

***Environmental Science: Nano***

## **Electronic Supporting Information**

### **Design of the nanoarray-pattern Fe-Ni bi-metal nanoparticles@M13 virus for enhanced reduction of *p*-chloronitrobenzene through micro-electrolysis effect**

Shuai Zhang<sup>1,2</sup>, Huimin Yu<sup>1,2, 3\*</sup>, Ji Yang<sup>1,2</sup> and Zhongyao Shen<sup>1,2</sup>

1 Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

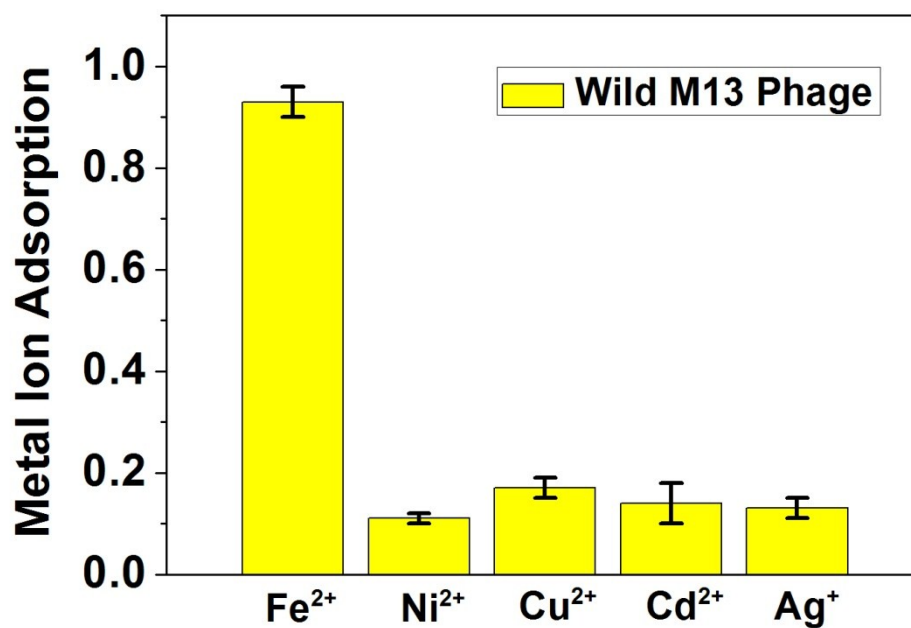
2 Key Laboratory of Industrial Biocatalysis (Tsinghua University), the Ministry of Education, Beijing 100084, China

3 Center for Synthetic and Systems Biology, Tsinghua University

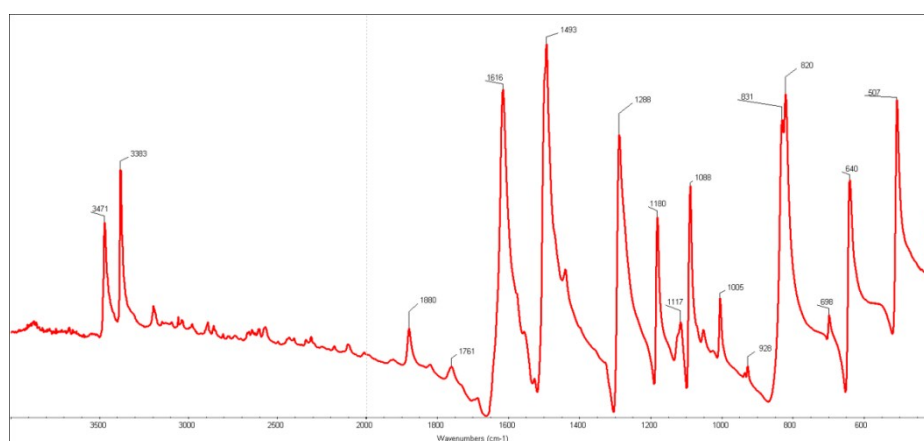
\* Corresponding author:

