The synthesis of greenish phosphorus on carbon substrates

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Experimental procedures

Synthesis of greenish phosphorus (greenish P)

Red phosphorus (red P >98.5%, energy-chemical) was treated by KOH-solution and deionized water washing. Carbon paper (CP, Toray Industries) was cut into 12 mm diameter sheets. Glassy carbon (GC) and silicon wafer were used without treatment. After pretreatment, 0.10 g red P and different substrates (CP 12 mm diameter, glassy carbon 10×10×1 mm and silicon wafer 10×10×1 mm) were sealed in a 12 cm long quartz tube with an inner diameter of 10 mm and a thickness of 2 mm under vacuum degree of -0.1 MPa. The quartz tube was heated from room temperature to 480 °C at a heating rate of 4 °C min^{-1} and maintained for 4 h, followed by cooling to 260 °C for 24 h. After cooling to room temperature, the final product was washed with CS_2 to remove the residual white P, and dried in a vacuum oven at 50 °C overnight.

Characterization

Ultraviolet-visible spectrum were performed using a U-3900 spectrophotometer. The morphologies of sample were characterized on scanning electron microscopy (SEM, Regulus 8100). X-ray photoelectron spectroscopy (XPS) data were measured on an ESCALAB Xi+ photoelectron spectrometer. Raman spectrum were obtained using LabRAM HR Evolution Confocal Raman Microscopy with a 532 nm laser. Grazing incidence X-ray diffraction (GIXRD) were measured on a Rigaku smartlab with Cu Kα radiation. Powder X-ray diffraction (PXRD) patterns were recorded on a D8-Focus diffractometer with Cu Kα radiation. Transmission electron microscopy (TEM) were measured by JEM-2100F

Electrochemical characterization

To evaluate the electrochemical performance of greenish P, the materials (CP, greenish P@CP, red P, black phosphorus (black P)) were made into electrodes and tested in detail by cyclic voltammetry (CV) in half cells at a scan rate of 0.05 mV s^{-1} between 0.01 and 3 V on a CHI1000C electrochemical workstation. CP and greenish P@CP sheets can be used as working electrodes directly without treatment and the working electrodes of red P and black P were prepared by mixing active materials, super-P and poly(vinylidene fluoride) (PVDF) binder in a weight ratio of 8:1:1 to form a homogeneous slurry, which was then coated on the copper foil. Electrochemical measurements were performed in CR2032-type coin cells with a Li metal counter electrode and polypropylene (PP) separator. The electrolyte was 1 M LiPF6 in the solvent of ethylene carbonate/ethyl methyl carbonate (EC/EMC=1:1, v/v) with 1% vinylene carbonate (VC) and 2% 1,3-propane sultone (PS) additives. The cells were assembled in an argon-filled glove box.

Computational Methods

All density functional theory calculations were carried out using CASTEP module in the Material Studio software. The functional of Perdew, Burke, and Ernzerhof (PBE) and the generalized gradient approximation (GGA) were employed. The electronic wave functions were expanded in a plane wave basis set with an energy cutoff of 408.2 eV to ensure an accuracy of the energy of 10^{-5} eV per atom. The Monkhorst-Pack grid on a 1×2×2 mesh were used in k-point sampling.

The adsorption energy $E_{(ad)}$ for P_4 molecule adsorbed on surface carbon and edge carbon was defined by the following method:

$$E_{(ad)}=E_{(\text{edge carbon-red P})}-E_{(\text{edge carbon})}-E_{(\text{red P})};\ E(as)=E_{(\text{surface carbon-red P})}-E_{(\text{surface carbon})}-E_{(\text{red P})}$$

$E_{(\text{edge carbon-red P})}$ and $E_{(\text{surface carbon-red P})}$ represent the total energy of edge carbon-red P and surface carbon-red P adsorption system respectively. $E_{(\text{edge carbon})}$, $E_{(\text{surface carbon})}$ and $E_{(\text{red P})}$ denote the energy of the edge carbon, surface carbon and P_4 respectively.

