

Research Article

Green Synthesis of Ag and Pd Nanospheres, Nanowires, and Nanorods Using Vitamin B₂: Catalytic Polymerisation of Aniline and Pyrrole

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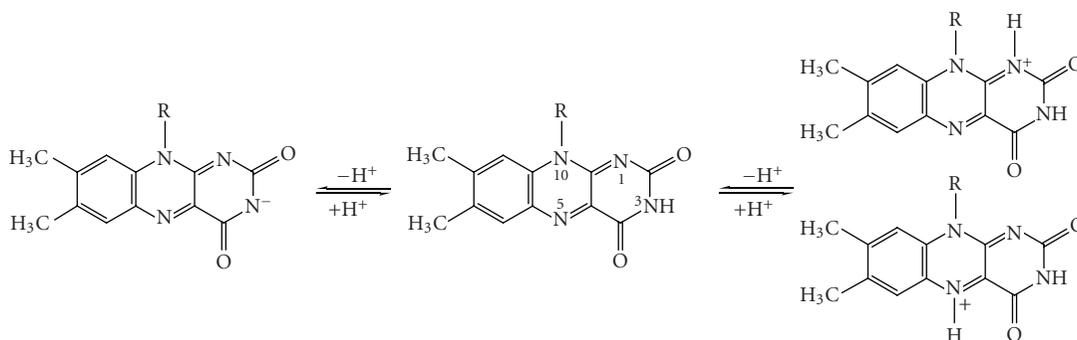
For the first time, we report green chemistry approach using vitamin B₂ in the synthesis of silver (Ag) and palladium (Pd), nanospheres, nanowires, and nanorods at room temperature without using any harmful reducing agents, such as sodium borohydride (NaBH₄) or hydroxylamine hydrochloride and any special capping or dispersing agent. Vitamin B₂ was used as reducing agent as well as capping agent due to its high-water solubility, biodegradability, and low-toxicity compared with other reducing agents. The average particle size of nanoparticle was found to be Ag (average size 6.1±0.1 nm) and Pd (average size 4.1±0.1 nm) nanoparticles in ethylene glycol and Ag (average size 5.9±0.1 nm, and average size 6.1±0.1) nanoparticles in acetic acid and NMP, respectively. The formation of noble multiple shape nanostructures and their self assembly were dependent on the solvent employed for the preparation. When water was used as solvent media, Ag and Pd nanoparticles started to self-assemble into rod-like structures and in isopropanol Ag and Pd nanoparticles yielded wire-like structures with a thickness in the range of 10 to 20 nm and several hundred microns in length. In acetone and acetonitrile medium, the Ag and Pd nanoparticles are self-assembled into a regular pattern making nanorod structures with thicknesses ranging from 100 to 200 nm and lengths of a few microns. The so-synthesized nanostructures were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) analysis, and UV spectroscopy. The ensuing Ag and Pd nanoparticles catalyzed the reactions of aniline and pyrrole to generate polyaniline and polypyrrole nanofibers and may find various technological and biological applications. This single-step greener approach is general and can be extended to other noble metals and transition metal oxides.

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1. INTRODUCTION

Recently, much effort has been devoted to the controlled synthesis of nanostructured materials because of their unique chemical and physical properties that are different from those of the bulk materials [1]. Particularly, metal nanomaterials have attracted considerable attention because of their unique magnetic, optical, electrical, and catalytic properties and their potential applications in nanoelectronics [2]. Hierarchical assembly of solution-based nanocrystals as building blocks is of great interest because of their potential in controlling morphologies of nanostructures, and hence their properties [3–6] wherein structured nanoparticle assemblies such as wires, rings, and superlattices, can be prepared [7–

13]. However, the challenge of synthetically controlling particle shape had limited success. Nevertheless, some physical and solid state chemical methods have been developed for making semiconductor, metal nanowires, nanobelts, and nanodots [14–18] in addition to wet-chemical methods [19–26]. Presently there are some methods available for making rods with controllable aspect ratio using seeding approaches [27], electrochemical and membrane-templated syntheses [28–30]. In solution phase, pH-dependent assembly of gold nanorods [31] and streptavidin-linked nanorods [32] is possible but requires elevated temperatures and, in most cases they afford poor yield of desired particle shape. Thus, the developments of bulk solution synthetic methods that offer shape control are very desirable to realize the full potential



SCHEME 1: Structure of anionic (left), neutral (center), and cationic (right) vitamin B₂ species in the fully oxidized redox state (R = -CH₂(CHOH)₃CH₂OH).

