

Article

Expeditious Synthesis of Noble Metal Nanoparticles Using Vitamin B₁₂ under Microwave Irradiation

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Abstract: A greener synthesis protocol for noble nanometals is developed using vitamin B₁₂ as a reducing and capping agent in conjunction with the use of microwaves. Successful assembly of nanoparticles or microparticles with varied shapes and sizes have been demonstrated. The synthesized Ag, Au, and Pd samples were thoroughly characterized with X-ray diffraction, scanning electron microscopy, transmission electron microscopy, high resolution transmission microscopy, and UV-visible spectrophotometry, confirming that metallic Ag, Au, and Pd were synthesized by the green chemistry method.

Keywords: green synthesis; microwave irradiation; noble metal nanoparticles; vitamin B₁₂

1. Introduction

Noble metals such as gold (Au), silver (Ag), and palladium (Pd) have been widely used for many applications, including catalysis, electronics, photonics, optoelectronics, sensing, and pharmaceuticals [1–5]. In order to synthesize noble nanometals, various methods have been established, including a polyol process, sodium borohydride (NaBH₄) reduction, and photoreduction [6–12]. Nevertheless, these conventional synthesis methods have several disadvantages, including the use of noxious reagents and volatile organic solvents as well as the production of hazardous by-products [6–10]. Therefore, it is of great importance to eliminate the use of toxic reducing agents for the synthesis of noble metal nanoparticles.

Several efforts have been made recently to utilize naturally occurring reducing compounds, namely vitamins and polyphenolic extracts of tea and fruit [13–18]. For example, vitamin B₁ effectively reduced Pd ions and the structures of the ensuing Pd nanoparticles could be well controlled as nanobelts, nanoplates, and nanotrees at different concentrations of palladium precursors [17]. Vitamin B₂ was used as a reducing and capping agent for the synthesis of metal nanoparticles [18]. In view of its antioxidative properties, water-soluble vitamin B₁₂ is used now in the present work to synthesize Ag, Au, and Pd metal nanoparticles [19,20].

In addition to the use of greener reagents, alternative or renewable energy sources show significant promise in helping to reduce the amount of by-product formation and energy used. Not only do they safeguard against these harmful by-products, but the use of alternative energy helps to preserve many of the natural resources that we currently use [21]. For example, Komerneni *et al.* [22] reported that hematite could be synthesized with a microwave (MW)-assisted hydrothermal method and it is 36 times faster compared to a conventional synthesis. Microwave heating has emerged as an alternative and powerful energy source for nanomaterial synthesis [23], which can accomplish chemical transformations in a short span of time (e.g., minutes instead of hours or days) since enough energy for the chemical reaction can be directly provided by molecular vibrations due to MW [24]. A variety of highly crystalline nanomaterials with uniform sizes such as titanium dioxide, copper, and iron oxides have been expeditiously synthesized in minutes [25–27]. The fusion of both the use of safer reagents and MW heating ideally suits the development of a sustainable technology to create noble nanometals of uniform, smaller size by reducing or eliminating the formation of undesired wastes.

In this study, vitamin B₁₂ was used as both a reducing and capping agent for the synthesis of Ag, Au, and Pd nanoparticles in conjunction with MW irradiation. The synthesized samples were thoroughly characterized by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-visible spectroscopy, and high resolution-transmission electron microscopy (HR-TEM). The MW irradiation was critical to synthesizing noble metals using vitamin B₁₂; no particle formation was discerned at room temperature and oil bath heating at 100 °C without the use of MW irradiation.

2. Experimental Section

Vitamin B₁₂ (Cobalamin, Sigma-Aldrich, St. Louis, MO, USA) 0.1% w/w solution was prepared using MilliQ water. For the synthesis of Ag, 0.1 M silver nitrate (AgNO₃, Sigma-Aldrich, 99%) was mixed

with vitamin B₁₂ solution (see Table 1). For the synthesis of Au, 0.01 M gold (III) chloride (AuCl₃, Sigma-Aldrich, 99%) solution was added to the vitamin B₁₂ solution. For the synthesis of Pd, 0.1 M palladium acetate (Pd(O₂CCH₃)₂, Sigma-Aldrich, 98%) was admixed with vitamin B₁₂ solution. All prepared solutions were hand-shaken for 1 min and then placed in a CEM Discover focused MW synthesis system and irradiated at 100 °C for varying irradiation times; the experimental conditions are summarized in Table 1.

