Supporting Information

Porous Cobalt-Nitrogen-Doped Hollow Graphene Spheres as Superior Electrocatalyst for Enhanced Oxygen Reduction in both Alkaline and Acidic Solutions

Qiangmin Yu,[abc] Jiaoxing Xu,[ab] Chunying Wan,[abc] Chuxin Wu,[ab] and Lunhui Guan*[ab]

[a.]   *Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences,*
YangQiao West Road 155#, Fuzhou, Fujian 350002, P.R. China. Fax: (+) 86-591-6317 3550; Tel: 86-591-6317 3550 E-mail: guanlh@fjirsm.ac.cn

[b.]   *Fujian Key Laboratory of Nanomertials, Fuzhou, Fujian 350002, China*

[c.]   *University of Chinese academy of sciences, Beijing 100049, China*

Exprimental section
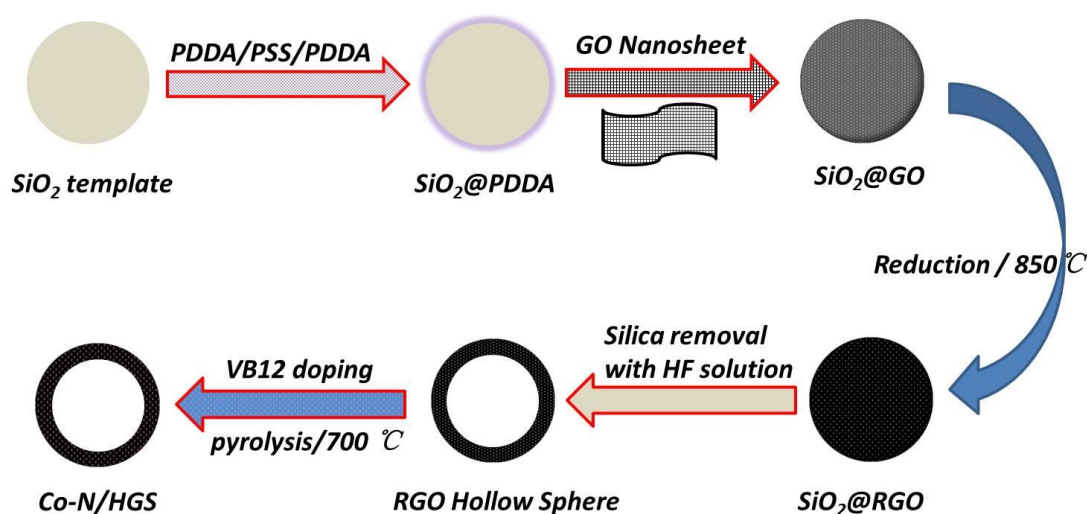
Scheme S1. Formation processes of the Co-N/HGS catalyst.

Synthesis of silica spheres and graphene oxide (GO) sheets

Solid silica spheres were synthesized by the classical Stöber method.[1] Initially, 3 mL of TEOS (tetraethyl orthosilicate) was injected into the mixture of 35 mL ethanol, 4 mL deionized water and 3 mL aqueous ammonium solution (25%). Then the above mixed solvent was stirred at room temperature for 6 h. Finally, 320 µL 3-(Methacryloxy) propyltrimethoxysilane was introduced to the mixture under stirring and reaction for 24 h. The final silica spheres were collected through centrifugation and drying overnight at 80 ℃.The monodisperse silica nanoparticles were obtained, whose SEM image was shown in Figure S1a. Graphene oxide (GO) sheets were synthesis by modified Hummers method.[2] 1 g Graphite was added to 30 ml concentrated sulfuric acid, and ultrasonic for 10 min. Then, 3 g potassium permanganate was added to the graphite

solution under vigorous stirring. The reaction was allowed to proceed at 50 ℃ for 3h before the solution was cooled in an ice bath and diluted with 300 ml deionized water. After stirring for 20min, 30ml hydrogen peroxide was added to the reaction solution. The mixture was then centrifuged and washed several times with 10% hydrochloric acid and water. The resultant GO solution was attained by centrifugation at 14000 rpm. The upper GO dispersion was sonicated 3h by ultrasonic disintegrator. The final products were prepared for further synthesis.

