Synthesis of atomic form nickel co-catalysts on TiO$_2$ for improved photocatalysis by RAFT technique

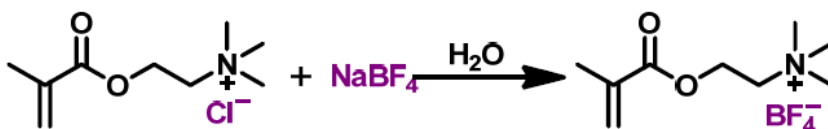Bo Zhang（**Corresponding author**　email：mnbvcxzxh@163.com）

Baohua Zhang（email：17751739703@163.com）　Guohua Wu（email：1125412583@qq.com）

Supporting Information

1. Synthesis of Ionic Monomers

1.1 Synthesis of [META$^+$][BF$_4^-$]

[META$^+$][BF$_4^-$] was prepared according to a previously published procedure (Cao, X.; An, Z. Macromol. Rapid Commun., 2015, 36, 2107-2110). In brief, [2-(methacryloyloxy)ethyl]trimethylammonium chloride solution (8.7g, 0.072mol) and sodium tetrafluoroborate (10.9 g, 0.099 mol) were dissolved in 45 mL of water. The solution was stirred at room temperature overnight, which was then filtered and washed with cold water. The collected solid was isolated via lyophilization.

1.2 Synthesis of [META$^+$][(CF$_3$SO$_2$)$_2$N$^-$]
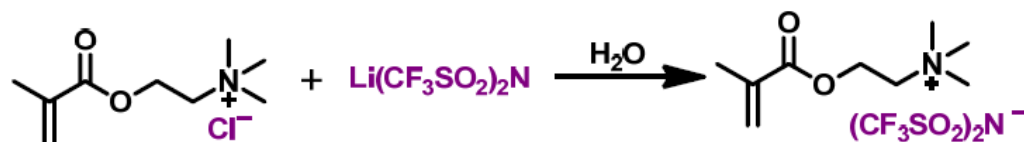
[META$^+$][(CF$_3$SO$_2$)$_2$N$^-$] was prepared according to a previously published procedure (Tokuda, M.; Minami, H.; Mizuta, Y.; Yamagami, T. Macromol. Rapid Commun., 2012, 33, 1130-1134). [2-(Methacryloyloxy)ethyl]trimethylammonium chloride solution (20.2 g, 78.0 mmol) and lithium bis(trifluoromethanesulfonyl)imide (23.3 g, 81.1 mmol) were mixed and stirred for 1.5h. Then the oily lower layer was collected and washed with cold water and lyophilized for 3 days to get [2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)imide ([META$^+$][(CF$_3$SO$_2$)$_2$N$^-$]) as a viscous oil.
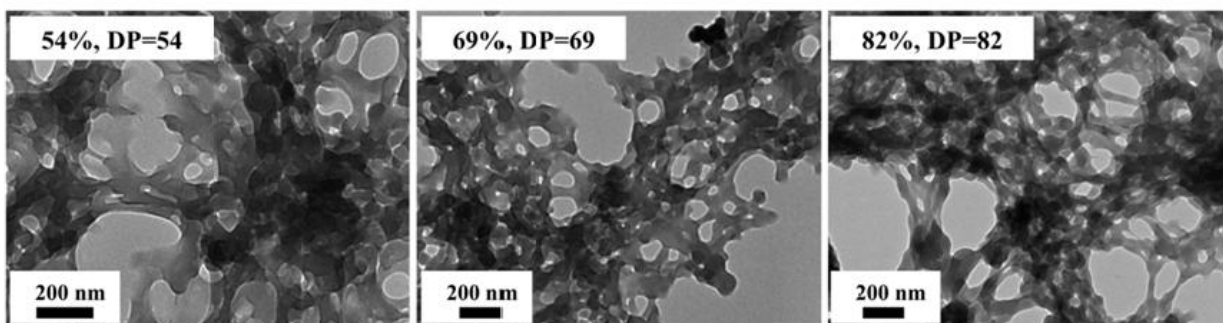
2. RAFT Dispersion polymerization of [META$^+$][PF$_6^-$]

