Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Scalable synthesis of copper submicron/nanoplates with high stability and their recyclable superior catalytic activity towards 4-nitrophenol reduction

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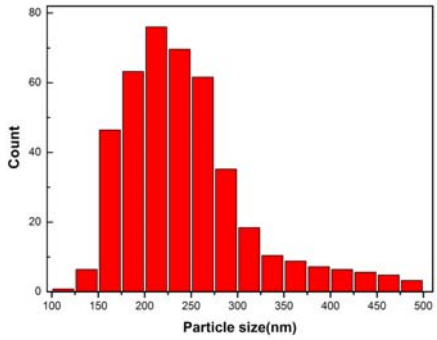


Fig.S1 The size distribution of copper submicroplates as-prepared (pH=4.5) in a typical synthesis

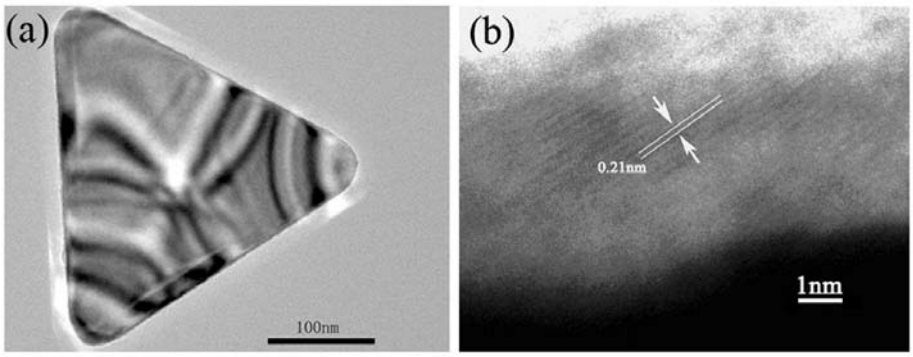


Fig.S2 (a-b) HR-TEM images of a triangular copper submicroplate.

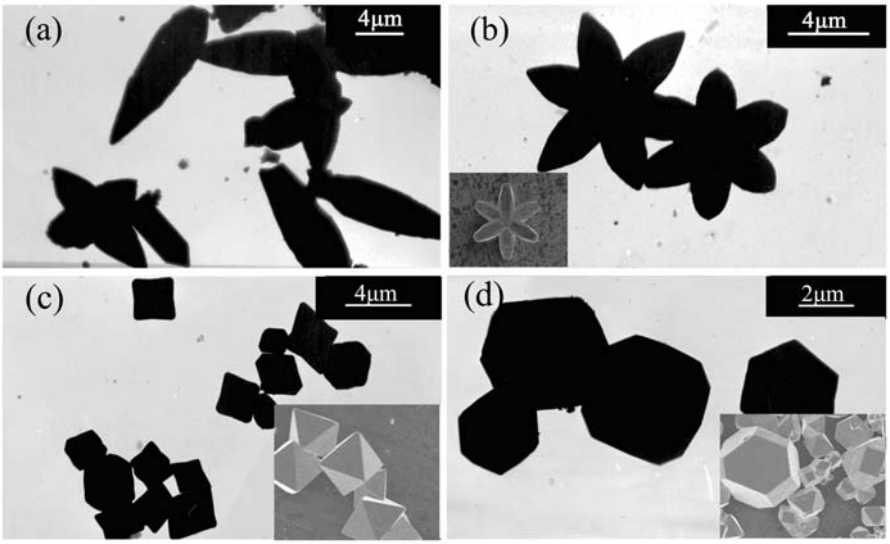
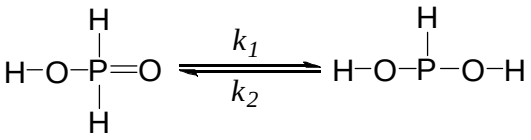


Fig.S3 TEM images of Cu_2O sampled at different pH of the initial reaction solution:

(a) pH~7.0, (b) pH~8.0, (c) pH~9.0,(d) pH~10.0.



