Freezing-mediated polymerization of Ag nanoparticle-embedded polyaniline belts with polyoxometalate as doping acid exhibiting UV-photosensitivity

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Experimental Section

Materials: Aniline (Beijing Chemical Co) was distilled twice under vacuum before use. Iron (III) nitrate [$Fe(NO_3)_3$], and silver nitrate ($AgNO_3$) were purchased from a Beijing chemical factory without further purification. In our experiment, SiW_{12} was prepared and characterized according to the literature.[S1]

Characterization: The morphology of resulting PANI was observed with an XL-30 ESEM FEG SEM operated at 20 kV. Samples dispersed in ethanol were transferred to copper grids for transmission electron microscopy (TEM, Philips JEM-2010). FT-IR spectrum was obtained by using an Alpha Centauri 560 Fourier transform infrared spectrophotometer (frequency range 4000−400 cm^{-1}) with a KBr

pellet. XRD was performed on a D/Max IIIC X-ray diffractometer by using a Cu Kα radiation source. Scans were made from 3 to 90^{o} (2θ) at a speed of 2^{o} min^{-1}. The conductivity of PANI was measured by RTS-9 four-point probes resistivity measurement system (China). Disk-shaped samples were prepared from powders using 2 MPa pressure at room temperature. Electrochemical experiments were all performed with a CHI 800B electrochemical workstation. Indium tin oxide (ITO) substrate (4cm×1cm) as work interface was pretreated before used. It was sonicated in ethanol for 5 min, followed by rinsing with water, and ultrasonic agitation in concentrated NaOH in 1:1 (v/v) water/ethanol bath for 15 min. The ITO substrate was then rinsed further with water for another 15 min under sonication, and dried with nitrogen stream.

Thermal effect test: On the one hand, we put one alcohol thermometer on one black substrate (black color strongly absorbs the light at all wavelength), and make it expose to 365 nm UV lamp light (room temperature is 20.0 ℃) while the distance of the lamp-to-device was greater than 5 cm. After a long time UV lamp illumination (about 30 mins, ~1800s), we found the thermometer's temperature is 20.1 ℃, it doesn't have obvious increase. On the other hand, we put our device contained the samples on one heater which can keep the temperature in a steady state, we tested the I-T curves of SiW_{12}-doped PANI/Ag samples under different temperature (30 ℃ and 40 ℃) by electrochemical workstation.

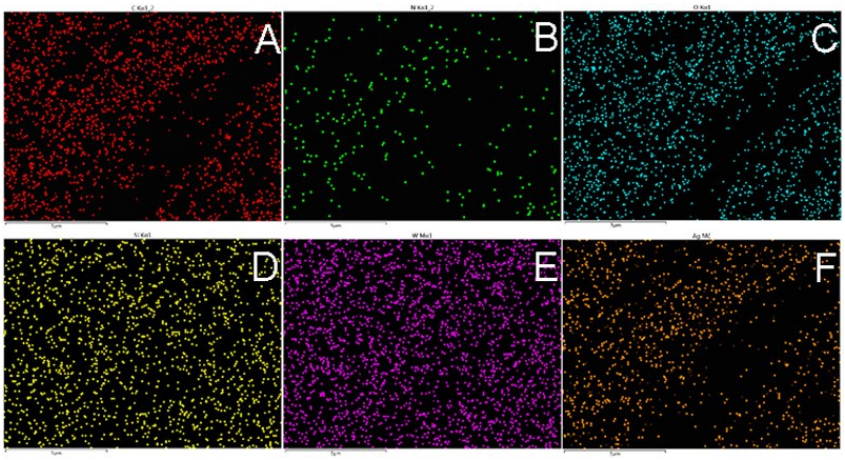

Fig. S1 EDX elemental mapping images of different elements in PANI samples. (A) C, (B) N, (C) O, (D) Si, (E) W, (F) Ag