Table 1. Experimental conditions for the synthesis of Ag, Au, and Pd ^a.

Sample	Metal Precursor (mL)	Amount of Vitamin B ₁₂ (mL)	Irradiation Time (min)
Ag	1	1	5
	2	2	4
Au	1	1	5
	2	2	4
Pd	1	1	5
	2	2	4

^a All experiments were conducted at 100 °C.

After MW irradiation, samples were cooled down to room temperature and then characterized. Scanning electron microscopy (SEM, Philips XL 30 ESEM-FEG, Eindhoven, The Netherlands) and transmission electron microscopy (TEM, Philips CM 20, Eindhoven, The Netherlands) were performed to investigate the surface morphology of the synthesized samples. In order to obtain detailed lattice information, high resolution TEM (HR-TEM, JEM-2010F, JEOL, Tokyo, Japan) was employed with a field emission gun at 200 kV. The samples were prepared by dispersing in isopropyl alcohol (99.8%, PHARMCO-AAPER, Brookfield, CT, USA) and sonication using a 2510R-DH sonicator (Branson, Danbury, CT, USA) for 20 min. The samples were dropped on a TEM copper grid (FCF400-Cu, EMS, Hatfield, PA, USA) and then air-dried. The obtained images of SEM, TEM, and HR-TEM were analyzed using the software ImageJ (National Institute of Health, Bethesda, MD, USA). UV absorption spectra were obtained using a UV-visible spectrophotometer (Cary 50 Conc, Varian, Agilent, Santa Clara, CA, USA). The XRD pattern was obtained using PANalytical Xpert Pro θ -2 θ diffractometer (Almelo, The Netherlands) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the two theta range from 20° to 80°. The pattern analysis was performed using the Jade + software v.7 or later (MDI, Inc., Livermore, CA, USA) by following the ASTM D934-80 procedure. Reference patterns were from the 2002 PDF-2 release from the ICDD (International Center for Diffraction Data, Newtown Square, PA, USA).

3. Results and Discussion

Vitamin B₁₂ comprises a *Corrin* ring in which a cobalt atom is bound to four nitrogen molecules (molecular structure shown in Figure 1) [28]; the redox potential of cob(II)alamin/cob(I)alamin being 0.49 V at pH 7 [29]. The formation of metallic Ag, Au, and Pd nanoparticles via this greener method was scrutinized by XRD analysis. Figure 2 shows XRD patterns of the synthesized samples; Ag, Au, and Pd samples were well crystallized during the synthesis process using vitamin B₁₂ under both 3 min and 6 min of MW irradiation, thus indicating that vitamin B₁₂ effectively reduced metal ions in the solution. However, control reactions carried out at room temperature and 100 °C (oil bath heating) did

not yield specified products. For Ag samples, the peaks corresponding to (111), (200), and (220) planes were observed at $2\theta = 38.2, 44.4$ and 64.66° , respectively (see Figure 2a). As shown in Figure 2b for Au, the peaks at $2\theta = 38.17, 44.37, 64.56$ and 77.55° were observed, which correspond to (111), (200), (220), and (311) planes, respectively. Peaks corresponding to (111), (200), and (220) planes of Pd were observed at $2\theta = 40.15, 46.70$ and 68.18° , respectively, for Pd samples (see Figure 2c).