Normal state metastable state

Fig.**S4** The structure changes of NaH_2PO_2 with variation of the pH in aqueous solution

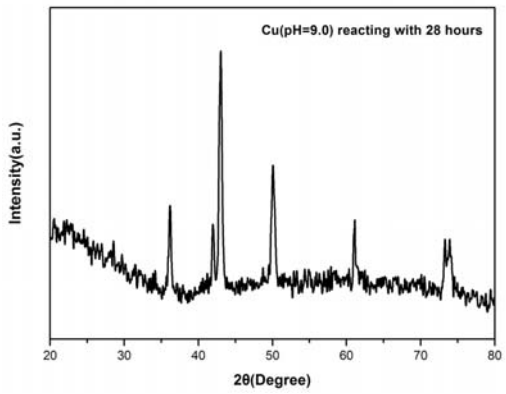


Fig.S5 XRD pattern of the obtained copper nanoplates at pH~9.0 reacting with 28hours

Section1:

The secondary reaction can be expressed by:

$$2H_2PO_2^- + H^+ = P + HPO_3^- + H_2O + 1/2H_2$$

With the large amount H^+ ions in solution and the continuous generated H^+ ions from the $H_2PO_2^-$, part of sodium hypophosphate would react with H^+ and finally convert into HPO_3^- and P. Therefore NaH_2PO_2 as reductant in the solution (pH=4.0) can't reduce copper ion completely and the products obtained were the compound of Cu and Cu_2O. If the amount of NaH_2PO_2 was increased twice at pH~4.0, the copper product was obtained that proved in Fig.S6.

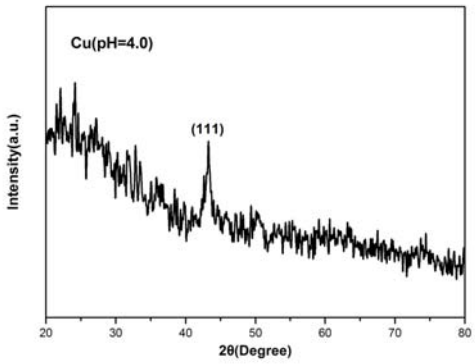


Fig. S6 XRD pattern of the obtained copper nanoplates at pH~4.0, adding twice amount of NaH_2PO_2 to solution

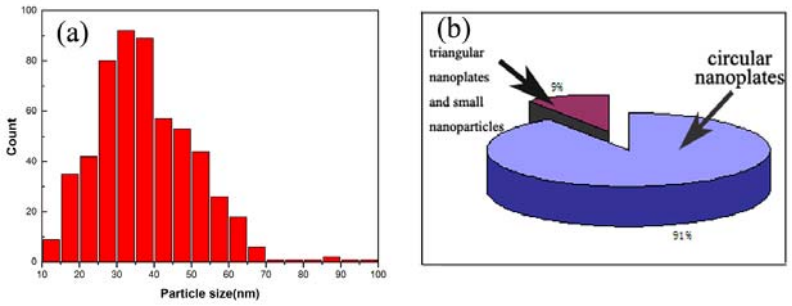


Fig. S7 (a) The size distribution of copper nanoplates as-prepared with 0.35g $KNaC_4H_4O_6$

