Electronic Supplementary Material (ESI) for RSC Advances.

Immobilization of Ag(0) Nanoparticles on Quaternary Ammonium Functionalized Polyacrylonitrile Fiber as Highly Active Catalyst for 4-nitrophenol Reduction

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1. Reagents and instruments

Commercially available polyacrylonitrile fiber (PANF, the number average molecular weight of the spinning solution is 53000 to 106000, with 93% acrylonitrile, 6.5% methyl acrylate and 0.4%-0.5% sodium styrene sulfonate as the monomers) was cut into 10 cm segments and stored in a desiccator at 60 ^{o}C before use. The chemicals of amines, $AgNO_3$, organic solvents, halohydrocarbons, NH_2NH_2(80% aq), 4-NP, NaOH and hydrochloric acid were purchased commercially. Additionally, water is deionized.

The model of rotary evaporator is EYELA N-1300 (Japan). The weights of fibers and chemicals were tested by the electronic analytical balance BSA124S (Sartorius

Company, Germany). The mechanical properties of fibers were determined by electronic single fiber strength tester YG(B)001A (Wenzhou Textile Instrument Company, China). The fourier transform infrared spectra (FT-IR) of original and functionalized fibers were detected by the AVATAR360 FTIR spectrometer (Thermo Nicolet). The C, H and N contents of fibers were recorded by Elementar Vario MACRO cube (Germany). The XRD spectra of fibers were measured by the D/MAX-2500 X-ray diffractometer (Rigaku Corporation). The X-ray photoelectron spectra (XPS) of PANF-supported Ag(0) nanoparticle catalysts were detected by the PH1600 spectrometer (PERKIN ELMER). The micro physical morphology of fibers were determined by scanning electron microscope (SEM) (Hitachi, model S-4800). The size of Ag(0) nanoparticle in fiber catalyst was measured by transmission electron microscope (TEM) (model FEI Tecnai G2 F20). The thermal stabilities of fibers were measured with TA409PC TGA/DSC simultaneous thermalanalyzer (Netzsch company, Germany). The concentrations of 4-NP were detected by the UV-visible spectrophotometer (Beijing Puxi General Instrument Co., Ltd., China).

2. Experimental

Preparation of $PAN_{TA}F$: The PANF (1 g), 45 mL of *N,N*-dimethyl-1,3-propanediamine and 30 mL of deionized water were added to a single-necked flask and reflux for 5 h. Then, the functionalized fiber was taken out by tweezers and washed with 1 L of 60 ^{o}C water until the eluant was neutral, and then dried at 60 ^{o}C over night. The functionality of $PAN_{TA}F$ determined by acid-base titration is 1.985%.

Preparation of $PAN_{PY}F$: The 1.0 g of PANF, 10 mL of deionized water and 10.0 g

of 4-pyridinemethaneamine were added to a single-necked flask and reflux for 24 h. Then, the resulting $PAN_{PY}F$ fiber was taken out and cleaned with 1 L of 60 °C water until the eluant was neutral, and then the $PAN_{PY}F$ was dried overnight at 60 °C. The weight gain and functionality of $PAN_{PY}F$ were 10.3% and 0.875 mmol/g, respectively.

Preparation of $PAN_{IM}F$: The 1.0 g of PANF , 15 mL of deionized water and 10.0 g *N*-(3-aminopropyl)imidazole were added to a single-necked flask and reflux for 18 h. Then, the resulting $PAN_{IM}F$ fiber was taken out and cleaned with 1 L of 60 °C water until the eluant was neutral, and then The $PAN_{IM}F$ was dried overnight at 60 °C. The weight gain and functionality of $PAN_{IM}F$ were 14.4% and 1.088 mmol/g.

Preparation of $PAN_{PY\text{-}C4}F$: The 0.2 g of 0.875 mmol/g $PAN_{PY\text{-}C4}F$, 20 mL of ethanol (95% aq) and 1.37 g *N*-bromobutane were added to a 50 mL single-necked flask and reflux for 12 h. Then, the resulting $PAN_{IM}F$ fiber was taken out and cleaned with 200 mL of 60 °C 50% ethanol aqueous solution until the eluant was neutral, and then The $PAN_{IM}F$ was dried overnight at 60 °C. The weight gain and functionality of $PAN_{IM}F$ were 13.5% and 0.869 mmol/g.