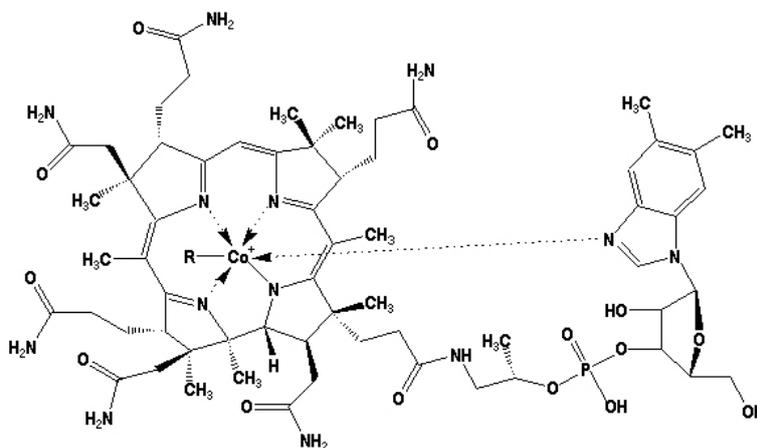


Figure 1. The molecular structure of vitamin B12.

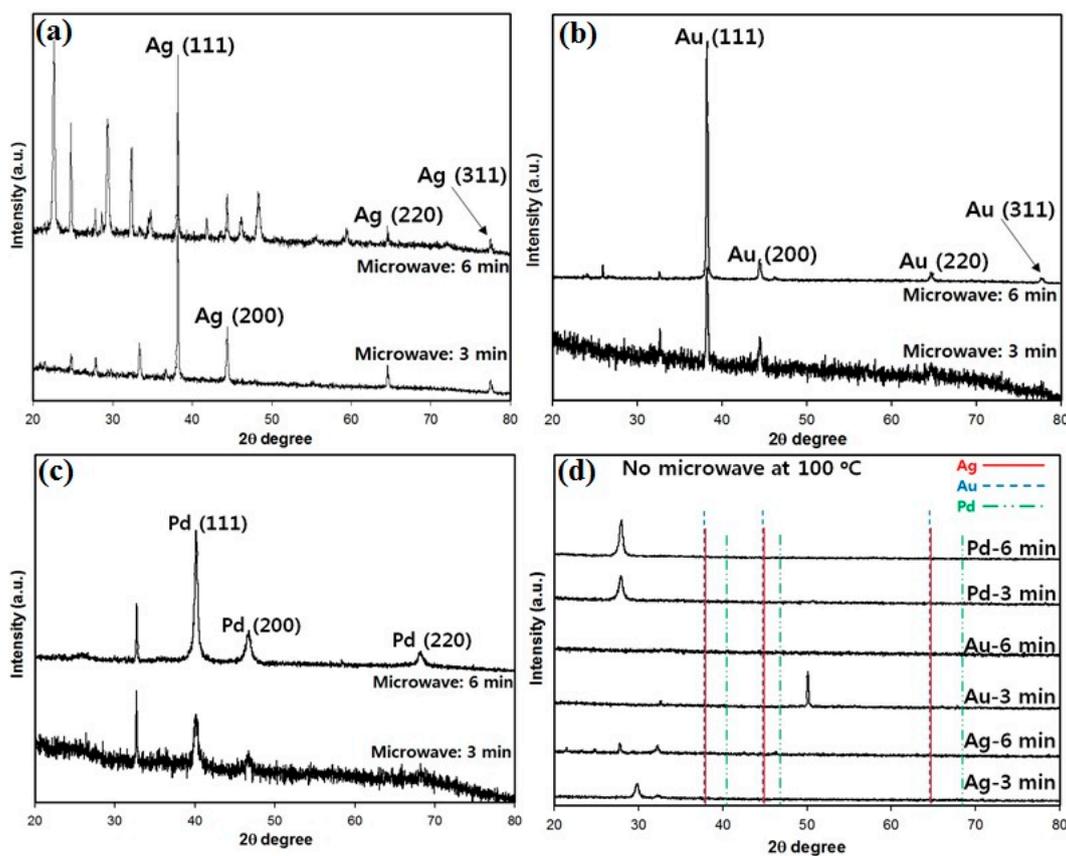


Figure 2. XRD patterns of synthesized samples: (a) Ag; (b) Au; (c) Pd; and (d) all samples treated at 100°C without the MW irradiation.