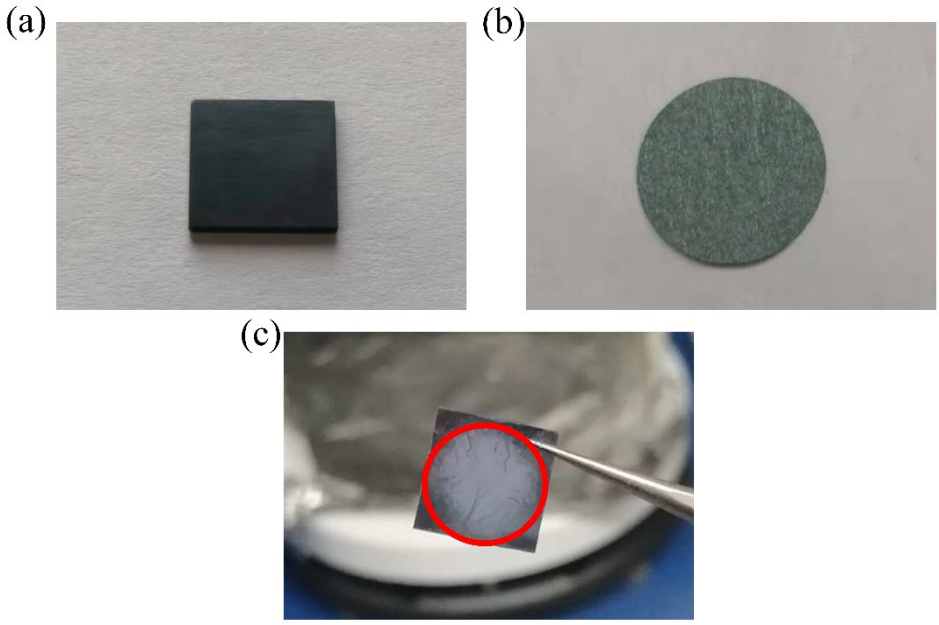

Figure S1 Digital photos of (a) GC, (b) greenish P@CP and (c) red P (marked by red circle in image) on silicon substrate.

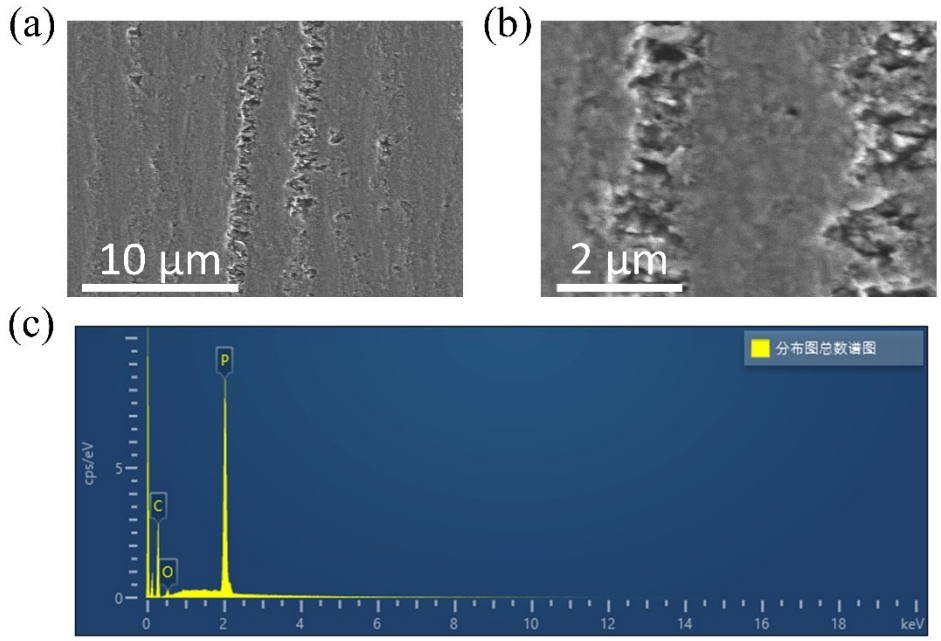

Figure S2 (a-b) SEM images of GC under different magnifications. (c) Energy-dispersive X-ray Spectroscopy of greenish P@GC.

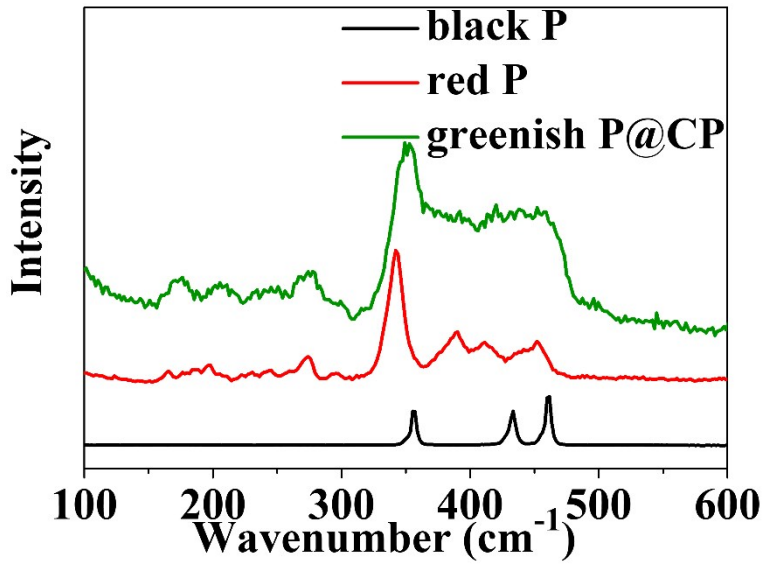

Figure S3 Raman spectrum of black P, red P and greenish P@CP.

