Functional trialkoxysilane mediated rapid synthesis of noble metal nanoparticles and their multimetallic analogues for catalytic applications

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DOCTOR OF PHILOSOPHY

By

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Summary

The thesis entitled "**Functional trialkoxysilane mediated rapid synthesis of noble metal nanoparticles and their multimetallic analogues for catalytic applications**" has been divided into five chapters.

- General introduction
- Trialkoxysilane-functionalized monometallic, bimetallic, and trimetallic noble metal nanoparticles mediated non-enzymatic sensing of glucose by resonance Rayleigh scattering
- Functional trialkoxysilane mediated controlled synthesis of fluorescent gold nanoparticles and fluoremetric sensing of dopamine
- Trialkoxysilane-functionalized synthesis of mesoporous supported palladium-nickel nanocatalyst for selective hydrazine decomposition and sensing
- Synthetic incorporation of palladium-nickel bimetallic nanoparticles within mesoporous silica/silica nanoparticles as efficient and cheaper catalyst for both cationic and anionic dyes degradation

Chapter 1

The first chapter gives a brief overview of noble metal nanoparticles and a discussion of the conventional methods for noble metal nanoparticle synthesis. The various sizes and shapes of noble metal nanoparticles, as well as their properties and applications, have been investigated in this chapter. Furthermore, the analytical behaviour of these noble metal nanoparticles in terms of their physical and chemical properties has been extensively studied. The significance of multimetallic analogues over monometallic noble metal nanoparticles has been discussed briefly. Throughout the chapter, the justification for utilizing trialkoxysilane as a nanomaterial stabiliser is explored. The introductory chapter also discusses the properties of trialkoxysilane, specifically 3-APTMS, which make it a useful material for functionalization.

Chapter 2

Chapter 2 addresses the microwave-assisted controlled synthesis of noble metal nanoparticles using 3-APTMS and 3-GPTMS as reducing, stabilising, and structure-directing agents that influence the geometry and crystallinity of noble metal nanoparticles. By changing the amount of functional trialkoxysilane, the particle size of noble metal nanoparticles was regulated. Under controlled concentrations of trialkoxysilane, large nanostructures are transformed into tiny spherical particles. This chapter discusses the synthesis of monometallic nanoparticles such as AuNPs, AgNPs, and PdNPs in a homogeneous solution, as well as bimetallic nanoparticles such as Au-Ag, Au-Pd, and Ag-Pd, and trimetallic nanoparticles such as Au-Ag-Pd. The presence of different sizes of noble metal nanoparticles was revealed by TEM microscopy, which supported the size of synthesised noble metal nanoparticles. XRD measurements revealed the crystalline nature of noble metal nanoparticles. Noble metal nanoparticles have the potential to be used in fluorescence-based applications. This chapter used several noble metal nanoparticles to present a synchronous fluorescence-based glucose sensor. When compared to other noble metal nanoparticles, synchronous fluorescence intensity data showed that gold and palladium (metal ratio of 80:20) have enhanced catalytic non-enzymatic sensing of glucose. The specific changes in the intensity of synchronous fluorescence emission for various noble metal nanoparticles were also investigated.

Chapter 3

Chapter 3 describes the successful synthesis of fluorescent gold nanoparticles were successfully synthesized using a controlled concentration of 3-APTMS and 3-GPTMS. The size of the synthesized fluorescent gold nanoparticles was confirmed by TEM microscopy, which revealed the average particle size was 6 nm. EDX analysis confirmed the prepared fluorescent gold nanoparticles were composed of Au and Si. In the XRD spectrum, plane (111) has shown high intensity and some other planes were observed with low intensity, confirmed the crystalline nature of fluorescent gold nanoparticles. The chemical bonding present in NMNPs, their elemental state, and composition were further determined by the XPS analysis. Furthermore, the optical properties of synthesized fluorescent gold nanoparticles were analyzed which exhibited blue fluorescence at the excitation wavelength of 365 nm under UV light along with a CIE co-ordinate index (0.16, 0.28). Moreover, the as-prepared fluorescent gold nanoparticles demonstrated QY up to 13% using quinine sulfate as a reference. Application of synthesized fluorescent gold nanoparticles for DA detection with excellent sensitivity and selectivity for clinical applications.