Interestingly, no metallic nanoparticles were observed with conventional heating at 100°C

(see Figure 2d). Also, no particles formed in the samples aged for 24 h at room temperature or without MW treatment (see supplemental Figure S1). These results surmise that the MW irradiation is crucial for the synthesis of noble metal particles using vitamin B₁₂. UV-visible absorption of the synthesized samples and vitamin B₁₂ was investigated (Figure 3). It can be seen from Figure 3b that the absorbance at wavelengths ranging from 500 to 570 nm increased due to surface plasmon resonance (SPR) of silver nanoparticles [30] compared to that of vitamin B₁₂; Ag nanoparticles normally exhibit resonance peaks at 400–450 nm.

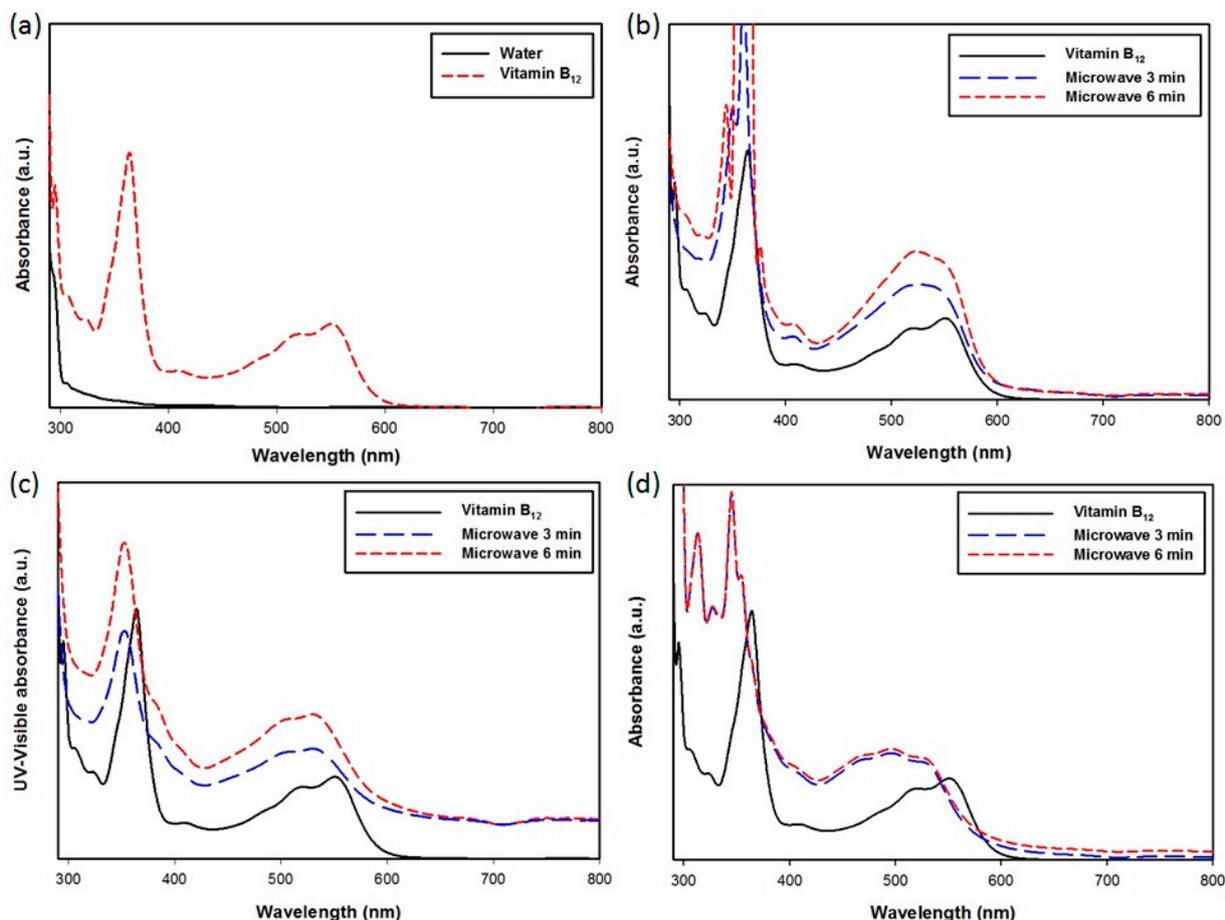


Figure 3. UV-visible absorbance for (a) vitamin B₁₂, and synthesized (b) Ag NPs; (c) Au NPs; and (d) Pd NPs.