Telephone: 86-10-62795492, Fax: 86-10-62770304,

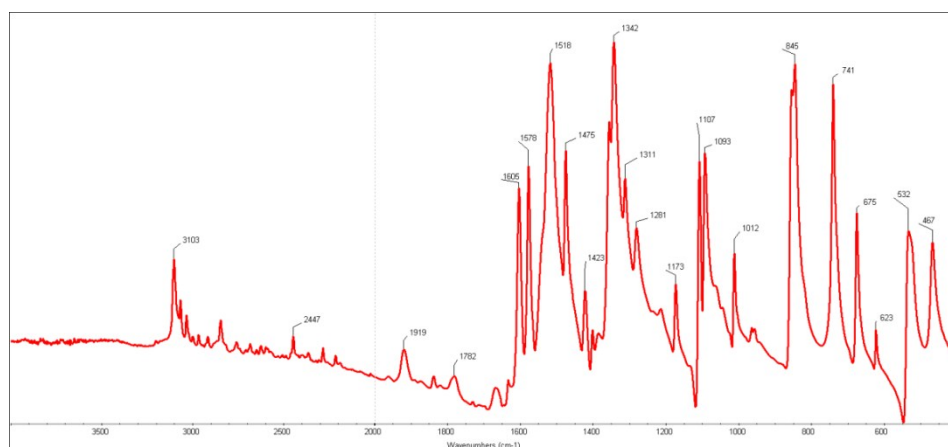
E-mail: [yuhm@tsinghua.edu.cn](mailto:yuhm@tsinghua.edu.cn)



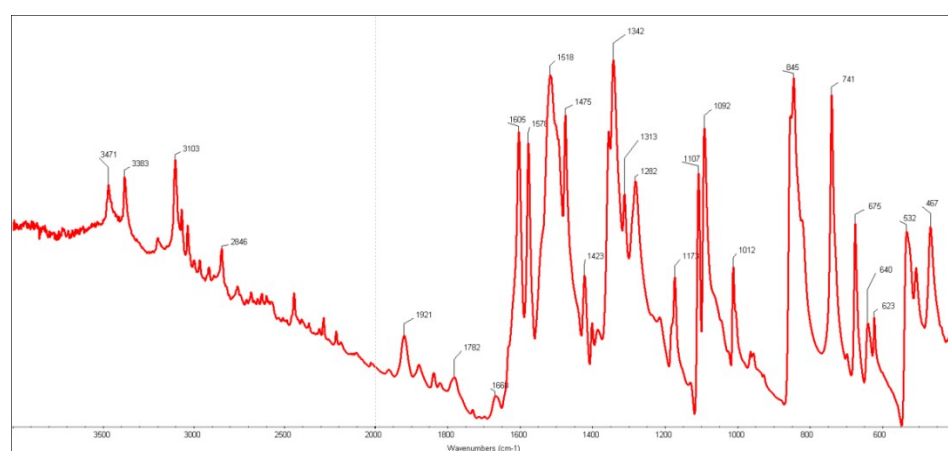
**Fig. S1** Affinity of the w-M13 viruses to various metal ions. The measuring method by ICP-OES was described in section 2.3. Experiments were performed in triplicate. The terminal sequence of the pVIII capsid protein of w-M13 is negatively charged AEGDDPAK.



(A)

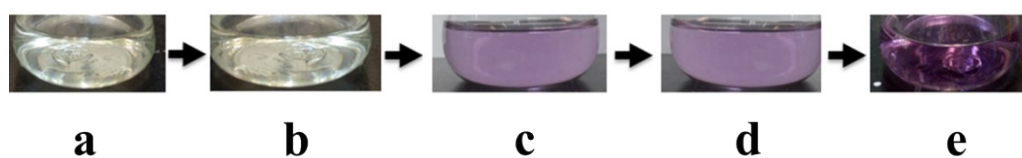


(B)



(C)

**Fig. S2.** Infrared spectrum of for *p*-CNB (A), *p*-CAN (B) and the reduction product of *p*-CNB after Fe-Ni@w-M13 reduction (C), respectively.



**Fig. S3** Potassium dichromate titration of the oxidized product of FeNPs after Fe-Ni@w-M13 reduction of *p*-CNB. With the drop by drop addition of  $C_{12}H_{10}NNaO_3S$ , the solution color was maintained transparent first(a→b), then turned into lavender (b→c), next stayed lavender for a while (c→d), finally turned into modena (d→e).