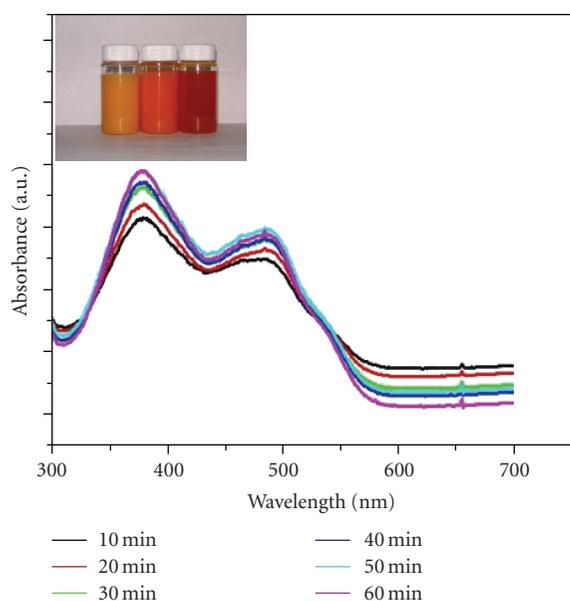


FIGURE 1: Reaction of vitamin B₂ with silver nitrate over the time in water media. The inset figure shows control vitamin B₂ (from left), reduced silver nanoparticles in water, and NMP solvent media after 60 minutes.

of these materials. Herein, we report a simple strategy using different solvents under which noble metal nanoparticles effectively self-assemble into spheres, nanowires, and nanorods in presence of vitamin B₂ (Riboflavin) and the ensuing self-assembled Ag and Pd nanoparticles can catalyze monomers such as pyrrole and aniline to afford conducting polymer nanocomposites. The study also serves the need for a greener protocol as there is a renewed interest in using green chemistry to synthesize metal nanoparticles [6, 33]. Green chemistry is the design, development, and implementation of chemical products and the process to reduce or eliminate the use and generation of substances hazardous to human health and the environment [34–37]. Strategies to address mounting environmental concerns with current approaches include the use of environmentally benign solvents, biodegradable polymers, and nontoxic chemicals [34–37]. In the synthesis of metal nanoparticles by reduction of the corresponding

metal ion salt solutions, there are three areas of opportunity to engage in green chemistry: (i) choice of solvent, (ii) the reducing agent employed, and (iii) the capping agent (or dispersing agent). In this area, there has also been increasing interest in identifying environmentally friendly materials that are multifunctional. For example, the vitamin B₂ used in this study functions both as a reducing and capping agent for Ag and palladium nanostructures, in addition to its high-water solubility, low toxicity and biodegradability; and water serves as a benign media. Herein, we describe a general method to prepare noble nanostructures such as Ag and Pd and their catalytic application to make polyaniline and polypyrrole nanofiber nanocomposites. This greener and general approach used to produce multiple shaped nanostructures such as Ag and Pd and their nanocomposites could find newer technological and medicinal applications.

2. EXPERIMENTAL PROCEDURE

All reagents were used as received without further purification. Vitamin B₂ (Riboflavin), silver nitrate (99.99%), and palladium chloride (99.99%) were purchased from Aldrich. In all experiments, Milli-Q water was used. The synthesis and self-assembly were accomplished by reacting respective metal salts with vitamin B₂ dissolved in solvents of different chemical nature. The reaction mixture was allowed to stand for 24 hours at room temperature and then analyzed. In particular, 50 mg of Riboflavin was dissolved in 20 mL (glass vial) of solvents such as ethylene glycol, acetic acid, *N*-methylpyrrolidinone (NMP), water, isopropanol, acetone, and acetonitrile in separate experiments. To this, 2 mL of aqueous solution containing 1×10^{-1} M AgNO₃ were added at room temperature, hand-shaken for a minute and allowed to settle. The solution turned orange immediately after the addition of AgNO₃ and the formation of silver nanoparticles was confirmed using UV spectroscopy and energy dispersive X-ray analysis (EDX). Similarly, experiments were conducted using 1×10^{-1} M PdCl₂. TEM specimens were prepared by placing 1 μ L of the particle solution on a carbon-coated copper grid and dried at room temperature. Transmission electron microscopy (TEM) was performed with a JEOL-1200 EX II microscope operated at 120 kV.