RAFT aqueous dispersion copolymerization of [META$^+$][PF$_6^-$] was performed at 80℃, stirring rate of 500rpm and solids contents of 5~8% w/v using PMPS (or other based macro-CTAs). In a typical experiment, PMPS$_{31}$ (1.7 mg, 0.0070 mmol) was dissolved in water (3.5 mL), to which was added [META$^+$][PF$_6^-$] (0.066 g, 0.21 mmol). After the solution was degassed with nitrogen in an ice/water bath for 30 min, it was immersed into a preheated oil bath at 80℃. After the temperature was stabilized, a degassed V-50 solution (100 mL, containing V-50 0.38 mg) was injected via a microsyringe. The polymerization was allowed to continu for 8h under protection of nitrogen. The final conversion of [META$^+$][PF$_6^-$] was ~80% as indicated by ^{1}H NMR analysis. The mean degree of polymerization of each block was calculated vased on the monomer conversion and thus the obtained polymer was denoted as PMPS$_{31}$-MPS-P([META$^+$][PF$_6^-$]). Dynamic light scattering (DLS) analysis: D$_h$=39 nm, PDI=0.14.

Table S1. Summary of RAFT Aqueous Dispersion Polymerization of [META$^+$][PF$_6^-$] Using PMPS Macro-CTAs at 80℃.

macro-CTA	solids^a (w/v)	macro-CTA/M/V-50^b	conv.^{c} (%)	DP^d	weight fraction of P([META$^+$][PF$_6^-$])^e (%)	D_h (PDI)^f	TEM morphology^g
PMPS$_{31}$	3%	1:40:0.7	75	30	37.64	62(0.21)	spheres+worms
		1:50:0.7	72	36	42.01	122(0.18)	worms
		1:60:0.7	75	45	47.52	997(0.87)	worms
		1:70:0.7	76	53	51.61	1554(0.58)	networks
	5%	1:30:0.2	80	24	32.57	39(0.14)	spheres
		1:40:0.2	82	33	39.91	41(0.11)	spheres
		1:45:0.2	100	45	47.52	79(0.39)	spheres+short worms
		1:55:0.2	85	47	48.61	66(0.13)	worms
		1:60:0.2	83	50	50.15	123(0.15)	worms
		1:70:0.2	84	59	54.28	4026(0.26)	networks
		1:80:0.2	87	70	58.48	3127(0.23)	networks
		1:90:0.2	88	79	61.39	3643(0.20)	networks
		1:100:0.2	92	92	64.93	3020(0.27)	networks
		1:130:0.2	90	117	70.19	3678(0.31)	networks
	8%	1:30:0.2	99	30	37.64	67(0.14)	spheres
		1:40:0.2	85	34	40.62	302(0.35)	spheres+worms
		1:50:0.2	88	44	46.96	70(0.36)	spheres+worms
		1:60:0.2	94	56	52.98	518(0.27)	networks
PMPS$_{22}$	5%	1:40:0.2	88	35	49.64	55(0.13)	spheres
		1:60:0.2	87	52	59.42	270(0.25)	worms
		1:80:0.2	93	74	67.58	2071(0.33)	networks

^{a}Solids=(W$_M$+W$_{macro-CTA}$)/V$_{water}$. ^{b}Molar ratio of macro-CTA/monomer/V-50. ^{c}Monomer conversion determined by ^{1}H NMR in d$_6$-acetone. ^{d}Actual degree of polymerization of [META$^+$][PF$_6^-$]. ^{e}Weight fraction of P([META$^+$][PF$_6^-$])=W(P([META$^+$][PF$_6^-$]))/W(PMPS-MPS-P([META$^+$][PF$_6^-$])). ^{f}Hydrodynamic diameter (D$_h$) and polydispersity (PDI) of nano-objects determined by dynamic light scattering (DLS). ^{g}Nano-object morphology identified by transmission electron microscopy (TEM).

