and $r_0(Au/G)$ is the initial reaction rate of Au/NG and Au/NG under the same conditions, respectively. And $r_{Au/G}$ and $r_{Au/NG}$ is the average radius of gold on graphene and NG by the TEM analysis, respectively.

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