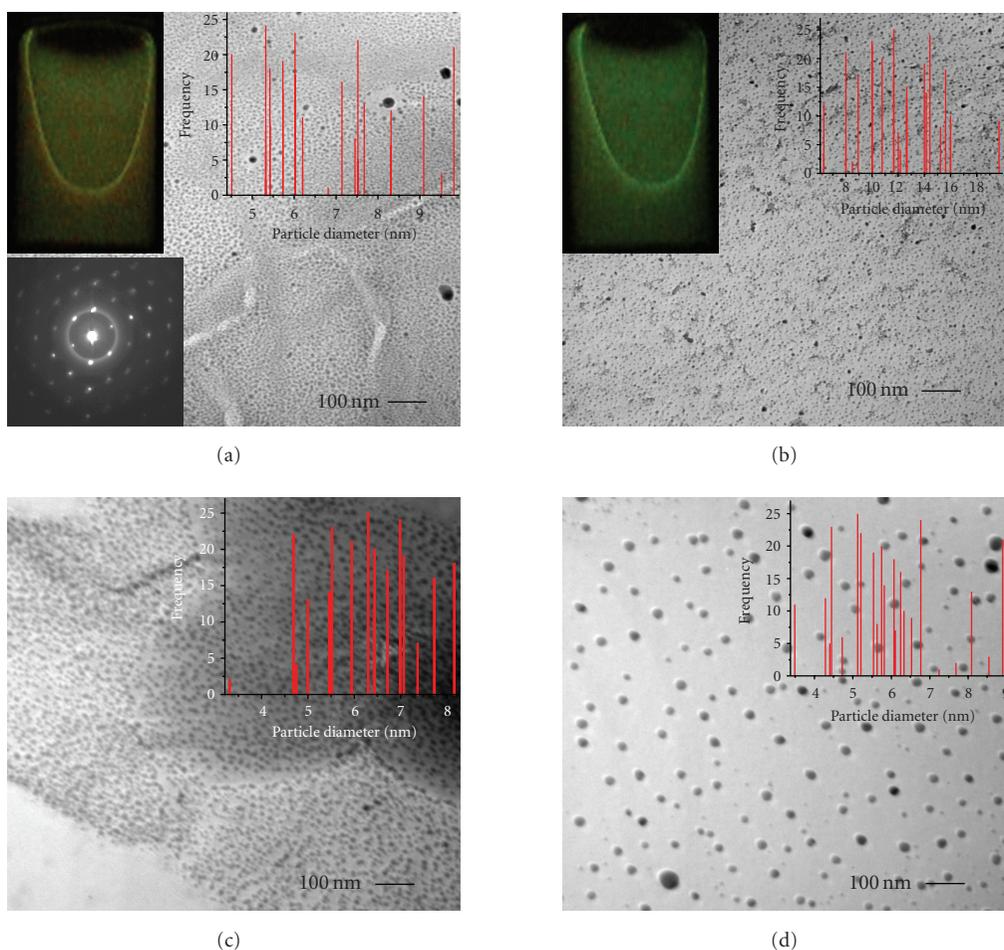


FIGURE 2: TEM image of Ag and Pd nanoparticles synthesized using vitamin B₂. (a) Ag (average size 6.1 ± 0.1 nm), (b) Pd (average size 4.1 ± 0.1 nm) nanoparticles in ethylene glycol, and (c), (d) Ag (average size 5.9 ± 0.1 nm, and average size 6.1 ± 0.1 nm) nanoparticles in acetic acid and NMP, respectively. Inset shows corresponding particle size distribution, electron diffraction, and UV excitation.

3. RESULTS AND DISCUSSION

Vitamin B₂ is the most frequently encountered organic cofactor in nature and it can assume three different redox states: fully oxidized, one-electron reduced, and fully reduced [38]. Each of these redox states exists in a cationic, neutral, and anionic form (see Scheme 1) depending on the pH of the solution. The reduction potential of vitamin B₂ is -0.3 V versus SCE [39] which is sufficient to reduce palladium (Pd, reduction potential 0.915 V versus SCE) and silver (Ag, 0.80 V versus SCE).

