


Effect of ethylene glycol as solvent on the composition and morphology of nickel phosphide

Lili Ren , Hanghui Xu

School of Chemical and Chemical Engineering, Southeast University, Nanjing, 211189, People's Republic of China

✉ E-mail: liliren@edu.cn

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Solvent, as one of the important factors, influences the composition and morphology of material during its preparing process. Ethylene glycol, as a good solvent, has good properties such as low toxicity, low cost, relatively high boiling point, good solubility and certain reducibility. Here, the work investigates the effect of ethylene glycol as the solvent on composition and morphology of nickel phosphide and find that the addition of ethylene glycol into aqueous solution will lead the composition of nickel phosphide from the pure Ni_2P phase to a mixture of Ni_2P and Ni_{12}P_5 , and the morphology from the close packed structure of nanoparticles to the loose structure.

1. Introduction: Transition metal phosphides (TMPs), as ‘quasi-platinum catalyst’, represent a class of materials that phosphorus atoms doping into the transition metal lattice, which could be widely used in various areas, such as hydrogenation reactions, magnetism, photonics and so on [1–9]. Among various TMPs, nickel phosphides have drawn great attention of researchers due to their plentiful various phases, such as Ni_2P , Ni_3P , Ni_5P_2 , Ni_{12}P_5 etc. So, it is an attractive and challenging subject to fabricate controlled phase or change morphology of nickel phosphide [10–14].

The solvent is one of the important factors influencing the phase and morphology of metal phosphides [15–19]. In the liquid synthesis, the solubility and transport behaviour of the precursor will be strongly affected by the properties of the solvent, which further leads to the change of the morphology, size, and phase of the final product. Xu *et al.* [15] reported that compared with water as a solvent, Bi_2WO_6 nanocrystals synthesised by ethylene glycol (EG) as solvent had a smaller particle size. Guo *et al.* [16] put forward that the different solvent induced the varied lateral structure sizes of bulk heterojunction films, which further resulted in the different device performance. Stuart *et al.* [20] reported that using different solvents could make sodium soap fibres having varying alkyl chain lengths. Oliveri *et al.* [21] investigated the solvent effects on the structure and morphology of molecular assembled nanostructures of a transition metal complex in the solid state, and found that the Lewis basicity, polarity, and volatility of the solvent controlled the molecular assembly of nano-architecture.

Normally, nickel phosphide is synthesised with water as a solvent. EG has low toxicity, low cost, relatively high boiling point, good solubility and certain reducibility. So, in this Letter, we investigated the change of the composition and morphology of nickel phosphide with the change of solvent from water to EG.

2. Experimental: The reagents we used are all analytical pure without further purification. Nickel phosphide was prepared using the following procedures. First moderate amount of nickel chloride was dissolved in deionised water under stirring, and a certain amount of red phosphorus according to the desired molar ratio of Ni and P was added and formed a slurry-like mixture with continuous stirring at room temperature for 20 min. Then the mixed solution was poured into a Teflon-lined stainless-steel autoclave, sealed and heated at 200°C for 12 h, then cooled naturally to room temperature. After centrifuging, washing and vacuum drying at 60°C for 6 h, the desired sample can be obtained.

X-ray diffraction (XRD) patterns were recorded on a D8 Discover diffractometer (Bruker) using $\text{Cu K}\alpha$ radiation with a nickel filter ($\lambda = 1.5406 \text{ \AA}$) at a respective voltage of 40 kV and generator current of 40 mA. The 2θ scans covered from 10° to 90° with a speed of 20° min^{-1} . Scanning electron microscopy (SEM) images were recorded on an FEI Inspect F50, equipped with an E-T secondary electron detector and an optional back scattering detector.