Preparation of $PAN_{IM\text{-}C4}F$: The 0.4 g of 1.088 mmol/g $PAN_{PY\text{-}C4}F$, 20 mL of ethanol (95% aq) and 7.91 g *N*-bromobutane were added to a 50 mL single-necked flask and reflux for 12 h. Then, the resulting $PAN_{IM}F$ fiber was taken out and cleaned with 400 mL of 60 °C 50% ethanol aqueous solution until the eluant was neutral, and then The $PAN_{IM}F$ was dried overnight at 60 °C. The weight gain and functionality of $PAN_{IM}F$ were 17.1% and 1.064 mmol/g.

Preparation of $PAN_{QA\text{-}C3}F$, $PAN_{QA\text{-}C4}F$, $PAN_{QA\text{-}C5}F$, $PAN_{QA\text{-}EB}F$, $PAN_{QA\text{-}C7}F$,

$PAN_{Q\text{-}C9}F$, $PAN_{QA\text{-}C10}F$ and $PAN_{QA\text{-}C12}F$: The 1 g of 1.985 mmol/g$PAN_{TA}F$, 7 eq of halogenated hydrocarbon relative to tertiary amine group and 20 mL of ethanol were added to a single-necked flask and reflux for 6 h. Then, the functionalized fiber was taken out by tweezers and washed with 1 L of 60 ^{o}C ethanol and water 1:1 mixed solution until the eluant was neutral, and then dried at 60 ^{o}C over night.

Preparation of Ag(I) functionalized fibers: The 0.2 g of corresponding functionalized fibers and 20-200 mL 5 ppm $AgNO_3$ (aq) were added to a single-necked flask and reflux for 10 h. Then, the functionalized fiber was taken by tweezers and washed with 200 mL, and then dried at 60 ^{o}C over night.

Preparation of Ag(0)-functionalized PANFs: The Ag(I)-functionalized PANFs (0.2 g), 1 g of NH_2NH_2 (80% aq), 30 mL of water were added to a single-necked flask and react for 4 h in room temperature. Then, the functionalized fiber was taken out by tweezers and washed with 200 nL of water until the eluant was neutral, and then dried at 60 ^{o}C over night.

General procedure for the $PAN_{QA\text{-}C4}F$-Ag(0) catalyzed the reduction of 4-NP

4-Nitrophenol (4-NP) solution (1 mmol/L, 40 mL), $NaBH_4$ (50-200 eq) and 0.1-1.5 mol% $PAN_{QA\text{-}C4}F$-Ag(0) were added to a glass stopper tube. The reaction was reacted at 15-35 ^{o}C temperature for appropriate time according to the color change of solution. After the reaction was finished, HCl solution (10 mL 1 mol/L) was put in the glass stopper so as to fully desorb the 4-NP attached to the fiber. The standard curves of 4-NP with pH=10 was accurately fitted by the UV-visible spectrophotometer. Then, the conversion rate of the reaction was accurately detected by the standard curve method.

3. TEM images of $PAN_{QA\text{-}C12}F$-Ag(0)

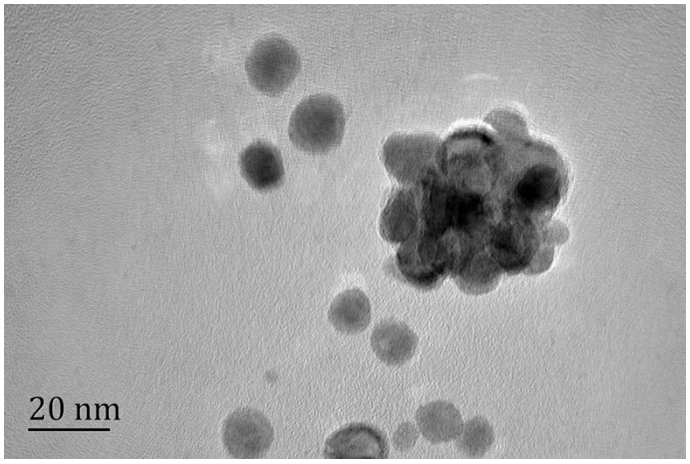

Fig. S1 TEM images of Ag(0) nanoparticles in $PAN_{QA\text{-}C12}F$-Ag(0).