The formation of noble nanostructures with vitamin B₂ probably occurs as follows: (i) vitamin B complexation with noble metal salts; (ii) simultaneous reduction of noble metal salts such as Ag (Ag, 0.80 V versus SCE) and Pd (Pd, reduction potential 0.915 V versus SCE) and formation of capping with oxidized vitamin B₂; (iii) solvent chemical nature with self-assembly of nanoparticles to form spheres, nanowires, and nanorods. The reaction of respective metal salts with vitamin B₂ in different solvents resulted in the reduction of metal and simultaneous oxidation and capping of vitamin B₂

as confirmed by UV spectroscopy (see Figure 1 for Ag). The increase in intensity over the time indicates the completion of the reaction. Plasmon absorption spectroscopy is usually used to examine the size- and shape-controlled nanoparticles because of their optical properties in aqueous suspensions related to these properties [40]. For example, the UV-vis spectrum for the colloidal solution of spherical Ag nanoparticles prepared shows a peak at approximately 375 nm. This broad extinction peak potentially results from inhomogeneity in morphology for the sample [40]. However, the plasmon absorption peak of the nanorods showed a more complex absorption pattern due to the absorption of visible light both along the length of the nanorods (the longitudinal plasmon band) and along the width of the nanorods (the transverse plasmon band). As the aspect ratio increases, the longitudinal surface plasmon resonance (SPR) band (λ_1) should be red-shifted significantly, whereas the transverse SPR (λ_T) band should only show a slight blue-shift [40].

The size of the Ag and Pd nanoparticles decreased with use of ethylene glycol and acetic acid. Solvents such as ethylene glycol yielded nanoparticles with average sizes of