Synthesis of hollow graphene spheres

0.2 g silica sphere templates were dispersed in 20ml deionized water by sonication 0.5 h. The above dispersed SiO_2 templates were modified for 3 h with poly (diallyldimethylammonium chloride) (PDDA, 8 mg/ml) and poly (sodium 4-styrenesulfonate) (PSS, 8mg/ml) in sequence, yielding positively charged PDDA/PSS/PDDA-modified SiO_2 templates. The final products were separated by centrifugation and overnight drying at 80 ℃.[3] The modified silica spheres was introduced into the as-prapared graphene oxide nanosheet suspension and stirred for 2 h. After 3 h standing, discarding the upper solution and drying the lower suspension overnight at 80℃. The dried products were heated at 850 ℃ for 3 h under flowing nitrogen. Finally, hollow graphene spheres were obtained after removal of templates by HF (10 wt. %) etching for 12 h at room temperature.

Synthesis of cobalt-nitrogen-Doped hollow graphene spheres

50 mg hollow graphene spheres was dispersed into 10 ml VB12 solution (50 mg VB12 dissolved in deionized water) and stirred for 3 h at 80 ℃. After filtration of solution and pyrolysis at 700 ℃ under nitrogen atmosphere for 3 h, cobalt-nitrogen-doped hollow graphene spheres catalyst were formed. Cobalt-nitrogen-doped active carbon (Co-N/AC) and reduced graphene oxide nanosheet (Co-N/RGO) were synthesized under the same procedure.

Preparation of the electrode

5 mg of catalysts and 100 μL of Nafion solution (DuPont Corp., 5 wt %) were dispersed in 1.9 mL of isopropanol alcohol and mixed solvent to form a homogeneous ink by an ultrasonic bath. Then, 30 μL of the catalysts ink were loaded onto a clean glass carbon electrode (GCE) surface with a diameter of 5 mm. Commercial Pt/C and other catalysts were also fabricated using the same procedure.

Characterizations

The morphology and elemental mapping of the Co-N/HGS catalyst were observed by using field-emission transmission electron microscopy (TEM, FEI, JEM-2010) and scanning electron microscopy (SEM, SU8010). BET test was conducted on Autosorb-iQ2-XR (Quantachrome Instruments). XPS measurements were performed on a VG Scientific ESCALAB 250Xi using AlKa radiation (1486.71 eV) and the C1s peak at 284.5 eV as internal standard. Electrochemical characterizations were performed on a CHI 760D electrochemical analyzer (CH Instruments, Inc., Shanghai, China), coupled with a RDE system (from Taizhou Keruite Analysis Instruments Co. Ltd.). A conventional three-electrode cell was used with a gas flow system. A GCE was used as the working electrode, an Ag/AgCl electrode (saturated KCl-filled) as the reference electrode, and a Pt wire as the counter electrode. All the experiments were carried out at ambient temperature. The electrochemical performance of the catalysts was explored by cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) measurements in an aqueous solution of 0.1 M NaOH and 0.5 M H_2SO_4. CV curves were obtained at a scan rate of 50 mV s^{-1}. LSV was performed at rotating rates of 500, 900, 1200, 1600, 2000, and 2500 rpm with a sweeping rate of 10 mV s^{-1}. All the

potential scan direction is from the positive to negative. The NaOH and H_2SO_4 solution was bubbled with pure N_2 (99.999%) or O_2 (99.999%) both before (at least 30 min) and during the electrochemical measurements. Chronoamperometric tests were performed at -0.20 V (alkaline medium) and 0.5 V (acidic medium) for 12 h with a speed of 1600 rpm.