(b) Percentage of circular and triangular nanoplates & small nanoparticles

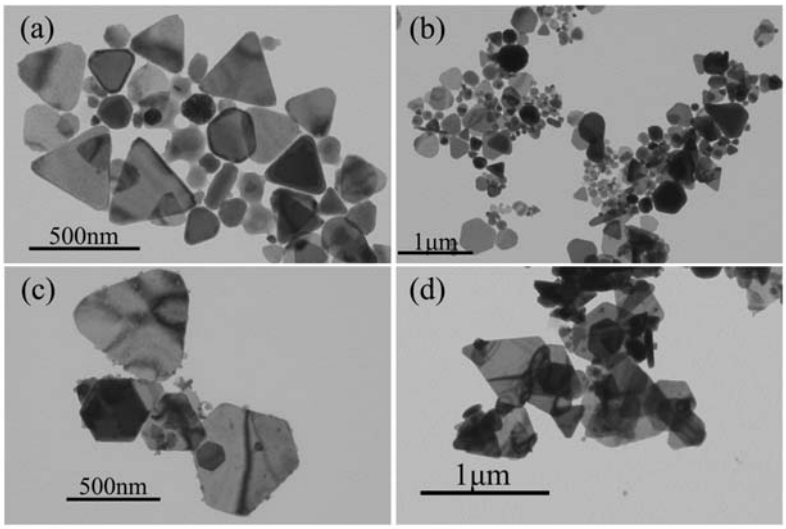


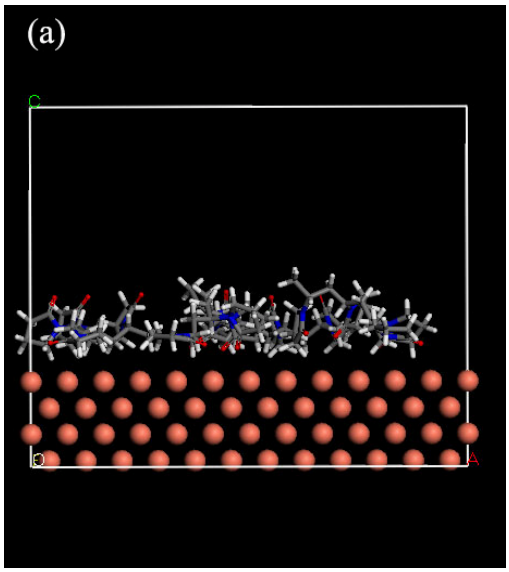
Fig. S8 TEM images of the Cu plates synthesized with different concentration of sodium potassium tartrate: (a) ~ (b) 1.75 g, (c) ~ (d) 2.10 g

Section 2:

The interaction energies (U) were calculated, expressed by:

$$U = E_{total} - (E_{surface} + E_{ploymer})$$

where E_{total} is the total energy of the Cu-surfactant system, $E_{surface}$ is the surface energy without the surfactant, $E_{ploymer}$ is the energy of PVP molecules.



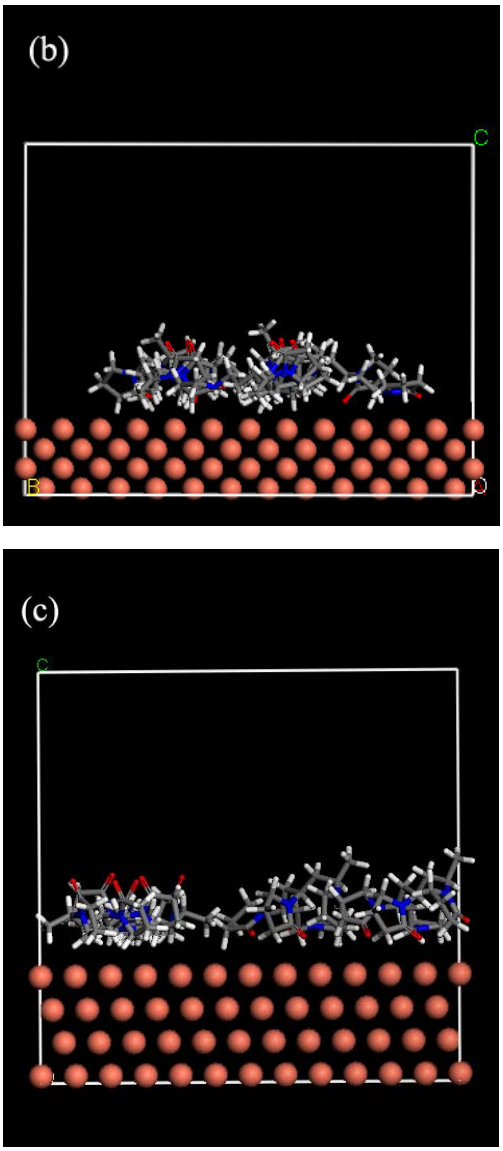


Fig. S9 The MD simulation shows PVP adsorbed on each of the copper surfaces (a) (100), (b) (110) and (c) (111)

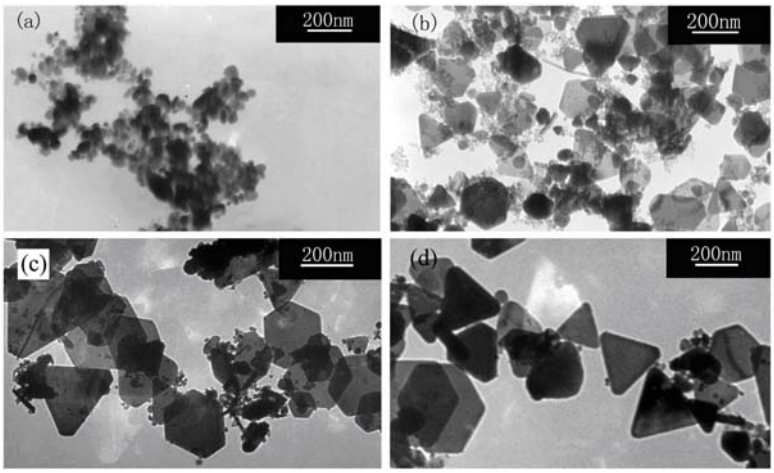


Fig.S10 TEM images of the synthesized copper submicroscale products at different stages: (a) 2h, (b) 4h, (c) 6h and (d) 8h