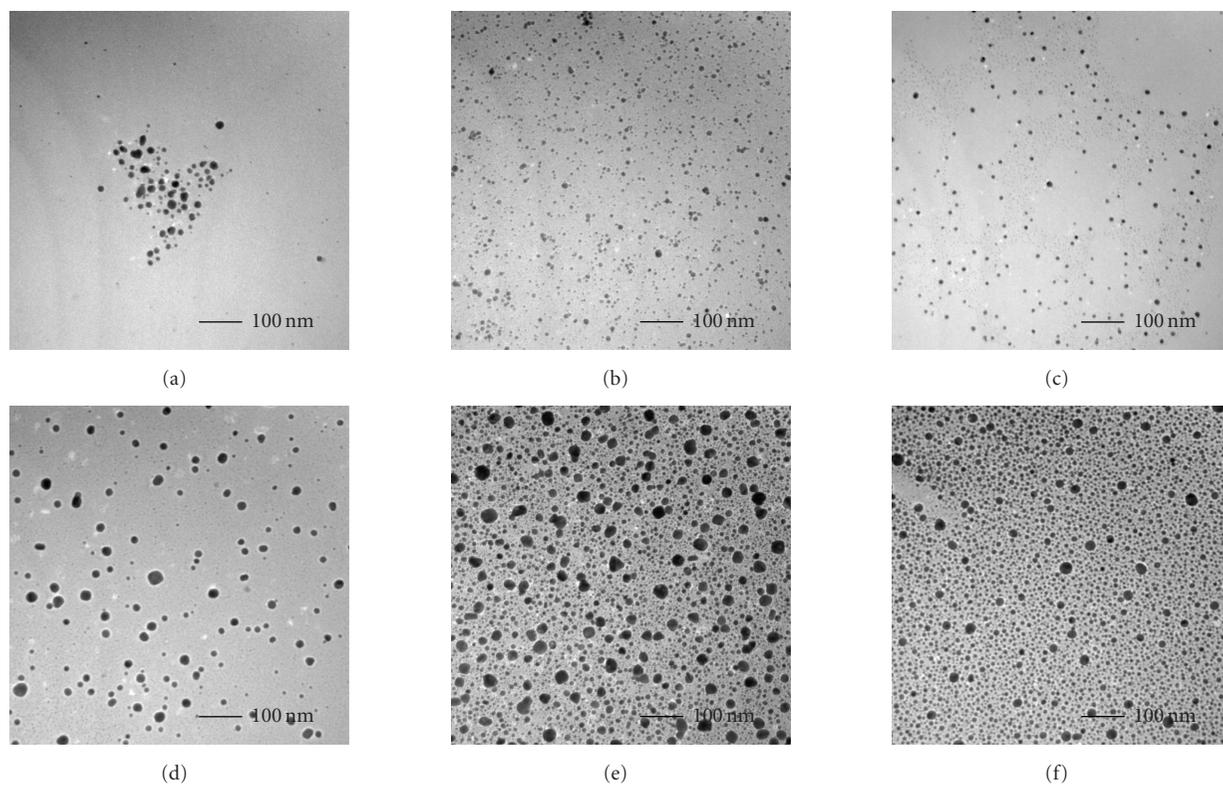


FIGURE 3: TEM micrographs of (a)–(c) Ag nanoparticles and (e), (f) Pd nanoparticles synthesized using vitamin B₂ in acetic acid, ethylene glycol, and NMP with sucrose as a capping agent, respectively.

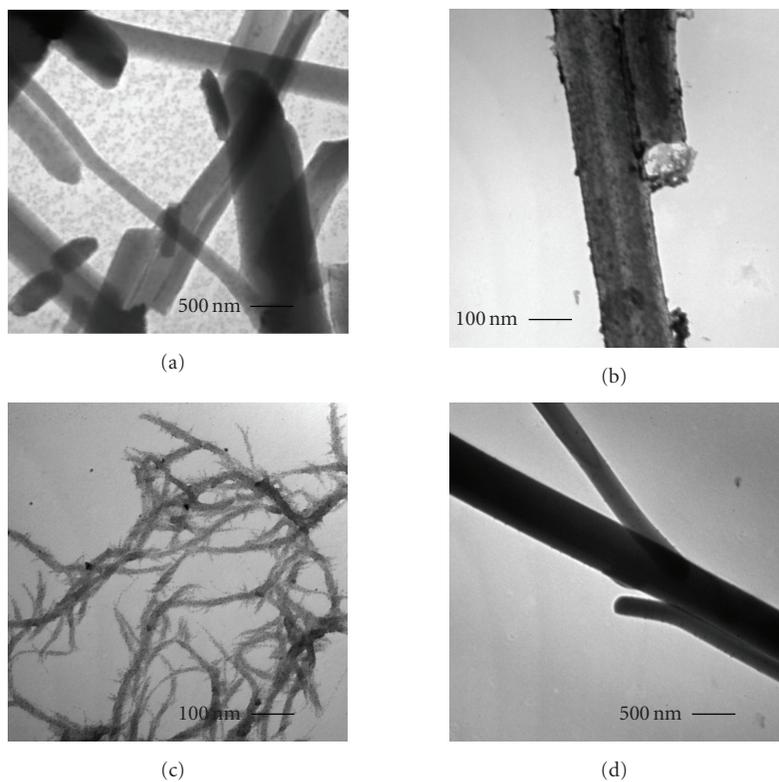


FIGURE 4: TEM micrographs of (a), (b) Ag and Pd nanostructures synthesized using vitamin B₂ in water and (c), (d) in isopropanol, respectively.