4. Standard curves of 4-NP and 4-AP

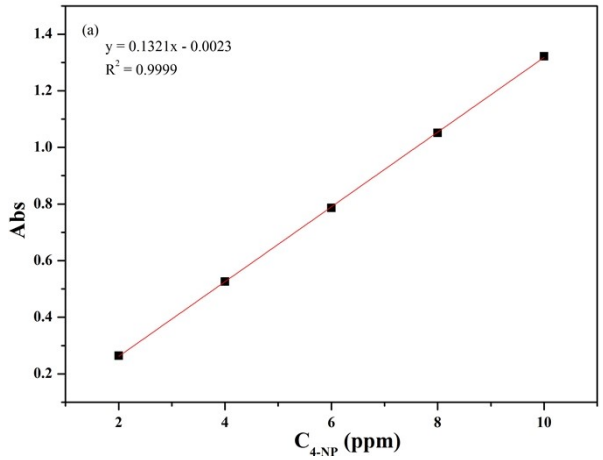

Fig. S2 The standard curves of (a) 4-NP at pH 10, (b) 4-AP at pH 3.

5. Catalysis kinetic of $PAN_{QA\text{-}C4}F$-Ag(0)-20

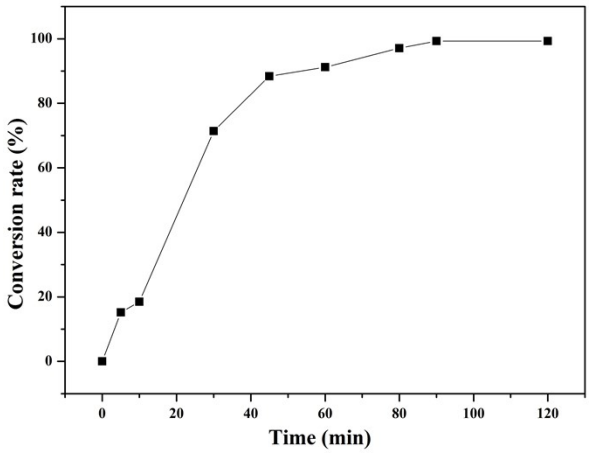

Fig. S3 Catalysis kinetic of $PAN_{QA\text{-}C4}F$-Ag(0)-20 for the reduction of 4-NP at room temperature

6. Comparison of $PAN_{QA\text{-}C4}F$-Ag(0) with other catalytic systems

Table S1 Comparison of various catalysts for the Heck reaction of iodobenzene and acrylic acid.

Entry	Cat./cat. Amount	T (°C)	Time (h)	Conv. (%)	Run[a]	Ref.
1	$Ag@SiO_2$ nanoparticles/2 mg (about 0.73 mol%)	25 °C	120 min	＞95%	20	[S1]
2	Fe_3O_4@PS@Ag/2 mg(about 78.4mol%)	25 °C	3 min	＞99%	7	[S2]
3	PEI-Ni/36.6 mol%	30 °C	5 min	＞99%	5	[S3]
4	TA@Fe_3O_4-AgNPs/0.75.9 mol%	25 °C	3 min	98.6%	5	[S4]
5	p(AAm)-CB-Ag composites/1.1 mol%	30 °C	80 min	＞99%	5	[S5]
6	CeO_2/g-C_3N_4/Ag/15 mg	25 °C	14 min	98.6%	--	[S6]
7	$PAN_{QA\text{-}C4}F$-Ag(0)/1mol%	25 °C	90 min	＞99%	20	This work

Reference

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