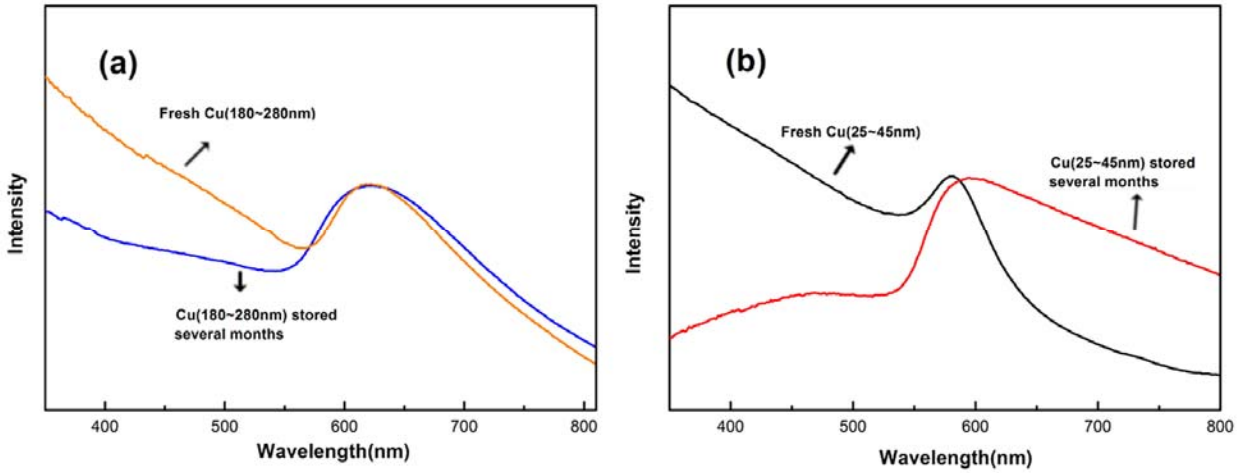


Fig.S11 Successive UV–Vis spectra of the different copper samples: (a) fresh Cu-1, Cu-1 after stored several months (b) fresh Cu-1, Cu-2 after stored several months

Table S1 Results of the reduction rate of 4-NP at room temperature catalyzed by the different catalysts

Catalyst	k (min^{-1})
Cu-1（obtained with 1.05g $KNaC_4H_4O_6$）	0.340
Cu-2 （obtained with 0.35g $KNaC_4H_4O_6$）	0.373
Cu-3（obtained with Na-citrate）	0.202
Cu-4（commercial Cu powder）	0.016

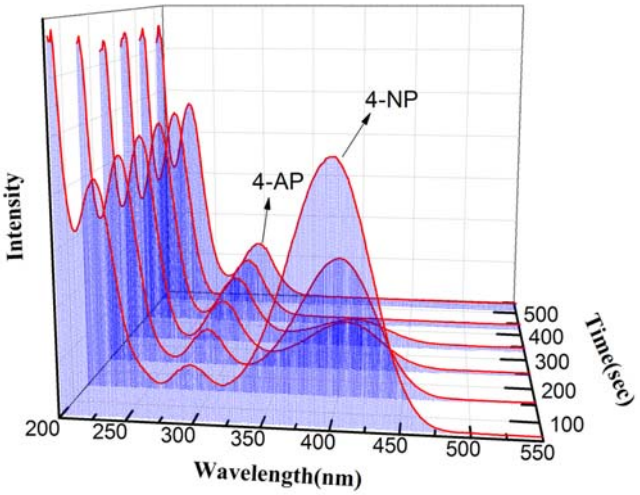


Fig. S12 Successive UV–Vis spectra of solutions of 4-NP sampled converted into 4-AP at different time with catalyst Cu-1.