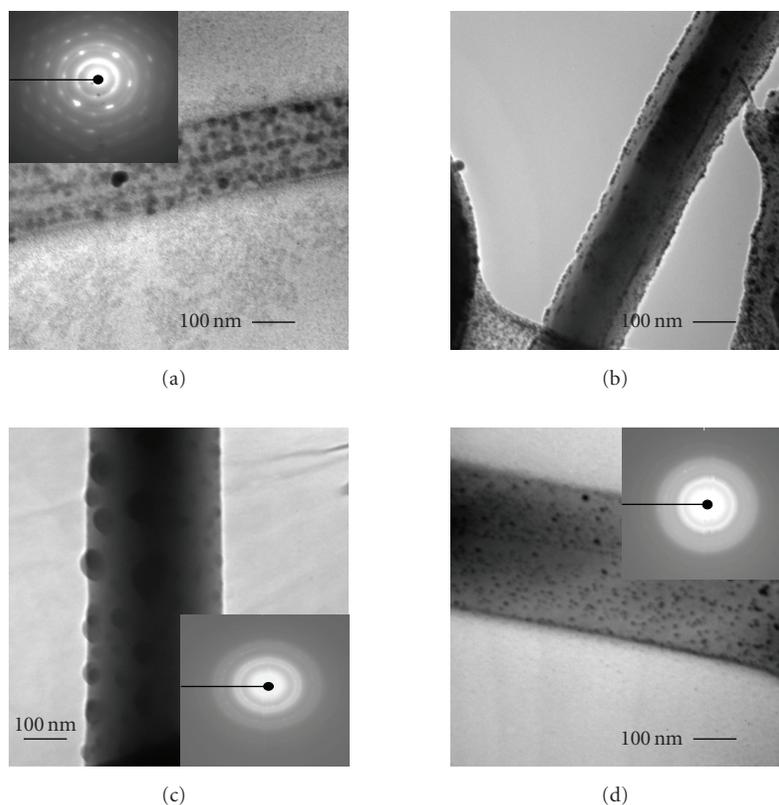


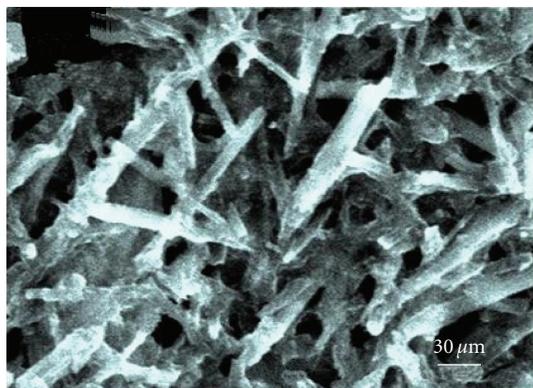
FIGURE 5: TEM image of self-assembled Ag and Pd nanowires/nanorods synthesized using vitamin B₂. (a), (b) Ag and Pd nanorods in acetone and (c), (d) Ag and Pd nanowires/nanorods in acetonitrile. Inset shows corresponding selected area electron diffraction patterns.

6.1 ± 0.1 nm for Ag (Figure 2(a)) and 4.1 ± 0.1 nm for Pd (Figure 2(b)). Acetic acid afforded nanoparticles ranging from 3 to 8 nm with an average of 5.9 ± 0.1 nm for Ag (Figure 2(c)) and 1 to 7 with an average size of 4.1 ± 0.1 nm for Pd (see Supplementary Material 1 Available online at doi:10.1155/2008/782358). Changing solvent, for example, using *N*-methylpyrrolidinone (NMP), yielded nanoparticles ranging from 3 to 9 nm with an average of 6.1 ± 0.1 nm for Ag (Figure 3(d)) and 5 to 13 nm with an average of 9.2 ± 0.2 nm for Pd (see Supplementary Material).

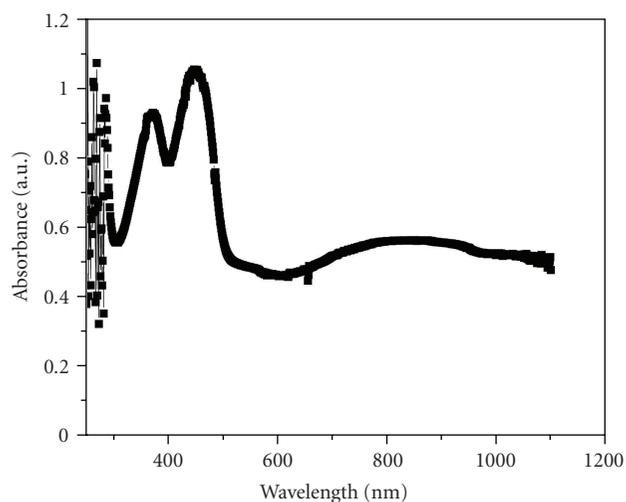
Solvents such as ethylene glycol, acetic acid, and NMP are not mere solvents but can modify the reaction conditions by virtue of their reducing character and pH, and so forth, and thereby change size and shape of the particles. For example, ethylene glycol is essentially a reducing agent and can help to reduce noble salts to corresponding metals when compared with other solvents such as NMP, water, and so forth. The more reduction nature atmosphere, the bigger the particle size formation. In contrast, NMP can form complexes with noble salts and can slow the metal reduction rate and hence, decrease in particle size. However, other solvents do not interfere a great deal in the reduction. In this context, we conducted control experiments using sucrose as a capping agent wherein we observed only nanoparticles with higher particle size (see Figure 3). This is due to masking of solvent effect (reducing and complexing behavior) on nanoparticles and hence the formation of bigger particle size. The TEM micro-

graphs of Ag and Pd nanoparticles self-assembled in water and isopropanol are shown in Figure 4.