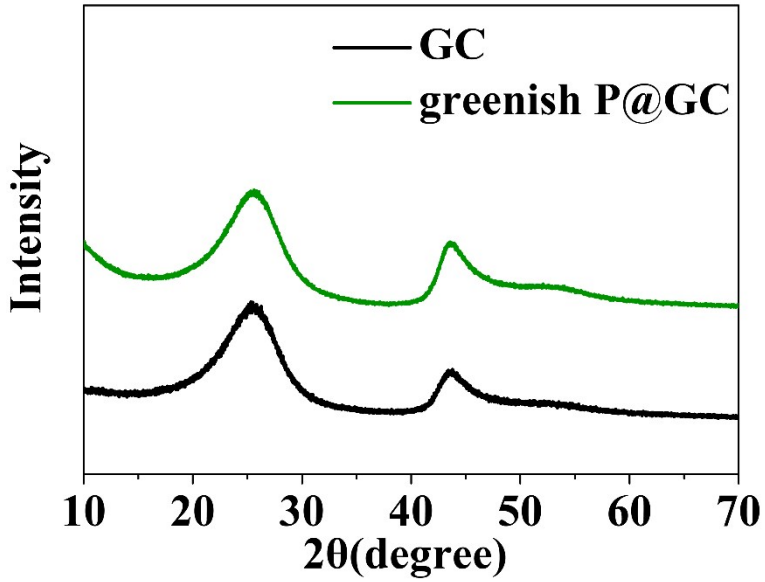

Figure S4 The XRD patterns of GC and greenish P@GC.

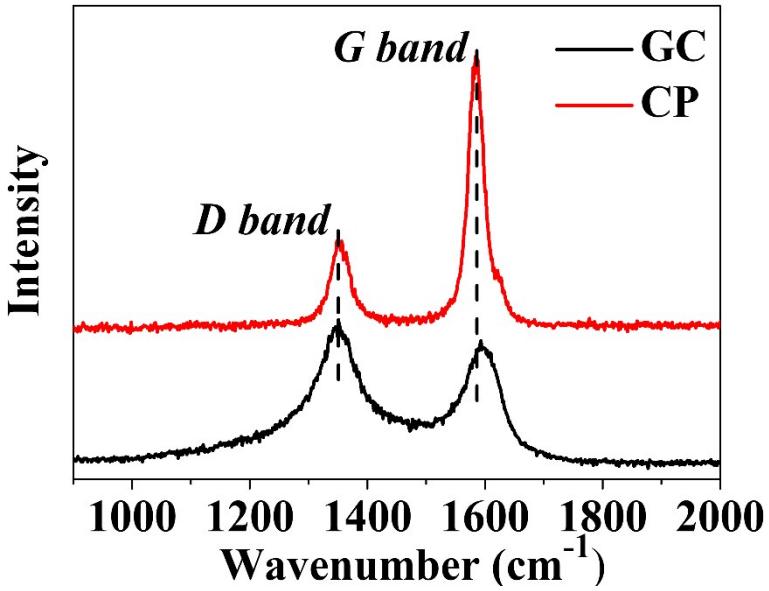

Figure S5 Raman spectrum of GC and CP.

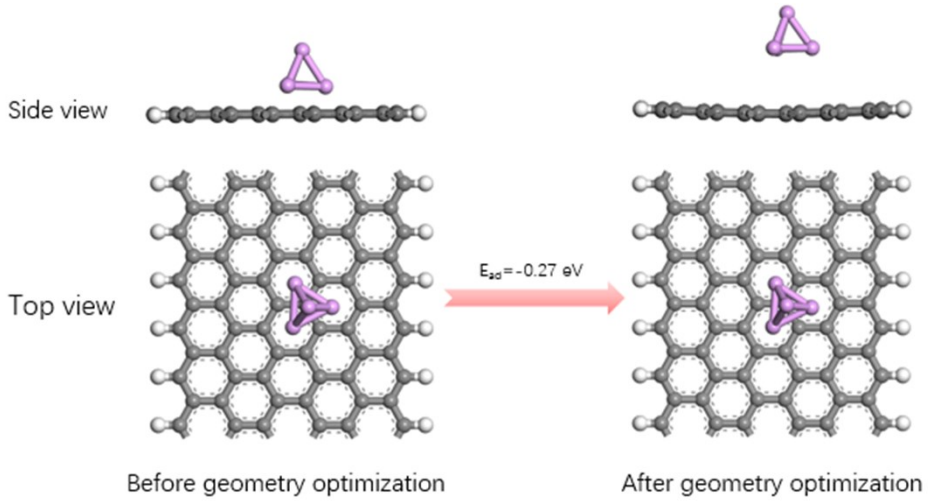

Figure S6 The adsorption process of surface carbon and P_4 based on DFT calculations.