However, in the present study, the shift in resonance peak is due to the formation of different shapes of particles in the presence of vitamin B₁₂. The absorbance for the sample subjected to MW irradiation for 6 min was higher than the sample that was heated for 3 min. These results are in good agreement with the XRD analysis (see Figure 2a), as well as with earlier reports exhibiting the SPR effect of Ag nanoparticles at wavelengths ranging from 500 to 570 nm [30]. For Au nanoparticles, a slight increase of the absorbance at wavelengths ranging from 520 to 550 nm was noticed compared to that of vitamin B₁₂, due to the localized surface plasmon resonance of Au (Figure 3c). This indicates that the formation of Au is in accordance with outcomes from XRD analysis (see Figure 2b) and earlier documented research [31,32]. For Pd samples, the specific light absorption patterns were not discerned due to the background light absorbance of vitamin B₁₂ (see Figure 3d), but decreased absorbance around

560–570 nm was observed; Jarret *et al.* reported that decreased absorbance accompanied the oxidation of cob(I)alamin to cob(II)alamin [29]. Cob(I)alamin is one of the intermediates of vitamin B₁₂ produced by the reduction of Co(III)-based cobalamins or cob(II)alamin [33]. Based on this observation, it may indicate that the released electron from the cobalamin oxidation can be used for the reduction of Pd ions.

In order to investigate morphological properties of the synthesized Ag, Au, and Pd samples, SEM and TEM analyses were performed. Figures 4–6 show the SEM and TEM images of each sample of Ag, Au, and Pd. As shown in Figures 4a and 4b, for Ag samples, large aggregates with irregular shapes and diameters ranging from 70 to 600 nm were synthesized using vitamin B₁₂. TEM images show the formation of nanoparticles and large aggregates synthesized using vitamin B₁₂. Nanoparticles with diameters less than 30 nm were observed in the sample treated with MW irradiation for 6 min (see red rectangles in Figure 4d).