Figure S1. Additional TEM micrographs for samples withdrawn during RAFT aqueous polymerization of $[META^+][PF_6^-]$ using $PMPS_{31}$ at 5% w/v solids and 80℃ with $[PMPS_{31}]/[monomer]/[V-50]$ being 1:100:0.1.
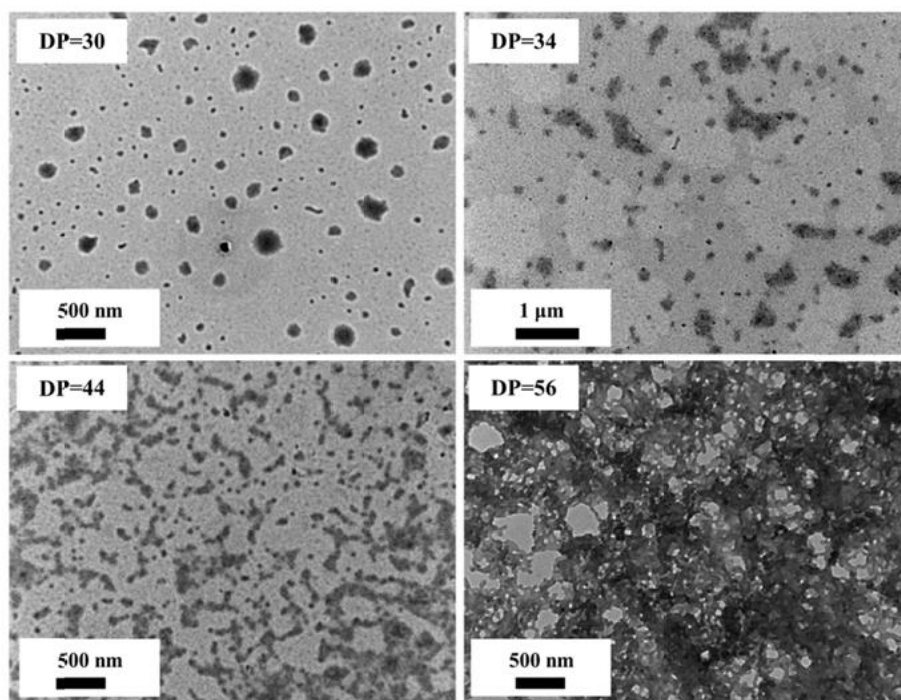
Figure S2. TEM micrographs for RAFT aqueous polymerization of $[META^+][PF_6^-]$ using $PMPS_{31}$ at 8% w/v solids and 80℃ targeting different DPs.
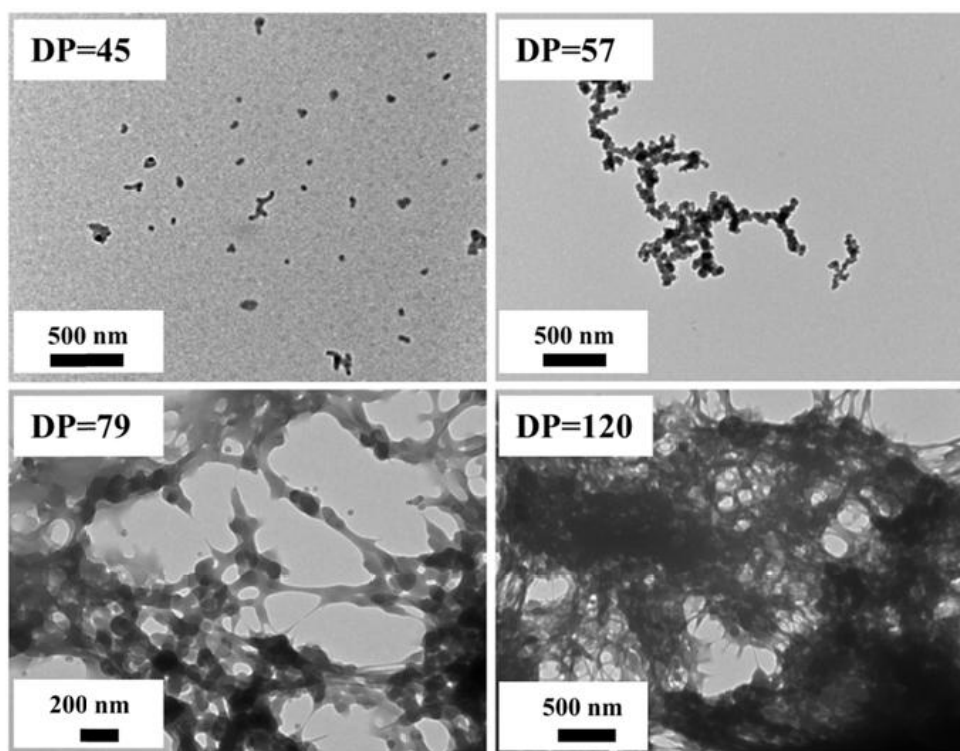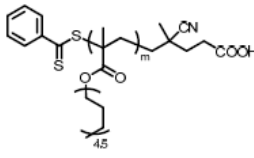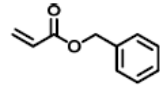
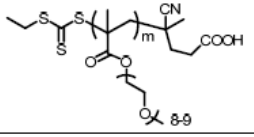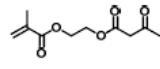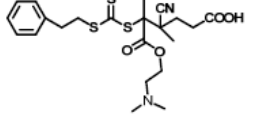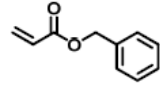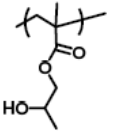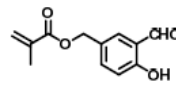**Figure S3.** TEM micrographs for RAFT aqueous polymerization of [META$^+$][PF$_6^-$] using PMPS$_{31}$ at 2% w/v solids and 80℃ with indicated DPs.
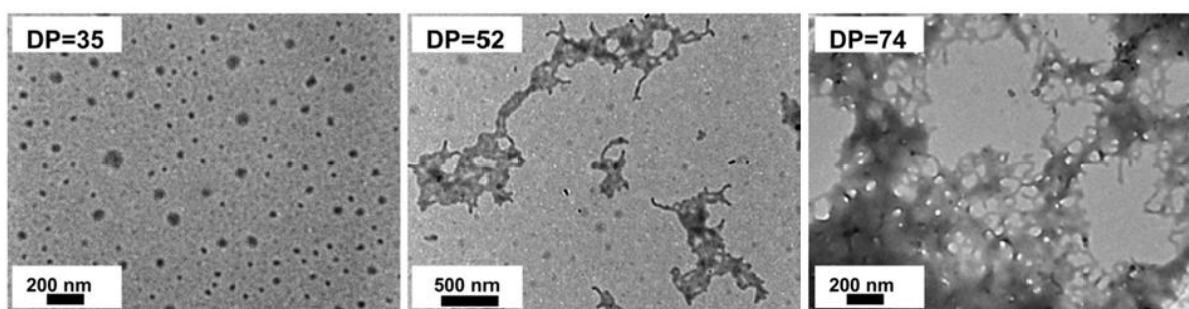
Figure S4. TEM micrographs for RAFT aqueous polymerization of [META$^+$][PF$_6^-$] using PMPS$_{22}$ at 5% w/v solids and 80℃ with indicated DPs.
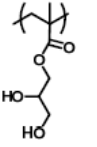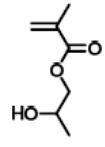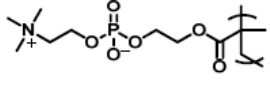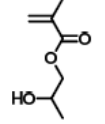
Table S2. Summary and Analysis of Some RAFT Dispersion Polymerization Formulations in Literature