Koutecky-Levich (K-L) equations were used to analyze from the data from RDE:

$$\frac{1}{j} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K}$$

$$B = 0.62nFC_0(D_0)^{2/3}v^{-1/6}$$

$$j_K = nFkC_0$$

Where, j is the measured current density, ω is the electrode rotation rate, F is the Faraday constant (F = 96485 C cm^{-1}), C_0 is the bulk concentration of O_2 (C_0 = 1.2×10^{-3} mol L^{-1}), D_0 is the diffusion coefficient of O_2 (D_0 = 1.9×10^{-5} cm s^{-1} or 1.15×10^{-5} cm s^{-1}) in 0.1 M NaOH or 0.5 M H_2SO_4, v is the kinetic viscosity of the electrolyte (0.01 cm^2 s^{-1}), and k is the electron-transfer rate constant. B can be determined from the slope of the K-L equation.
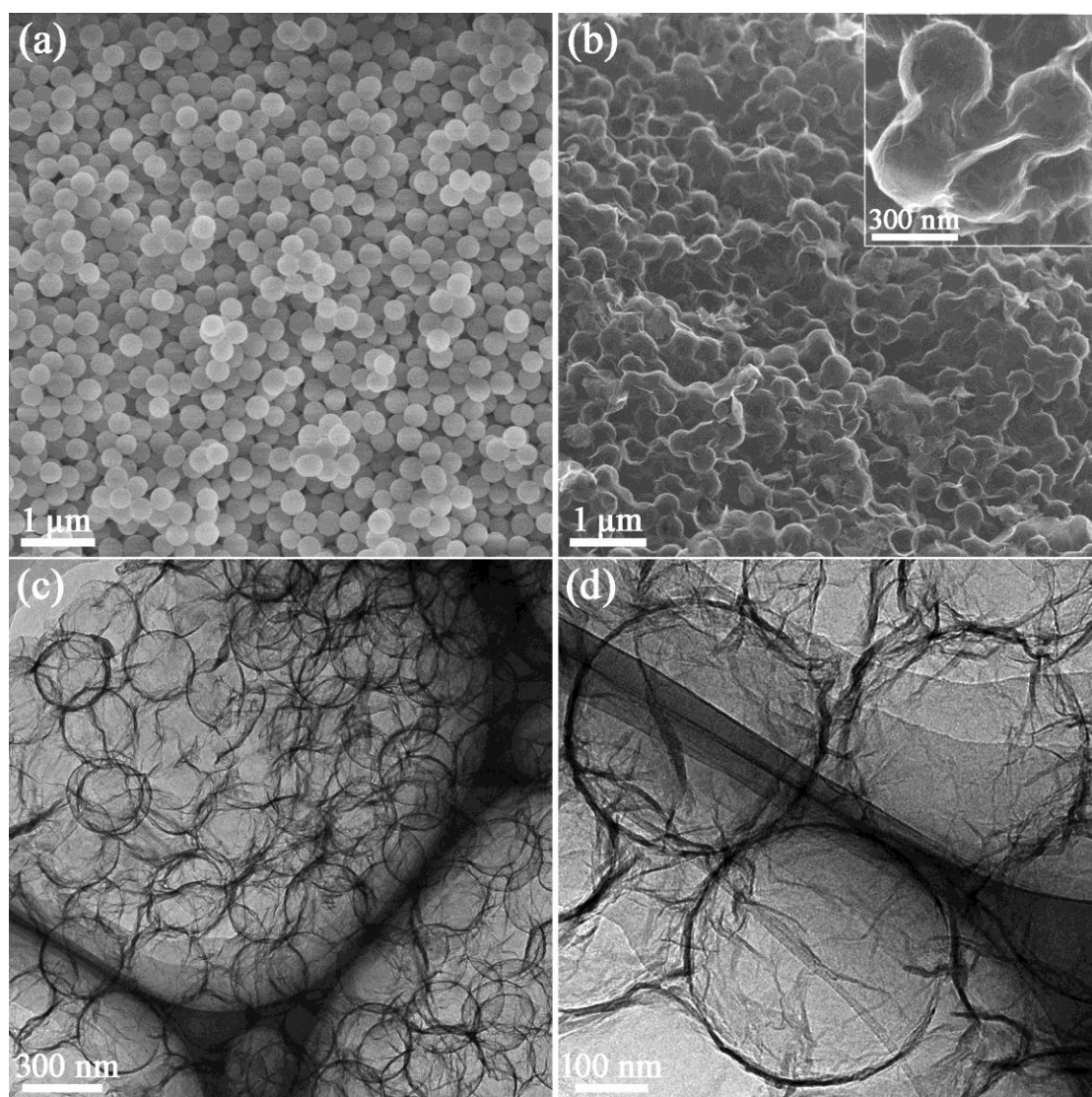

