ALCOHOL-MEDIATED SYNTHETIC APPROACH OF NANOMATERIALS: MECHANISM STUDY, MATERIALS PROPERTIES AND APPLICATIONS

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ABSTACT

Alcohol is a kind of common organic solvent with low cost, good accessibility, and low toxicity. Recently, alcohol-based synthesis of nanomaterials has been a very hot research topic due to their special advantages in realizing scalable controllable production of high-quality nanomaterials. In this thesis, alcohol-mediated synthesis of nanomaterials was focused on, and especial attention was paid to the different reaction mechanisms, material properties and related applications. Based on the types and roles of alcoholic solvents in the synthesis of materials, this thesis will be elaborated from three main aspects:

1) **Primary alcohol-mediated synthesis of inorganic materials**. Due to relatively simple and stable molecular structure, primary alcohols usually play two roles in material synthesis: the solvent and the reducing agent. In this part, the synthesis of two typical oxide semiconductors ZnO and TiO_2 were described. In the case of ZnO synthesis, the reaction system just involved the precursors and alcoholic solvent, and it was found that the morphology of ZnO can be determined by the type of precursors in which nanorods and nanoparticles can be well obtained. In the synthesis of TiO_2, $TiCl_4$ was used as the precursors, and it was found that the size of TiO_2 particles was strongly dependent on the type of alcoholic solvents. The products obtained from primary alcohol usually show much bigger size than for secondary alcohol, tertiary alcohol, benzyl alcohol.

2) **Polyol-mediated synthesis of inorganic materials**. Distint from primary alcohols, polyols usually have higher boiling point, better dissolving ability to inorganic salts and stronger bond with metal ions, and thus polyol synthesis is a more popular synthetic method. In this part, a two-step injection polyol method was first used for the preparation of silver nanowires. This method can easily realize rapid controllable high-concentration synthesis of silver nanowires. The aspect ratio of silver nanowires can be well controlled by adjusting the experimental parameters. The mutual attachment of silver nanowires was found in such high-concentration synthesis

and play an important role in controlling the growth of silver nanowires. Subsequently, as-prepared silver nanowires were used as basic unit to build macroscale transparent conductor. A new PEO-assisted solution-processed film-making method was first adopted to prepare nanowires-based PEO composite film on flexible PET substrate. Then PEO was *in-situ* thermal removed by low-temperature heat treatment attributed to easy thermal decomposition of PEO. As-prepared silver nanowires film show excellent stability, good light transmission and outstanding conductivity. A layer of PES was further coated on the surface of silver nanowires to stabilize the structure. The electromagnetic interference shielding effect (EMI SE) of PES/silver nanowires/PET sandwiched structured film was investigated. It was found that, when light transmission is above 80%, EMI SE was still above 25dB, which is much better than commercial application standard.

3) **Tertiary alcohol and benzyl alcohol-mediated synthesis of inorganic materials**. In this part, the differences of tertiary alcohol and benzyl alcohol from primary alcohol and polyols in physicochemical properties were elaborated. Due to better stability of carbocation, tertiary alcohol and benzyl alcohol exhibit stronger carbon-oxygen dissociative propensity and thus stronger chemical reactivity with nucleophilic agents. Due to the easier leaving of hydroxyl group, these alcohols can better play the supplier of oxygen in the synthesis of metal oxides. Generally, the reactions can be classified into two types: S_N1 reaction and E1 reaction. In benzyl alcohol-based synthesis, a series of oxide nanoparticles were prepared. S_N1 mechanism can be used to well explain the reaction process. It is the first detailed description of S_N1 mechanism for the synthesis of inorganic materials. Different from S_N1 reaction in benzyl alcohol route, E1 reaction was dominant in tertiary alcohol-mediated synthesis. The products obtained from the two approaches showed excellent dispersibility in some polar solvents and suited to being incorporated into polymer or other matrix for diverse applications. Also, these oxides can show good applied potential in optoelectronics, photocatalysis, energy storage, and so on, of which the photocatalytic performance of ZnO assembled structures was investigated especially as a case.

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