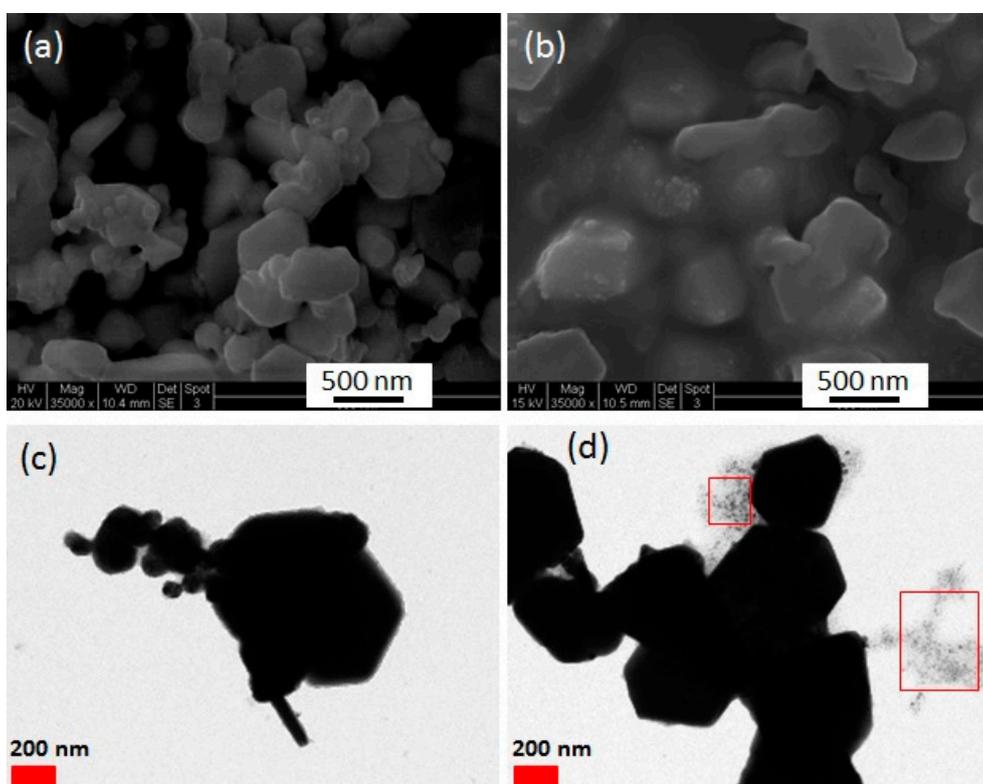


Figure 4. SEM (a,b), and TEM (c,d) images of synthesized Ag; samples with the present method: (a,c) for Ag sample MW-heated for 3 min, and (b,d) for Ag sample irradiated for 6 min.

Figure 5a–d for Au samples reveal the formation of particles of irregular shapes and sizes; small nanoparticles with an average diameter of 40 ± 11.7 nm were obtained under MW irradiation for 3 min, whereas much larger particles with a size over 500 nm were formed after 6 min of irradiation. Spherical-, triangular-, and decahedron-shaped microparticles were observed. The TEM images reaffirmed the formation of nanoparticles and microparticles for different durations of MW irradiation. For the MW-heated 6 min sample, nanoparticles of an average diameter of 9.9 ± 2.2 nm formed with the irregular, large micro-sized particles (see red rectangle in Figure 4d); the increase in particle size is presumably due to longer MW exposure time and crystal growth of the particles.

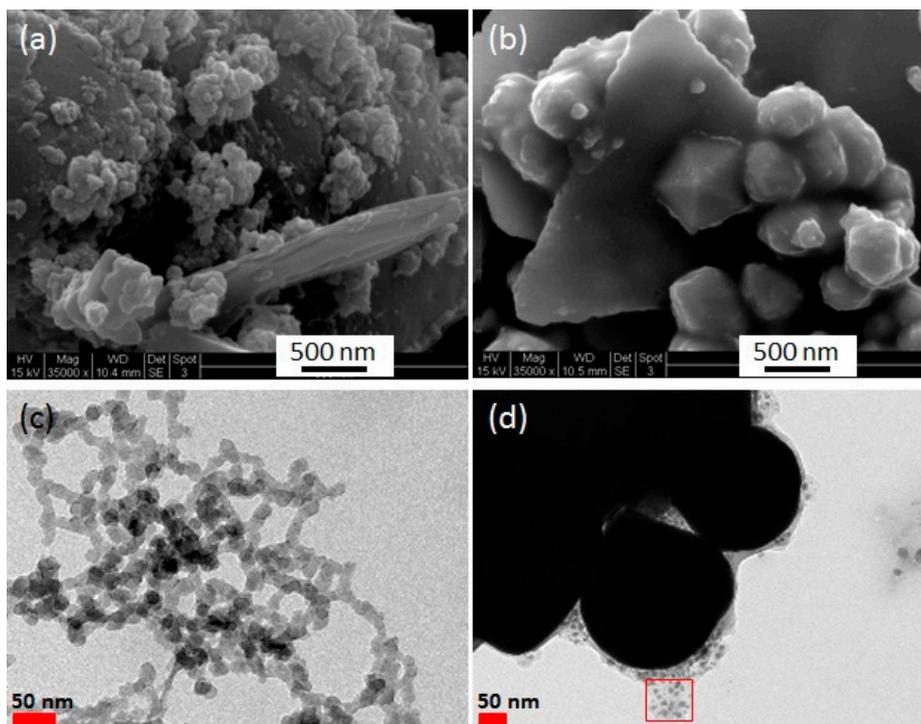


Figure 5. SEM (a,b), TEM (c,d) images of synthesized Au; samples with the green chemistry method: (a,c) for Au sample microwaved for 3 min, and (b,d) for Au sample microwaved for 6 min.