### Deduction of the ratio of FeNPs:NiNPs on the surface of w-M13

The initial concentration of Fe(II) ions was 2 mM and approximately 90% of the Fe(II) ions were adsorbed by pVIII protein (Fig. S1), that is to say, the actual concentration on w-M13 surface ( $C_{Fe^{2+}}$ ) was approximately 1.8 mM. So the amount of Fe(II) ions per w-M13 ( $n_{Fe^{2+}/M13}$ ) was

$$n_{Fe^{2+}/M13} = \frac{n_{Fe^{2+}}}{n_{M13}} = \frac{C_{Fe^{2+}} * V_{Fe^{2+}}}{n_{M13}}$$

From previous work,<sup>1-2</sup> the stable crystal form of FeNPs with size less than 10 nm was an icosahedron which contained 12 atoms in one unit cell, and the distance( $d_1$ ) between two iron atoms in the unit cell of FeNPs was 0.252 nm, so the volume of one unit cell of Fe( $V_{Fe-unit}$ ) was

$$V_{Fe-unit} = \frac{(15+5\sqrt{5})}{12} \times d_1^3 = \frac{(15+5\sqrt{5})}{12} \times (0.252nm)^3 \approx 3.49 \times 10^{-2} nm^3$$

The volume of one FeNP ( $V_{FeNP}$ ) was (the radius was obtained from Fig. 6C, and it was 2.8 nm in average)

$$V_{FeNP} = \frac{4}{3} \pi r^3$$

Therefore, the number of iron atom per FeNP( $n_1$ ) was

$$n_1 = \frac{V_{FeNP}}{V_{Fe-unit}} * 12$$

The number of FeNPs per w-M13( $n_{FeNPs/M13}$ ) was

$$n_{FeNPs/M13} = \frac{n_{Fe^{2+}/M13}}{n_1}$$

According to the ratio of Fe:Ni (element ratio) from TEM result (Fig. 6); therefore, the actual Ni(II) concentration on M13 surface( $C_{Ni^{2+}}$ ) was approximately 0.2 mM. The amount of Ni(II) ions per w-M13( $n_{Ni^{2+}/M13}$ ) was

$$n_{Ni^{2+}/M13} = \frac{1}{9} n_{Fe^{2+}/M13}$$

. From other researchers' work,<sup>3</sup> the crystal form of NiNPs with a size more than 4 nm was a face-centered cubic shape which contained four valid atoms in one unit cell, and the distance( $d_2$ ) between two nickel atoms in the unit cell of NiNPs was 0.352 nm, meaning that the volume of one unit cell of Ni( $V_{Ni-unit}$ ) was

$$V_{Ni-unit} = d_2^3 = (0.352nm)^3 \approx 4.36 \times 10^{-2} nm^3$$

. The size of NiNPs( $V_{NiNP}$ ) were close to FeNPs, so its volume was also approximately 92 nm<sup>3</sup>(Fig. 6). The number of nickel atom per NiNP( $n_2$ ) was

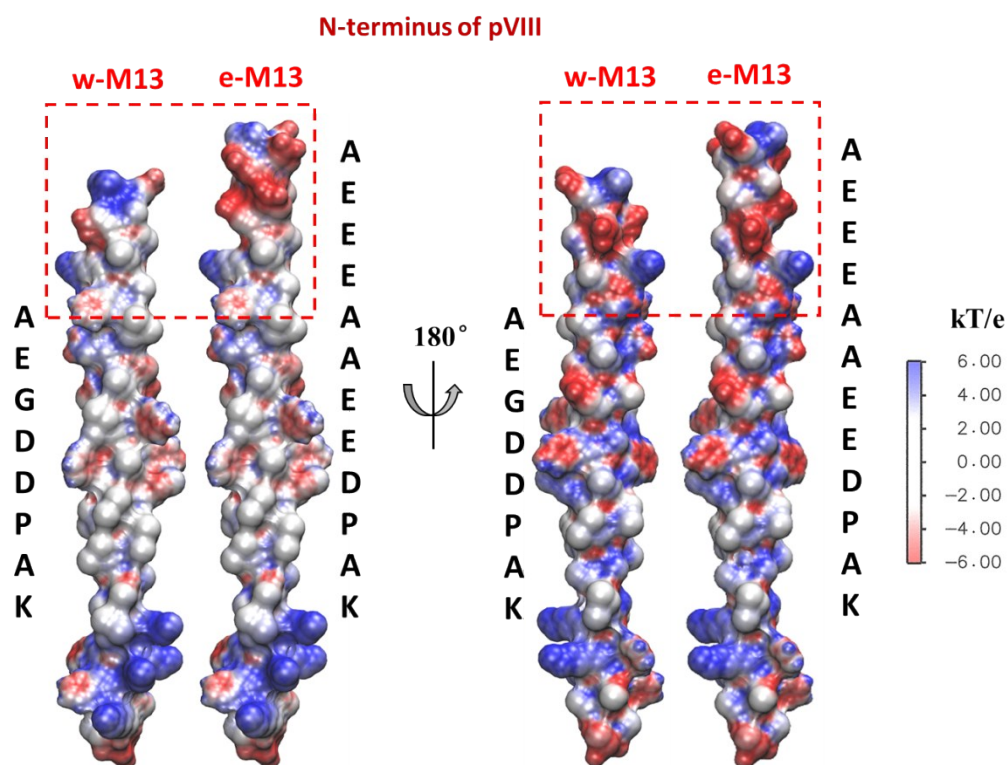
$$n_2 = \frac{V_{NiNP}}{V_{Ni-unit}} * 4$$