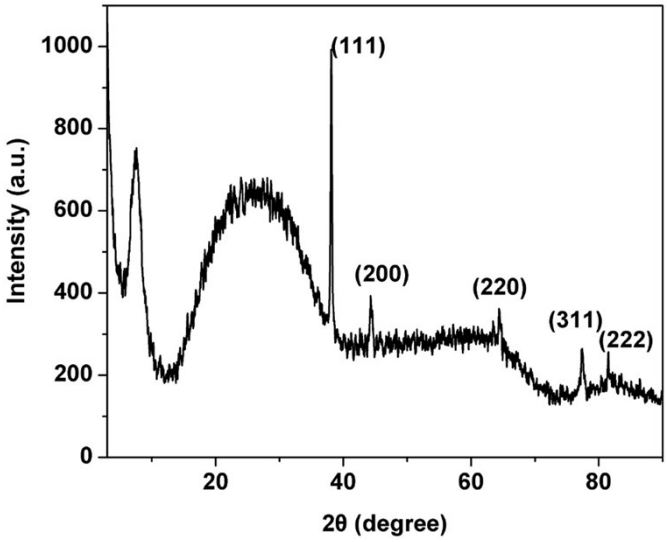

Fig. S2 XRD pattern of the Ag nanoparticles-embedded PANI belts.

The XRD pattern reveals the presence of Ag in the nanocomposites. Some sharp peaks centered at 2θ = 38°, 44°, 64°, and 77° are observed corresponding to (111), (200), (220), and (311) silver planes, respectively, which coincide well with the literature values (JCPDS No. 04-0783). Apart from the sharp peaks of Ag, one sharp band at 2θ = 7.1° appears, which is close to the PANI repetition unit. This result suggests that doping with SiW_{12} leads to a more ordered structure with relatively distinct Bragg reflections.[s2] In additional, three broad bands centered at 2θ = 25.78 °, 63.31 ° and 84.01 ° are also observed, which are related to the periodicity parallel and

perpendicular to the polymer chain.[s3]

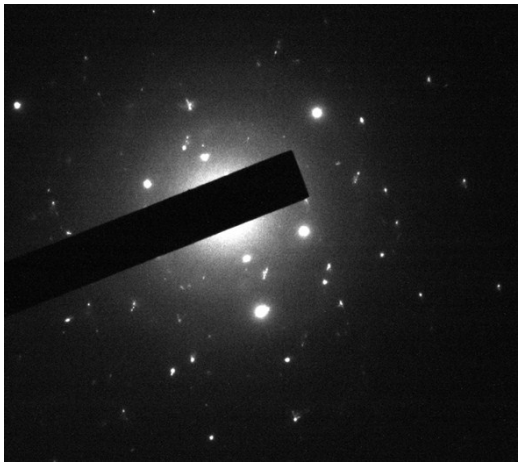

Fig. S3 SAED pattern of the PANI belts containing Ag nanoparticles.

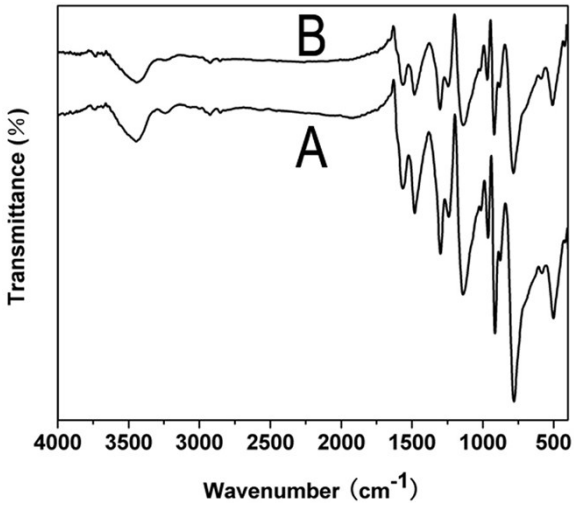

Fig. S4 FT-IR spectra of the Ag nanoparticles-embedded PANI belts with SiW_{12} doping acid (A) and only SiW_{12}-doped PANI (B).