Figure S1. (a) SEM image for the silica template. (b) Low- and high-magnification (inset) SEM images of Co-N/HGS. (c) TEM and (d) HRTEM images of Co-N/HGS.
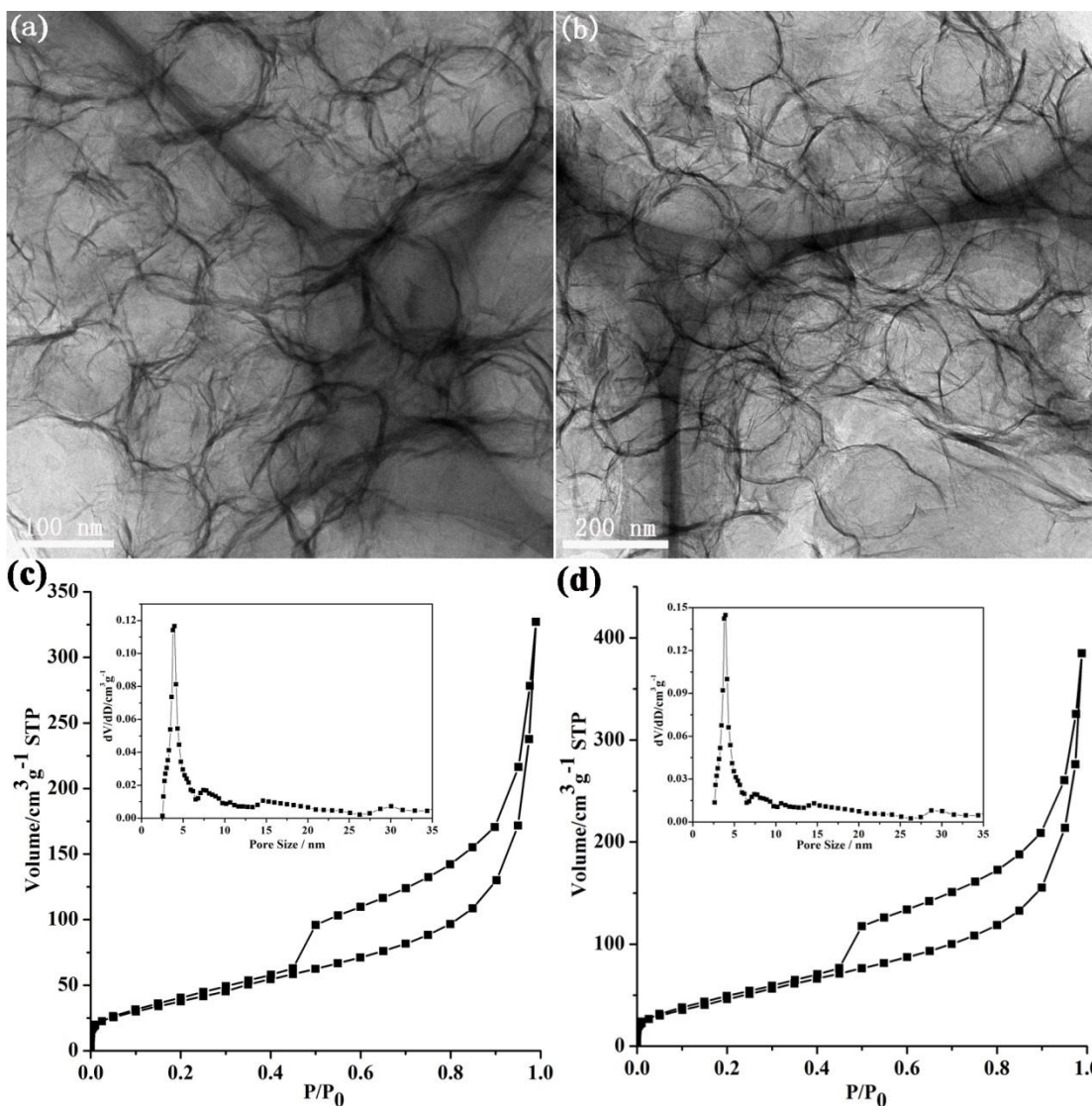
Figure S2. TEM image for the Co-N/HGS (a) ~80nm and (b) ~180 nm averaged diameter. (c) and (d) Nitrogen sorption isotherm and pore size distribution (inset) of Co-N/HGS (~80nm) and (~180 nm), respectively.