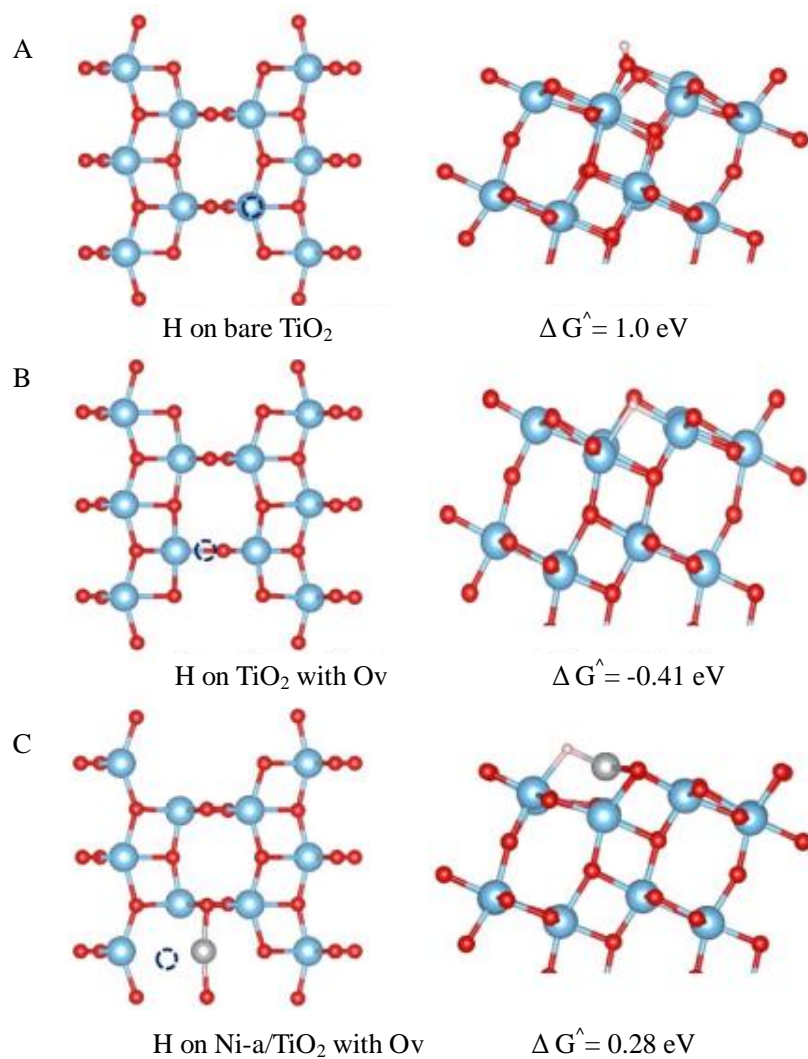| macro-CTA	monomer	solids	solvent	core block weight fraction	morphology	reference citation
(structure)	(structure)	10%	EtOH	61%	spheres	Boyer et al. ACS Macro Lett. 2015, 4, 984−990
				66%	sphere+ worms	
(structure)	(structure)	15%	EtOH	80%	spheres	An et al. ACS Macro Lett.2014,3,1220−1224
				85%	sphere+vesicles	
(structure)	(structure)	10%	EtOH	57%	spheres	Armes et al. Macromolecules 20 12, 45, 50 91−5098
				68%	spheres+worms	
		13%		52%	spheres	
				68%	spheres+worms	
(structure)	(structure)	15%	MeOH	83%	spheres	Lu et al. Polymer Chemistry, 2016, 7(29): 4761-4770
				84%	spheres+worms	
(structure)	(structure)	10%	H_2O	83%	spheres	Armes et al. J. Am. Chem. Soc. 2011, 133, 16581−16587
				84%	spheres+worms	
(structure)	(structure)	15%	H_2O	80%	spheres	Lewis et al.J. Am. Chem. Soc. 2011, 133, 15707− 15713
				83%	spheres+worms	