The FT-IR spectrum of the Ag nanoparticles-embedded PANI belts (A) is very similar to that of the only SiW_{12}-doped PANI (B), which shows all the bands of PANI-emeraldine salt. The peaks in the frequency range of 2900-3500 cm^{-1} are due to the N-H stretching vibrations of the leucoemeraldine component. The peak at 1139.81 cm^{-1} assigned to the characteristic of $Q=NH^{+}$-B (where Q and B denote quinoid ring and benzene ring, respectively) is also observed. The peak at 1299.32 cm^{-1} relates to

the C-N stretching vibration with aromatic conjugation. The well-resolved peaks at 1565.09 and 1481.45 cm^{-1} correspond to the C=C stretching vibration of benzeniod and quinoid rings, respectively.[s4] SiW_{12} with a Keggin structure consists of one $\{SiO_4\}$ tetrahedron surrounded by four $\{W_3O_{13}\}$ sets formed by three edge-sharing octahedra. There are four kinds of oxygen atoms in the SiW_{12}, which are Oa (oxygen in $\{SiO_4\}$ tetrahedron), Ob (cornersharing oxygen between different $\{W_3O_{13}\}$ sets), Oc (edgesharing oxygen bridge within $\{W_3O_{13}\}$ sets), and Od (terminal oxygen atom). Therefore, curves A and B appear four characteristic peaks of SiW_{12} around 780 cm^{-1} (ascribes to W—Oc—W), 878 cm^{-1} (W—Ob—W), 914 cm^{-1} (Si—Oa), and 963 cm^{-1} (W=Od), which demonstrate that SiW_{12} has been doped into PANI structure in PANI products.[s4]

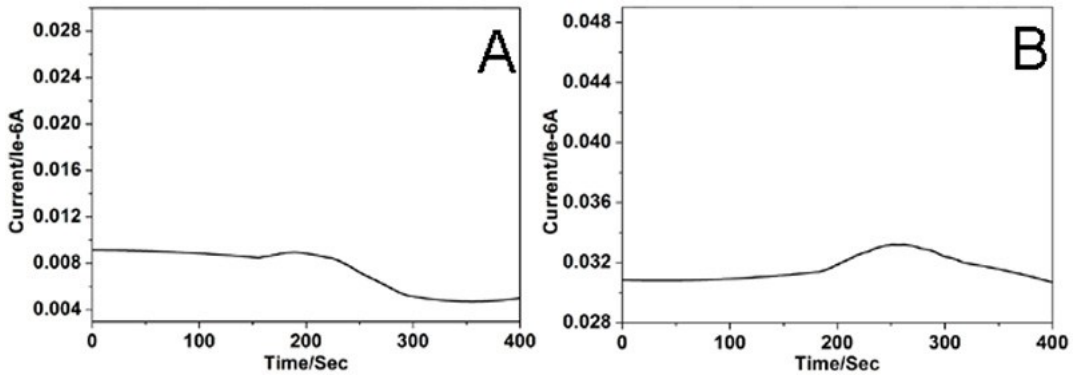

Fig. S5 I-T curves of SiW_{12}-doped PANI/Ag samples tested under different temperature. (A) 30 ℃. (B) 40 ℃.

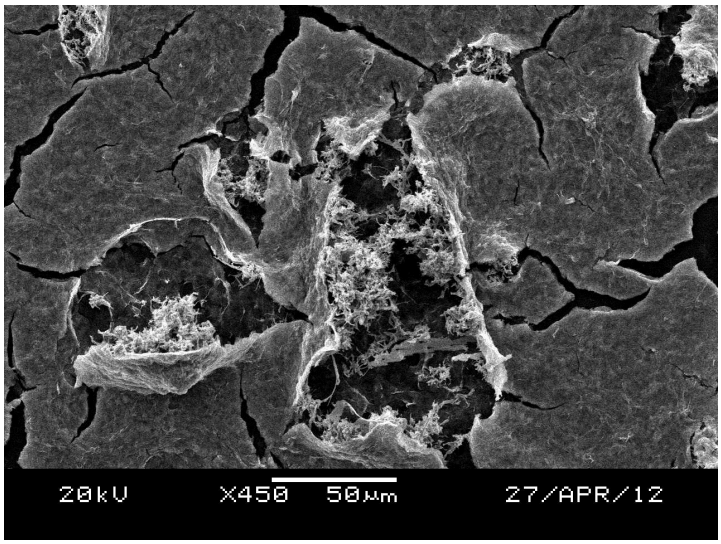

Fig. S6 SEM images of the SiW_{12}-doped PANI/Ag products synthesized in room temperature. (the molar ratio of aniline:oxidant:acid is 6:7:1, aniline=0.1 mL, $AgNO_3$ is 0.05g).