. The number of NiNPs per w-M13( $n_{NiNPs/M13}$ ) was

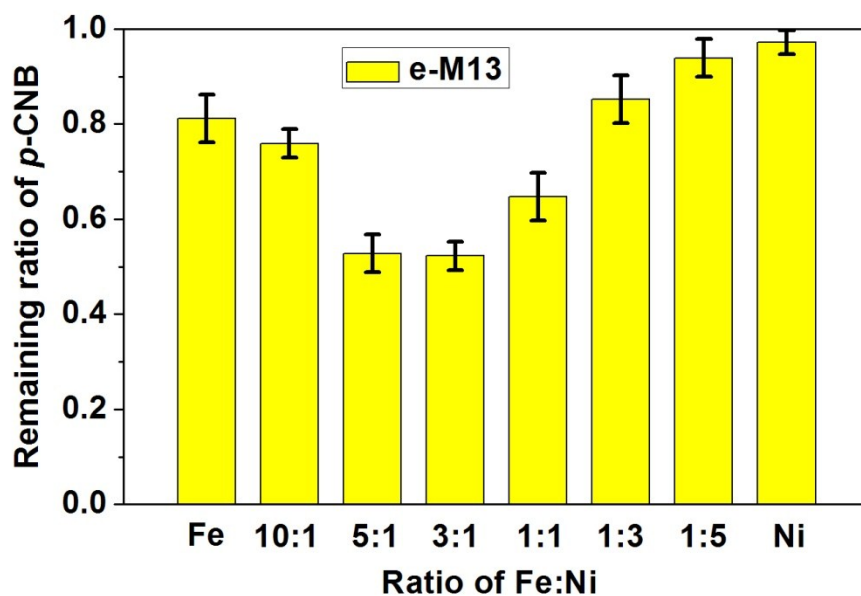
$$n_{NiNPs/M13} = \frac{n_{Ni^{2+}/M13}}{n_2}$$

. Finally, the ratio of FeNPs/NiNPs on the surface of w-M13( $R_{FeNPs:NiNPs}$ ) was:

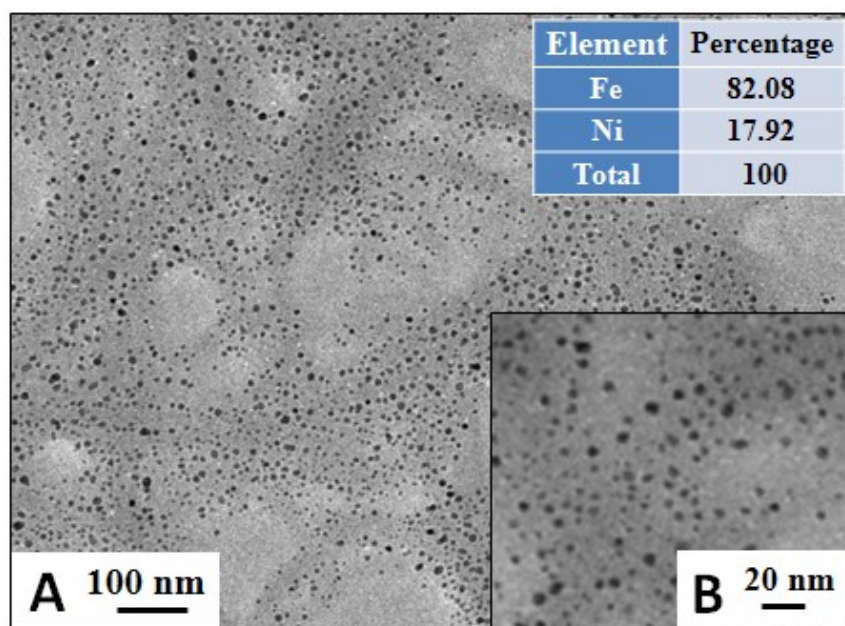
$$R_{FeNPs:NiNPs} = \frac{n_{FeNPs/M13}}{n_{NiNPs/M13}} = \frac{n_{Fe^{2+}/M13} / n_1}{n_{Ni^{2+}/M13} / n_2} = \frac{n_{Fe^{2+}/M13} / (\frac{V_{FeNP}}{V_{Fe-unit}} \times 12)}{\frac{1}{9} n_{Fe^{2+}/M13} / (\frac{V_{NiNP}}{V_{Ni-unit}} \times 4)} \approx \frac{9 \times 4 \times V_{Fe-unit}}{12 \times V_{Ni-unit}} \approx 2.40$$