Chapter 4

Functional trialkoxysilane containing an amino-glycidoxy moiety was used to synthesize the pair of monometallic (AuNPs-1 and AuNPs-2) and bimetallic (Pd-Ni NPs-1 and Pd-Ni NPs-2) nanomaterials. Monometallic and bimetallic nanomaterials have been demonstrated to be effective for sensing and decompose hydrous hydrazine, respectively. A concentration-dependent enhancement in resonance Rayleigh scattering is enabled by these materials, which might lead to the detection of hydrazine hydrous in water. The size of the synthesized gold nanoparticles (AuNPs-1 and AuNPs-2) was measured by TEM microscopy, which revealed the average particle size was 9 nm and 17 nm, respectively. Further, it was tested for hydrous hydrazine recognition using synchronous fluorescence spectroscopy, resulting in AuNPs-1 having greater catalytic efficiency for detection of hydrous hydrazine than AuNPs-2. Furthermore, Pd-Ni NPs-1 and Pd-Ni NPs-2 have been used to decompose hydrous hydrazine. A study conducted by EDX has shown that the Pd-Ni NPs 1 and 2 had a 1:1 and 1:5 ratio of

Pd to Ni metal, respectively. Therefore, the Pd-Ni NPs-1 exhibit a higher decomposition rate for hydrous hydrazine, which could be explained by their surface area.

Chapter 5

Chapter 5 is the study of palladium and palladium-nickel bimetallic nanocrystallite-supported mesoporous silica/mesoporous silica nanoparticles (MSPs/MSNPs) synthesized at a fixed ratio of Pd/Ni by functional trialkoxysilane-mediated reduction of palladium cations. Bimetallic Pd-Ni NPs-1 and Pd-Ni NPs-2 nanocrystallites with metal ratios of 1:1 and 1:5 are stabilised and assembled using the functional trialkoxysilane as a template. A TEM microscope was used to measure the particle size of the synthesized Pd and Pd-Ni NPs-1. The average particle size was 6 nm and 9 nm, respectively.The elemental mapping of the synthesised Pd and Pd-Ni nanocrystallite confirmed the presence of respective elements in the nanocrystallite, and EDX analysis confirmed the composition of Pd, Si, and Pd, Ni, Si, respectively. An XRD spectrum confirmed the crystalline nature of Pd and Pd-Ni nanocrystallite. According to an XRD spectrum, Pd and Pd-Ni nanocrystallite are crystalline. Both cationic and anionic dyes, such as Congo red and Rh B, have been degraded using these nanocrystallite supported MSPs/MSNPs. The degradation of 15 ppm Rh B within 50 s as compared to that of mesoporous silica within 110 s under similar conditions is justified by the nanocrystallite inserted MSNPs of diameter 200 nm, with a rate constant to the order of 6.9×10^{-2} s^{-1}, as opposed to that for MSPs of 50 m to the order of 3.2×10^{-2} s^{-1}. An analogous observation has been made for the degradation of (Rh B). The heterogeneously supported nanocrystallite continues to exhibit 100% catalytic activity even after five further applications.

Future projection

The potential role of trialkoxysilane-based noble metal nanoparticles has been investigated in this Ph.D. thesis. In order to analyze the flexibility of the fabricated materials, we carried out detailed investigations involving many different aspects in order to analyse the capabilities of the system. Organically functionalized alkoxysilanes (APTMs, GPTMS) were used as stabilisers, reducing agents, and secondary capping agents for the homogenous and heterogeneous phase synthesis of noble metal nanoparticles, along with variable concentrations of metal precursor. Functional trialkoxysilane together with a stablizer effectively controlled the morphological properties, promoting the directional growth of nanoparticles. This allowed the use of NMNPs as template-based multifunctional nanoparticles. Further, amino groups of functionalized noble metal nanoparticles reacted actively with foreign molecules to produce a class of nanohybrids and microscale composites. These nanoparticle model systems have shown promising catalytic properties for a number of reactions, as well as improved selectivity and efficiency.

However, there are considerable challenges to adopting these techniques as reliable tools in order to assure that the real-time demands of the catalyst can be met. NMNPs functionalised with trialkoxysilane have been shown to be a good alternative to those prepared via conventional routes. However, an even better system requires more technical analysis to be implemented for significant practical purposes. To achieve high sensitivity, the next step will be to develop more catalytically efficient models of nanoparticles. In addition, studies on heterogeneous matrix based on the stabilization and enhancement of nanoparticle catalytic activity are currently underway and will be concluded in the near future. Several studies of zeolites in the context of catalytic synthesis concluded that they are highly crystalline and porous in nature, and exhibit metal ions oriented along their axes, which facilitate the alignment of nanoscale particles. By confining functionalized nanoparticles in a mesoporous silica matrix, more nanodimensional metal particles can be accommodated while further controlling agglomeration possibilities. A heterogeneous silica matrix with cavities allows for the exposure of both mono-and multi-metallic nanoparticles or those in bulk to catalysed reactions. As a mesoporous silica-based solid matrix, nanoparticles bound within it will interact highly with the solid matrix. This interaction may lead to more application-oriented nanoparticles that are also commercially viable. The present work is being further extended by considering the advantages of immobilizing metal nanoparticles in aluminosilicate networks and mesoporous materials for their possible applications.