We have also synthesized smaller silica templates for further research. Their size could be controlled in the range from ~80 nm to ~300 nm by tuning the ratio of ammonium solution. Figure S2a-b shows TEM images for ~80 nm and ~180 nm Co-N/HGS, respectively. Compared with Co-N/HGS (~300 nm), the smaller size silica templates were coated inhomogeneity. The results might derive from tensile force of roll graphene oxide and agglomeration of small silica. Moreover, we have assessed the porous nature of the two samples. The surface area and total pore volume of these two samples were 144 m^2/g and 0.51 cm^3/g, 182 m^2/g and 0.6 cm^3/g, respectively. Obviously, smaller Co-N/HGS (80-180 nm) displays the similar porous properties with Co-N/RGO.
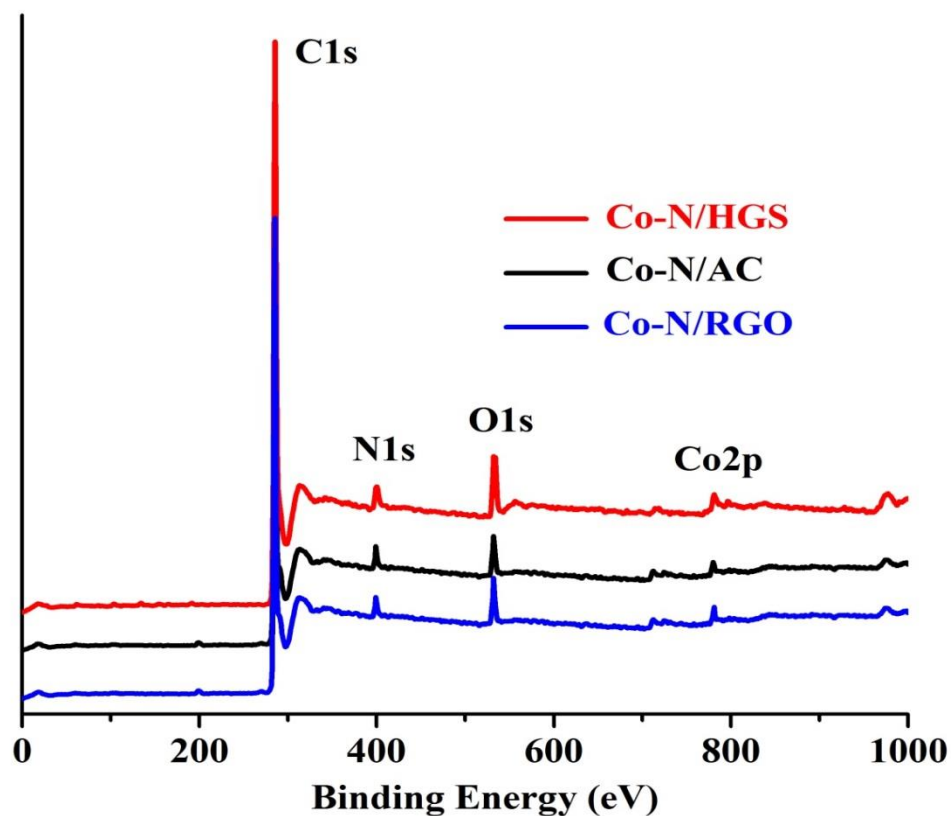
Figure S3. XPS survey spectra of the Co-N/HGS, Co-N/AC and Co-N/RGO catalysts