Conditions: [4-NP] $=5.0\times10^{-4}$ M; Cu=0.07mg; [NaBH4] $=3.0\times10^{-2}$ M; with T=25℃

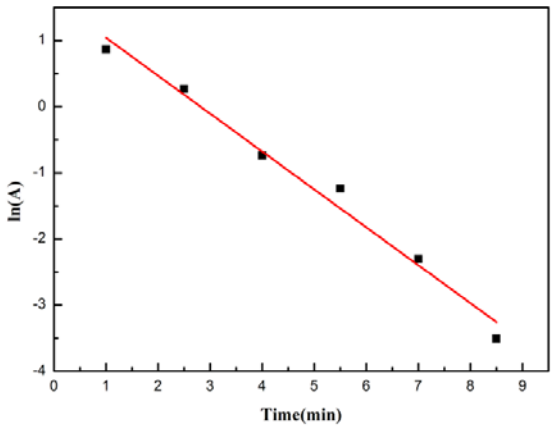


Fig. S13 Absorbance ln(*A*) vs. time plot for the reduction of 4-NP with Cu-1

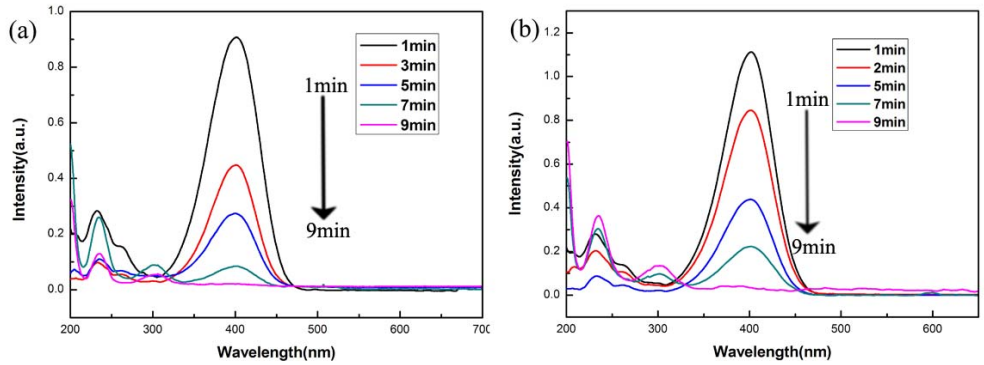


Fig**.** S14 Successive UV–Vis spectra of the reduction reaction after several months (a) the copper catalyst in size180~280 nm, (b) the copper nanocatalyst within 25~45 nm

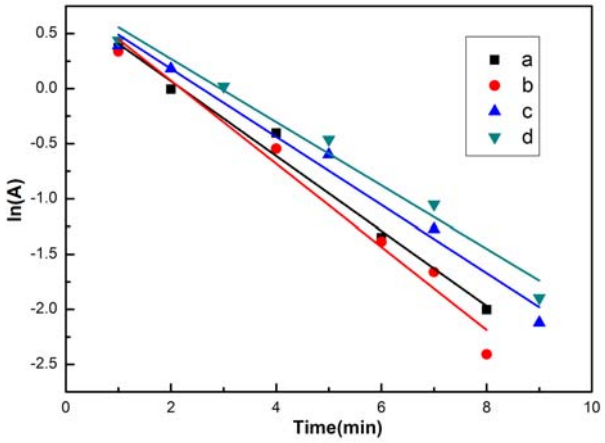


Fig. S15 Absorbance ln(*A)* vs. time plot for the reduction of 4-NP in the presence of solid catalyst: (a) the fresh Cu-1, (b) the fresh Cu-2, (c) the Cu-1 storing for 2 months, (d) Cu-2 storing for 2 months,

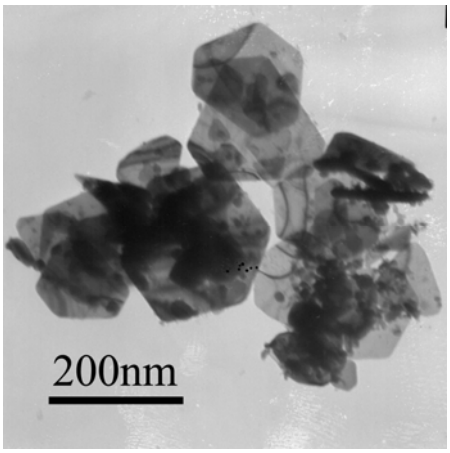


Fig. S16 TEM image of the used Cu as catalyst