3. Results and discussion
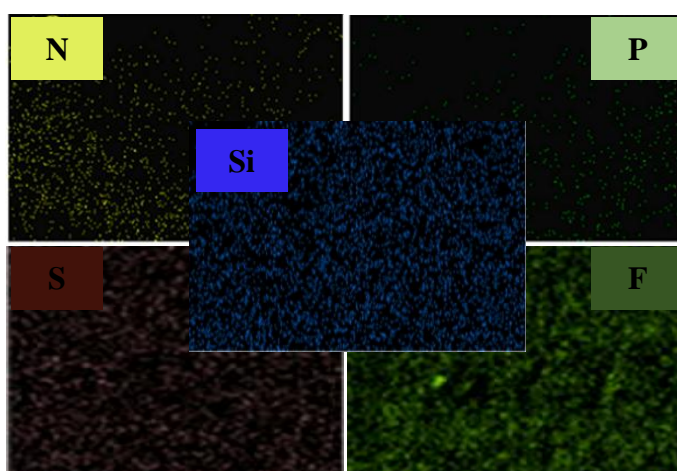
Figure S5. the energy dispersive X-ray spectrum mapping(EDS) of Ni-a/TiO$_2$

A H on bare TiO$_2$ $\Delta G^{\wedge} = 1.0$ eV

B H on TiO$_2$ with Ov $\Delta G^{\wedge} = -0.41$ eV

C H on Ni-a/TiO$_2$ with Ov $\Delta G^{\wedge} = 0.28$ eV

Figure S6. The molecular models of the adsorption of hydrogen on the surface of (A) bare TiO$_2$, (B) TiO$_2$ with Ov and (C) Ni-a/TiO$_2$ with Ov, respectively.

The HER reaction under standard condition includes 2 parts:

$$H^+ + e^- + * \rightarrow H^*$$ (1)

$$H^* \rightarrow * + \frac{1}{2}H_2$$ (2)

Where $*$ and H^* represent adsorption sites and hydrogen adsorbed on the surface. The whole process can be described as follows:

$$H^+ + e^- \rightarrow \frac{1}{2}H_2$$ (3)
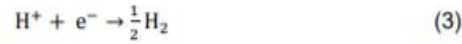
Since the total energy of $H^+ + e^-$ and $\frac{1}{2}H_2$ are equal, the Gibbs free energy of equation (3) is 0 eV. Therefore the Gibbs free energy of the adsorption of hydrogen (ΔG_{H^*}) on the surface of catalyst (equation (1)) is a key descriptor of HER activity. The closer ΔG_{H^*} is to 0, the higher HER activity the catalyst has[8]. In our calculations, ΔG_{H^*} is calculated by the following equation:

$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\,\Delta S$$ (4)

where ΔE_{H^*}, ΔE_{ZPE}, T and ΔS are the adsorption energy of hydrogen, the difference in zero-point energy, the temperature and the difference in entropy, respectively[9].