The SEM and TEM images of synthesized Pd samples are shown in Figure 6a–d. In keeping with the general trend, larger aggregates of an average size of 220 ± 45 nm were formed for the samples treated under longer durations of MW irradiation (*i.e.*, 6 min). In contrast, nanoparticles with an average diameter of 40.2 ± 7.3 nm were discerned in the sample irradiated by MW for 3 min (Figure 6a,c). Moreover, the TEM images show that the sample irradiated by MW for 6 min contained primary particles with two different average diameters of 43.9 ± 7.1 and 6.6 ± 2.1 nm (Figure 6b,d). As shown in Figures 4 and 5, micro-sized and nano-sized particles coexist, especially for Ag and Au samples irradiated with MW for 6 min.; the growth of particles is possibly due to a longer reaction time since no surfactants were used to control their structures.

In order to investigate the crystal phase in detail, HR-TEM analysis was performed on the synthesized samples. For the Ag sample, the lattice spacing of 0.145 nm was measured, which corresponds to the (220) plane of Ag (see Figure 7a) [34,35]. As shown in Figure 7b, the measured lattice spacing of 0.236 nm, corresponding to the (111) plane of Au, indicated that Au cations were well reduced via this method [36]. Additionally, as shown in Figure 7c, the lattice spacing of 0.137 nm was in good agreement with the lattice spacing of the (220) plane of Pd. [37] These HR-TEM analysis results corroborated the XRD analysis, thus reaffirming the prowess of this vitamin B₁₂ synthesis method to produce noble nanometals under MW irradiation conditions.

Based on the results, we postulate a plausible mechanism for the synthesis of metal nanoparticles. Metal ions could be reduced using vitamin B₁₂ due to the reduction and oxidation of cobalamin from cob(I)alamin to cob(II)alamin under MW irradiation. Metal nanoparticles are produced by the polyol

method with MW assistance, a common method for the synthesis of metal nanoparticles via reduction [38–40] due to hydroxyl groups of vitamin B₁₂.

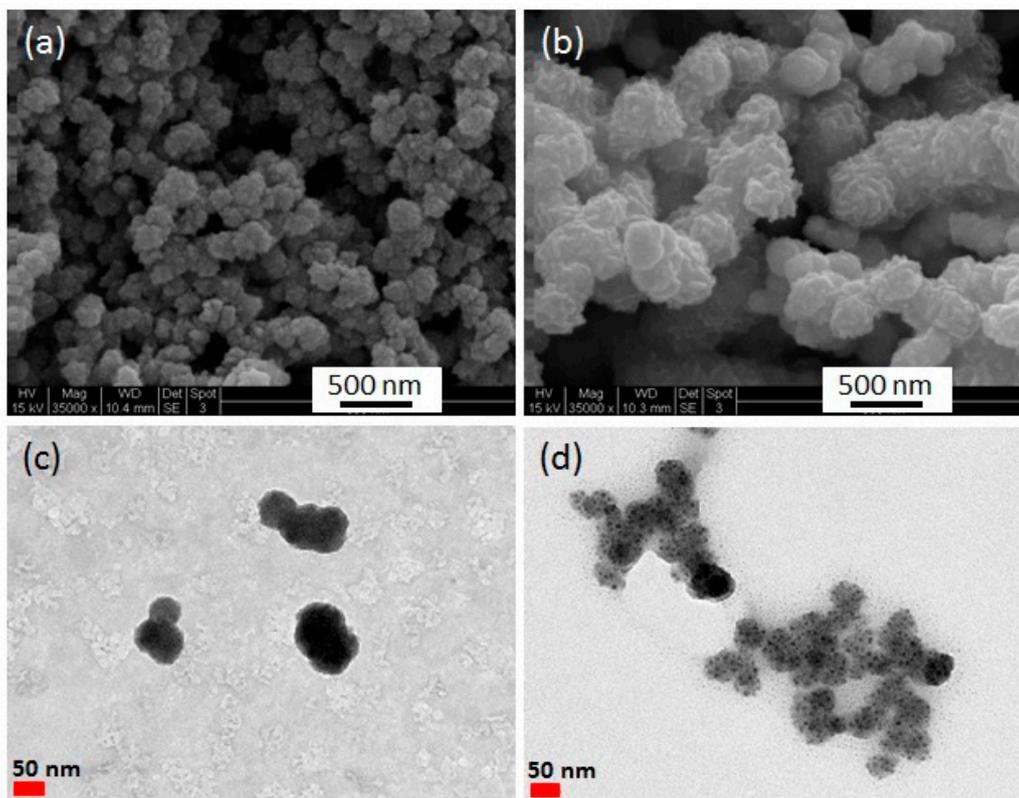


Figure 6. SEM (a,b), TEM (c,d) images of synthesized Pd samples; with the green chemistry method: (a,c) for the Pd sample MW-irradiated; for 3 min, and (b,d) for the Pd sample irradiated for 6 min.