3. Results and discussion: In the reaction environment, different reaction solvents will lead to different structures and morphologies of the product. To investigate the influence of solvents on the reaction products, we mixed a certain amount of EG with water and analysed the composition and morphology of nickel phosphide. Fig. 1 shows the XRD patterns of the nickel phosphide prepared with different reaction solvents. When the pure water is used as the reaction solvent, Ni_2P is the single phase in the XRD patterns. When the EG and water mixture is used as the solvent, the product is Ni_{12}P_5 and Ni_2P mixed crystals, as shown in Figs. 1b–d. From the figure, we can also find that the greater proportion of EG in the solvent leads to the weaker Ni_2P characteristic peak. It indicates that when adding EG into the aqueous solution as the reaction solvent, the growth of Ni_{12}P_5 will be promoted.

Fig. 2 shows the SEM pictures of the samples prepared under different reaction solvents. From the pictures, we can easily find that by simply changing the solvent in the proportion of each component, the morphology of the products varies widely. When water is used as the reaction solvent, the product is made up of irregular nanoparticles, and the particle size varies from several microns to more than tens of microns. When the amount of EG and water is the same, the product shows large blocks with a certain thickness, its size is tens of microns and the surface is smooth. Then as the amount of EG continually increases the sample changes to a large hollow particle. From the illustration of Fig. 2c, it can be clearly seen that the inner part of the particle is a flake structure composed of small nanometre-sized particles. When the pure EG is used as the reaction solvent, the sample presents a porous sheet structure, and the flake structure is also accumulated by small nanoparticles, as shown in Fig. 2d.

Table 1 summaries the effect of solvent EG on the composition and morphology of nickel phosphide. When the reaction solvent is pure water, Ni_2P is the only phase and it is formed by the accumulation of nanoparticles. When EG is added, the product becomes two kinds of mixed crystals of nickel phosphides (Ni_2P and Ni_{12}P_5). As the content of EG is increased, the proportion of Ni_2P becomes

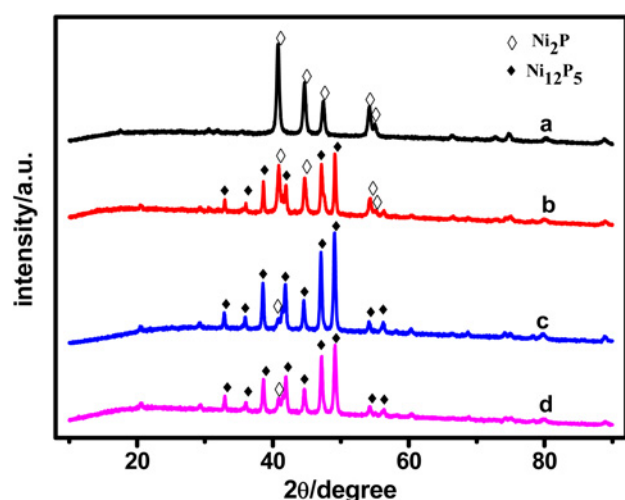


Fig. 1 XRD pattern of products at different reaction solvent (Ni/P = 1/10, $T = 200^\circ\text{C}$)
 a $V_{\text{EG}}/V_{\text{H}_2\text{O}} = 0:1$
 b $V_{\text{EG}}/V_{\text{H}_2\text{O}} = 1:1$
 c $V_{\text{EG}}/V_{\text{H}_2\text{O}} = 2:1$
 d $V_{\text{EG}}/V_{\text{H}_2\text{O}} = 1:0$