Table S1. Electrochemical performance of different electrocatalysts for ORR

| sample	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Onset potential (V)	Diffusion-limiting current (mA/cm^2)	Electron transfer number	Ref.
Fe-N-HCMS	1199	1.77	0.8V (RHE)	6.8 (1600 rpm)	3.8	*Adv Energy Mater* **2014**, *4*, 1400840 [4]
CoP-CMP800	480	----	0.74V (RHE)	4.84 (1600 rpm)	3.94	*Adv Mater* **2014**, *26*, 1450-1455 [5]
NDCN-22	589	1.52	0.72V (RHE)	3.57 (1600 rpm)	3.91	*Angewandte Chemie* **2014**, *53*, 1570-1574 [6]
Fe-N-CNFs	425	0.44	0.55V (Ag/AgCl)	4.8 (1600 rpm)	3.76	*Angewandte Chemie* **2015**,*54*,1-6 [7]
Co-N/HGS	321	1.8	0.65V (Ag/AgCl)	5.69 (1600 rpm)	3.90	This work
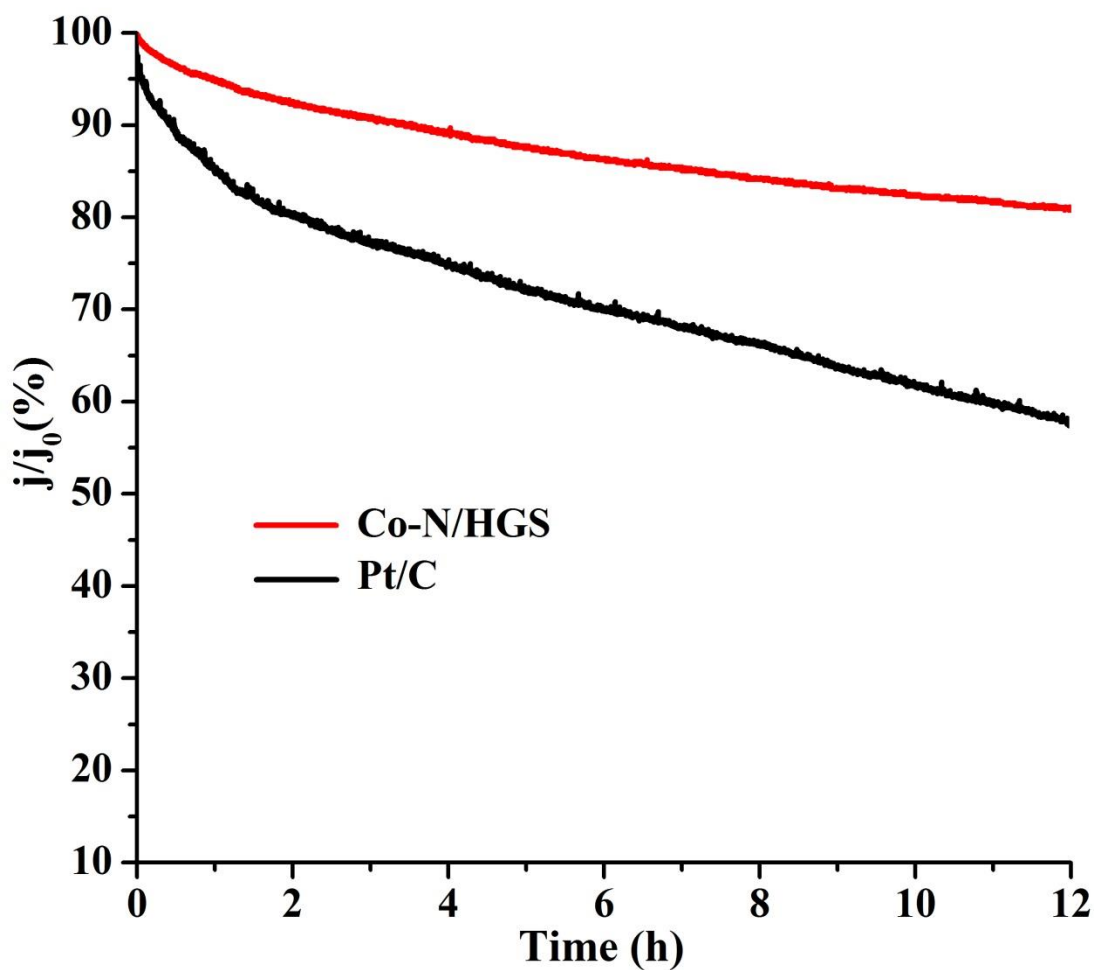
Figure S4. Current-time chronoamperometric responses at 0.3 V of Co-N/HGS and Pt/C for 12 h in O$_2$-saturated 0.5 M H$_2$SO$_4$ solution at a rotation rate of 1600 rpm.

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