In water, Ag, and Pd nanoparticles started to self-assemble into rod-like structures. In isopropanol, Ag and Pd nanoparticles yielded wire-like structures with a thickness in the range of 10 to 20 nm and several hundred microns in length. In acetone and acetonitrile medium, the Ag and Pd nanoparticles are self-assembled into a regular pattern making nanorod structures with thicknesses ranging from 100 to 200 nm and lengths of a few microns (see Figures 5(a)–5(d)). The formation of self-assembly was due to strong inter-particle van-der-Waals interactions and hydrophobic interactions in aqueous solutions. Irrespective of solvent used Ag and Pd crystallized in fcc symmetry. To take the advantage of self-assembly, we were able to measure two-probe conductivity. For instance, Ag nanorods prepared from acetonitrile solvent casted on a gold electrodes $5 \mu\text{m}$ apart gave a conductivity of $(40 \text{ to } 80) \times 10^6$ depending on electrode contact which is very much comparable to conductivity of the bare Ag reported [41]. It is interesting to note that self-assembled Pd nanoparticles can catalyze monomers such as pyrrole and aniline to afford polypyrrole and polyaniline nanocomposites (see Figure 6 for SEM and UV spectra and Figure 7 for TEM images). In the present study, Pd- and Ag-catalyzed polypyrrole yielded nanofiber nanocomposite formation in contrast with the literature reports that deliver spherical nanoparticle composites [42].



(a)



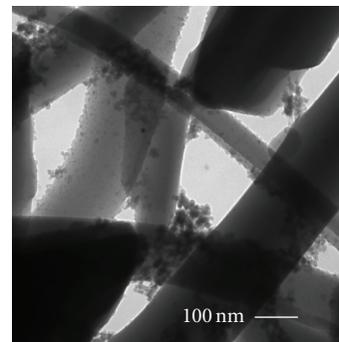
(b)

FIGURE 6: (a) SEM image of polypyrrole nanocomposites catalyzed by self-assembled Pd nanoparticles synthesized in water media using vitamin B₂ and (b) corresponding UV spectra.

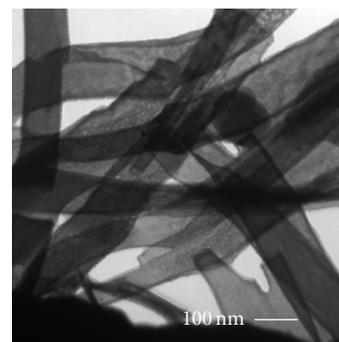
The broad absorption spectrum from 600 to 900 nm is due to the characteristic peak of polypyrrole formation [43]. We believe these one-dimensional fiber nanocomposites filled with noble nanoparticles may find applications in sensors, hydrogen-storage material, fuel cell membranes, catalysis, and other biological applications.

In summary, we report the following.

- (i) High yield, room temperature, solvent-assisted self-assembly to prepare noble nanostructures such as Ag and Pd nanospheres, nanowires, and nanorods using vitamin B₂ in different solvent media thereby providing new opportunities in a myriad of applications, such as catalysis, antibacterial coatings, fuel cell membranes, and so forth.
- (ii) The method employed no special capping, dispersing, or polymer as a coating agent.
- (iii) Formation of noble nanostructure multiple shapes and their self-assembly depended on the solvent used for the preparation.



(a)



(b)

FIGURE 7: TEM image of (a) polypyrrole nanocomposites and (b) polyaniline nanocomposites catalyzed by self-assembled Pd nanoparticles synthesized in water media.

- (iv) This single-step greener approach (when used in water) is general and may be extended to other transition metal oxides.
- (v) Self-assembled Ag and Pd nanoparticles catalyzed reactions of aniline and pyrrole to generate polyaniline and polypyrrole nanocomposites.

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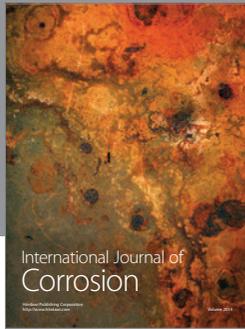
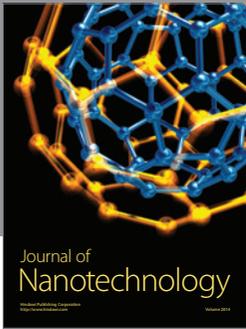
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