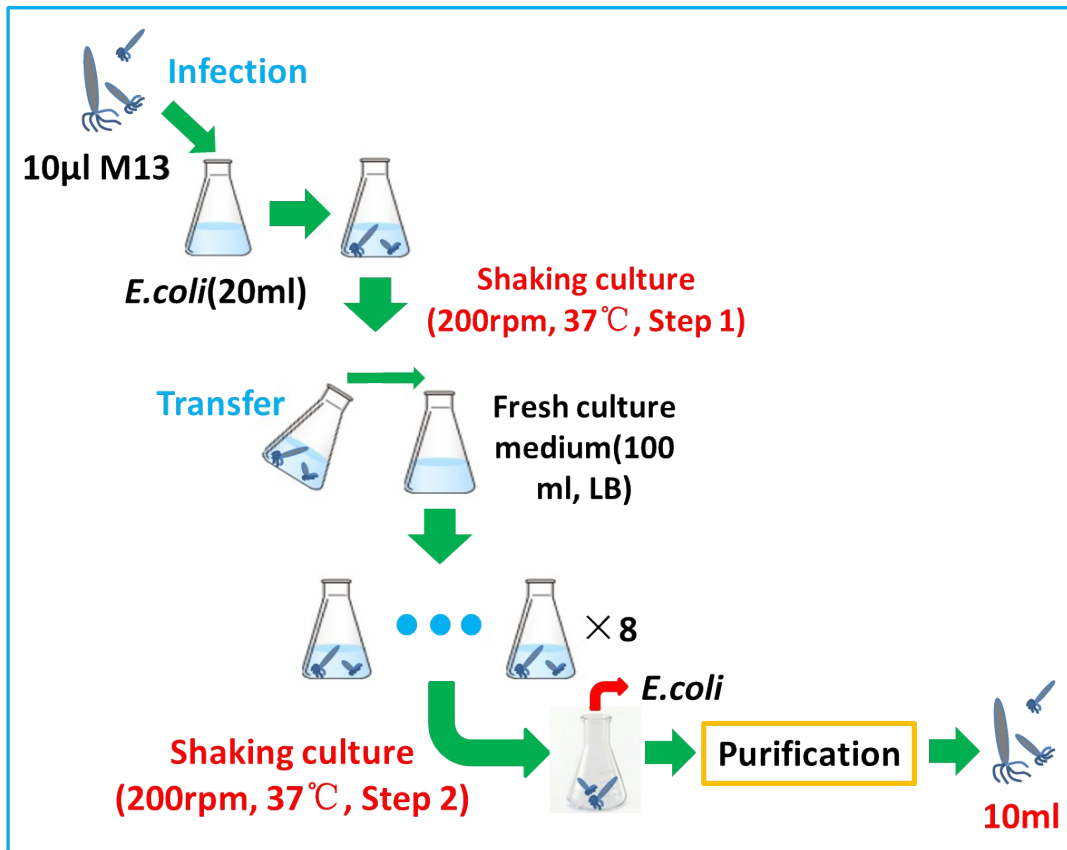
**Fig. S4** Electrostatic potential surfaces of pVIII proteins of M13. Solvent-accessible surfaces were calculated with a 1.4 Å solvent probe radius. Surface colorings are contoured over the same range for each structure (−6 to +69 kbT/ec). The N-terminal sequence of the wild-type and mutated pVIII proteins are AEGDDPA and AEEEEAEEDPA, respectively. The Electrostatic potential surfaces were constructed using visual molecular dynamics (VMD) software.<sup>4</sup>