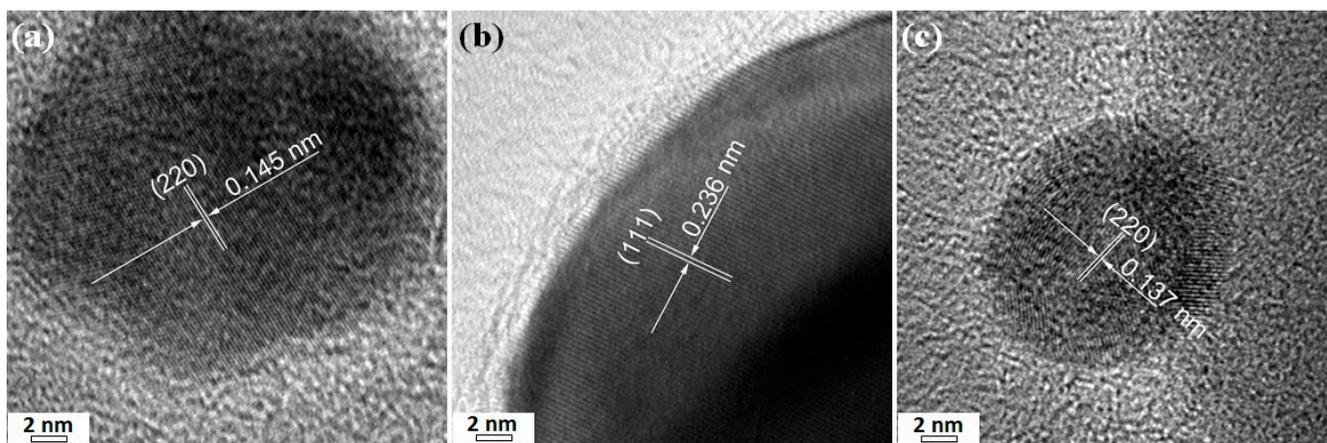


Figure 7. HR-TEM analysis for synthesized samples: (a) Ag NPs; (b) Au NPs; and (c) Pd NPs.

4. Conclusions

Noble metal nanoparticles or microparticles were successfully synthesized via the MW-assisted method using vitamin B₁₂, which played the dual role of a reducing and capping agent. The synthesized Ag, Au, and Pd samples were thoroughly characterized with XRD, SEM, TEM, HR-TEM, and

UV-visible spectrophotometry; XRD analysis indicated the crystalline phase and confirmed the formation of metallic Ag, Au, and Pd. No nanometal or microparticles were formed without MW irradiation at room temperature (for 24 h) and/or 100 °C. However, upon heating in the MW at 100 °C, the duration of MW irradiation was a key to control the shape and size of the formed metal particles. Since noble nanometals such as Pd, Ag, and Au have been widely used as sensing materials, catalysts, and non-toxic drug carriers due to their unique properties [41–44], these synthesized metal nanoparticles could find potential applications in numerous areas of sensing, catalytic processes, and clinical applications.

Supplementary Materials

X.R.D. patterns of synthesized Ag, Au, and Pd samples at room temperature without microwave irradiation.

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Author Contributions

Performing the experiment: Varun Nagendra, R. B. Nasir Baig; Characterizing synthesized materials: Changseok Han, Mallikarjuna N. Nadagouda; Drafting of manuscript: Changseok Han, Varun Nagendra, R. B. Nasir Baig; Critical revision: Rajender S. Varma, Mallikarjuna N. Nadagouda; Planning and supervision of the research: Rajender S. Varma, Mallikarjuna N. Nadagouda.

Conflicts of Interest

The authors declare no conflict of interest.

Disclaimer

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