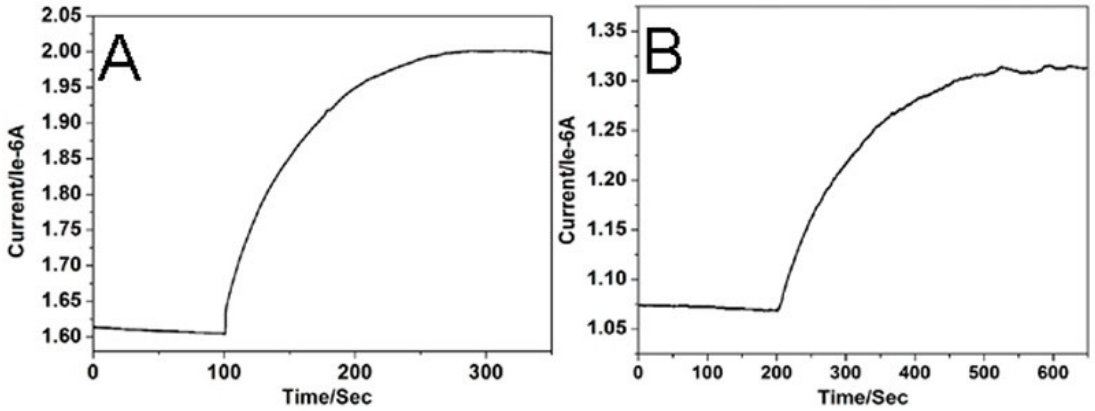

Fig. S7 Photocurrent curves of SiW_{12}-doped PANI/Ag samples synthesized by adding different quality of $AgNO_3$. (A). 0.045 g; (B). 0.089 g.

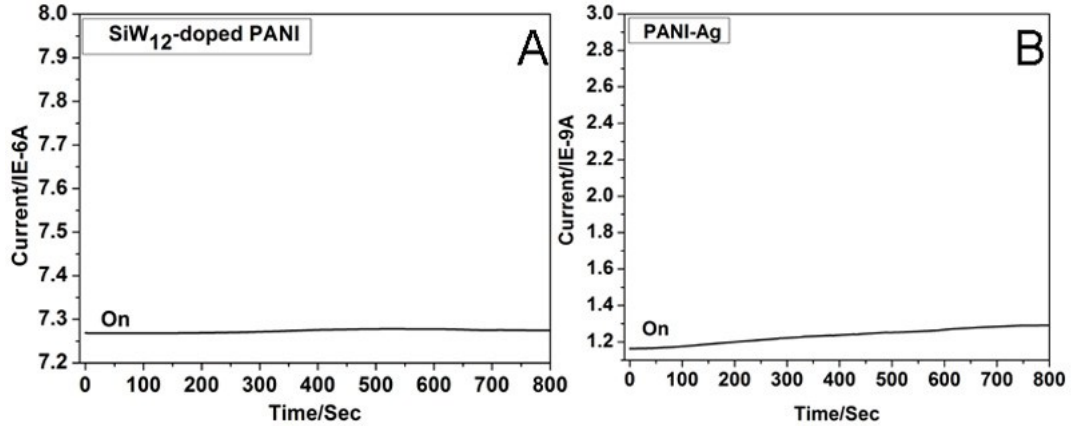

Fig. S8 Photocurrent curves of (**A**) SiW_{12}-doped PANI without Ag nanoparticles; and (B) PANI-Ag samples without SiW_{12} acid.

References

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S3. Y. Sun, A. G. MacDiarmid and A. J. Epstein, *J. Chem. Soc. Chem. Commun.* 1990, **7,** 529.
S4. H. Y. Ma, Y. Gao, Y. W. Li, J. Gong, X. Li and Y. L. Deng, *J. Phys. Chem. C* 2009**, 113***,* 9047.