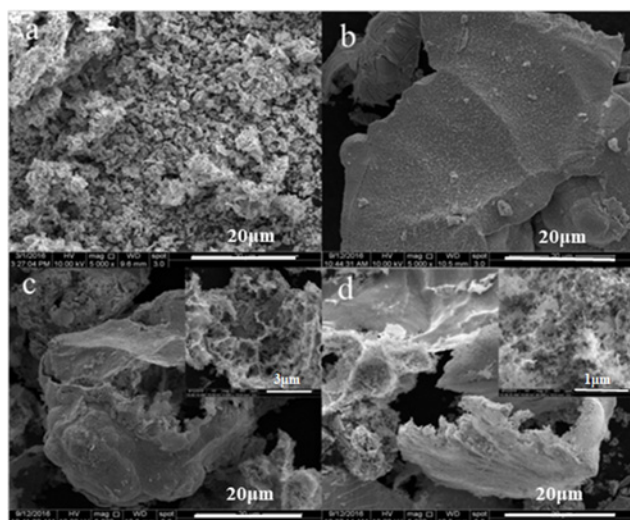


Fig. 2 SEM pictures of products at different reaction solvents (Ni/P = 1/10, $T = 200^\circ\text{C}$)
 a $V_{\text{EG}}/V_{\text{H}_2\text{O}} = 0:1$
 b $V_{\text{EG}}/V_{\text{H}_2\text{O}} = 1:1$
 c $V_{\text{EG}}/V_{\text{H}_2\text{O}} = 2:1$
 d $V_{\text{EG}}/V_{\text{H}_2\text{O}} = 1:0$

smaller and smaller and it presents an increasingly loose state. It is thought that the addition of EG increases the viscosity of the reaction solvent, which is more favourable for the formation of Ni₁₂P₅ under the reaction conditions. For the detailed transformation mechanism, please see Fig. 3.

The EG molecules on the outer surface of the particles play a decisive role in the formation of crystals with different shapes. As a chelating ligand molecule, EG can be easily chelated with Ni²⁺ ion on the crystal surface when it is adsorbed on small grains of hexagonal shape [22]. Since the Ni²⁺ ions at the edges and corners have more coordination positions than the Ni²⁺ ions at the crystal plane, the formation of the chelate coordination structure is favourable. Therefore, EG should be preferentially combined at the edges and corners of the crystal at lower concentrations,

Table 1 Effect of EG on composition and morphology of nickel phosphide (Ni/P = 1/10, $T = 200^\circ\text{C}$)

$V_{\text{EG}}/V_{\text{H}_2\text{O}}$	Reaction times, h	Product	Morphology
0:1	12	Ni ₂ P	nano particles
1:1	12	Ni ₁₂ P ₅ + Ni ₂ P	↓
2:1	12	Ni ₁₂ P ₅ + Ni ₂ P	
1:0	12	Ni ₁₂ P ₅ + Ni ₂ P	porous sheet

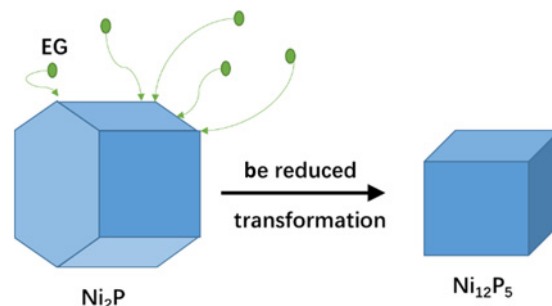


Fig. 3 Schematic diagram of Ni₂P crystalline phase transforming into Ni₁₂P₅ crystalline phase

which may be beneficial to the growth of the naked surfaces of the hexagonal phase and change the growth rate of different crystal planes, which further leads to the formation of the tetragonal phase. It is well known that EG also exhibits strong reducibility due to the presence of two hydroxyl groups [23]. Wang *et al.* have prepared high-quality quantum dots with EG than with water. They think EG can more easily accept the radicals than water because of its better reducibility, thus combining the features of good solvency and suitable viscosity. So, we think that the Ni metal ions in the solution will be reduced with the increase of EG concentration, and then the Ni₂P will gradually turn into Ni₁₂P₅ with weaker oxidation.

4. Conclusion: The reaction solvent can change the phase composition of products. The different reaction solvents lead to different crystal growth environments, which ultimately lead to the different composition and morphology of the nickel phosphide. The addition of EG into aqueous solution will lead the composition of nickel phosphide from the pure Ni₂P phase to a mixture of Ni₂P and Ni₁₂P₅, and the morphology from the close-packed structure of nanoparticles to the loose structure.

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6 References

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