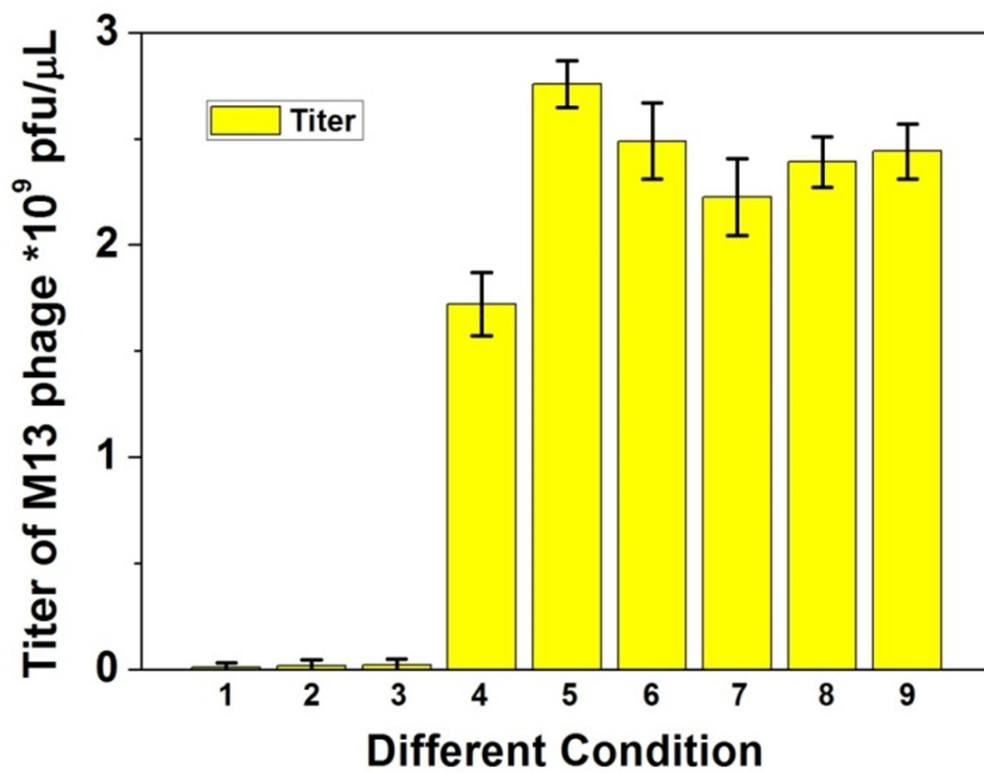
**Fig. S5** Reduction of *p*-CNB by Fe-Ni@e-M13 synthesized at different ratio of initial Fe(II):Ni(II) before NaBH<sub>4</sub> addition. Experiments were performed in triplicate. The initial concentration of Fe(II) was 2 mM.



**Fig. S6** Fe-Ni bi-nanoparticles synthesized on e-M13 supports. A, Fe-Ni nanoparticles were uniform in size, distributed along the e-M13. The ratio of the initial Fe(II):Ni(II) was 3:1. B, partial amplification of A. The element ratio of Fe:Ni was measured as 82.08:17.92.



A



B



**Fig. S7** The amplification cultures of the M13 phages. A, schematic process of M13 amplification (two cycles). After being infected by M13, the host *E.coli* ER2738 would be cultured and M13 would be released at some time. The mixture would be transferred into a larger-scaled culture medium after shaking for a while for amplification. The two processes continued for different hours, then, after purification (details could be seen in section 2.1), about 10ml phages stored in TBS solution could be obtained. B, optimization of the time for culturing of the M13 phages in two cycles of amplification. Condition 1 stands for 1 hour in Step1 and 3 hours in Step2; Condition 2, 1 hour in Step1 and 4 hours in Step2; Condition 3, 1 hour in Step1 and 5 hours in Step2; Condition 4, 2 hours in Step1 and 3 hours in Step2; Condition 5, 2 hours in Step1 and 4 hours in Step2; Condition 6, 2 hours in Step1 and 5 hours in Step2; Condition 7, 3 hours in Step1 and 3 hours in Step2; Condition 8, 3 hours in Step1 and 4 hours in Step2; Condition 9, 3 hours in Step1 and 5 hours in Step2. Under the optimal Condition 5, about  $2.8 \times 10^9$  pfu/ $\mu$ l M13 were obtained.

## References

- 1 T. Ling, H. M. Yu, Z. Y. Shen, H. Wang, J. Zhu, *Nanotechnol*, 2008, 19, 115608-115613.
- 2 T. Ling, J. Zhu, H. M. Yu and L. Xie, *The Journal of Physical Chemistry C*, 2009, 113, 9450-9453.
- 3 S. Illy, O. Tillement, F. Machizaud and J. M. Dubois, *Philos. Mag. A*, 1999, 79, 1021-1031.
- 4 W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graph.*, 1996, 14, 33-38.