

Photoinduced synthesis of CdTe nanoparticles using Te-modified gold electrode in poly(vinyl pyrrolidone)-containing electrolyte

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Abstract Photocathodic stripping of a pre-deposited tellurium film on a gold electrode in 0.1 M Na₂SO₄ electrolyte containing Cd²⁺ ions and poly(vinyl pyrrolidone) (PVP) was used as a route to the photoelectrosynthesis of CdTe nanoparticles. Thus illumination of a Te-modified gold surface generated Te²⁻ species, which were removed from the surface into the bulk electrolyte containing Cd²⁺ and PVP by vigorous stirring. The reaction of Te²⁻ and Cd²⁺ produced PVP-protected nanosized CdTe particles dispersed in solution in the size range 20–40 nm. In this approach, PVP played a critical role as a stabilizer to form discrete CdTe particles instead of larger (agglomerated) ones. Electrochemical quartz crystal microgravimetry was used to monitor stripping of Te films during the light illumination and the synthesized CdTe nanoparticles were characterized by scanning electron microscopy, energy dispersive X-ray analyses and laser Raman spectroscopy.

Keywords Semiconductor nanoparticles · Photoelectrochemistry · Photocorrosion · Photoelectrosynthesis

1 Introduction

Semiconductor nanocrystals are of fundamental and practical interest stemming from size quantization effects, which result in unique size dependent properties [1–3]. Among them, Group II–VI semiconductor nanocrystals such as CdSe and CdTe are of much interest because of applications in solar photovoltaic cells, sensors and optoelectronic devices [4–6]. Nanosized particles of these materials have been successfully synthesized by chemical methods using reagents such as trioctylphosphine oxide [5, 6]. While such preparative approaches often require severe experimental conditions such as high reaction temperatures and toxic chemicals, electrochemical syntheses can be performed under much more benign environments. We describe here one such “photoelectrosynthesis” route based on the combined use of photocorrosion of an immobilized Te precursor and subsequent nanoparticle formation in Na₂SO₄ supporting electrolyte containing Cd²⁺ ions and poly(vinyl pyrrolidone), (PVP).

Recently, we described an approach to deposit CdTe nanoparticles using illumination of a Te-modified polycrystalline gold electrode in Cd²⁺ containing electrolyte [7]. Light illumination generated Te²⁻ species in situ at the electrode surface and subsequent precipitation resulted in nanosized CdTe particles on the Au substrate surface. As an extension to this work, we now describe a simple strategy to produce nanosized CdTe nanoparticles *in bulk solution*. In this approach, illumination of a Te-modified electrode generates Te²⁻ species on the electrolyte/

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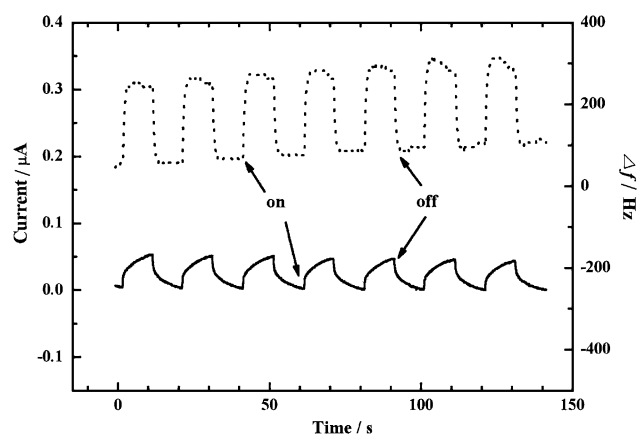


Fig. 1 Photocurrent transients (—) and corresponding EQCM frequency change (---) for a Te modified Au electrode in 0.1 M Na₂SO₄ at a fixed bias potential of -0.2 V. A gold electrode was previously modified with Te by holding the potential at -0.3 V for 120 s in 0.1 M H₂SO₄ electrolyte containing 1 mM TeO₂

electrode interface and mechanical convection affords formation of CdTe nanoparticles in the presence of PVP in the bulk electrolyte dosed with Cd²⁺ ions. As in our earlier work [7–9], electrochemical quartz crystal microgravimetry (EQCM) was used in the present study to investigate the photocorrosion process accompanied by mass changes.

2 Experimental

An EG&G Princeton Applied Research (PAR) 263A instrument equipped with Model M250/270 electrochemistry software was used for film deposition and voltammetry. The EQCM (Seiko EG&G, Model QCA 917) instrument consisting of an oscillator module (QCA 917-11) and a 9 MHz AT-cut gold-coated quartz crystal (geometric area, 0.2 cm²) working electrode, a Pt counter electrode, and a Ag/AgCl/3 M NaCl reference electrode, was used for monitoring mass changes during illumination of the working electrode. All potentials are quoted with respect to the Ag/AgCl/3M NaCl reference electrode.

Cadmium sulfate hydrate (purity 98+%), tellurium dioxide (purity 99+%), sodium sulfate (purity 99+%), sulfuric acid (purity 98+%) were from Aldrich and they were used as received.

A Müller Elektronik-Optik tungsten halogen lamp was used as the light source. The light intensity measured on the electrode surface with a Newport Model 70260 radiant power meter combined with a Model 70268 probe was ~ 100 mW cm⁻² in all the experiments described below; this value is uncorrected for cell reflection and electrolyte absorption losses. Raman spectra were measured using the 514 nm line of an Ar⁺ ion laser (HORIBA-LABRAM) at room temperature. Film morphology and composition were

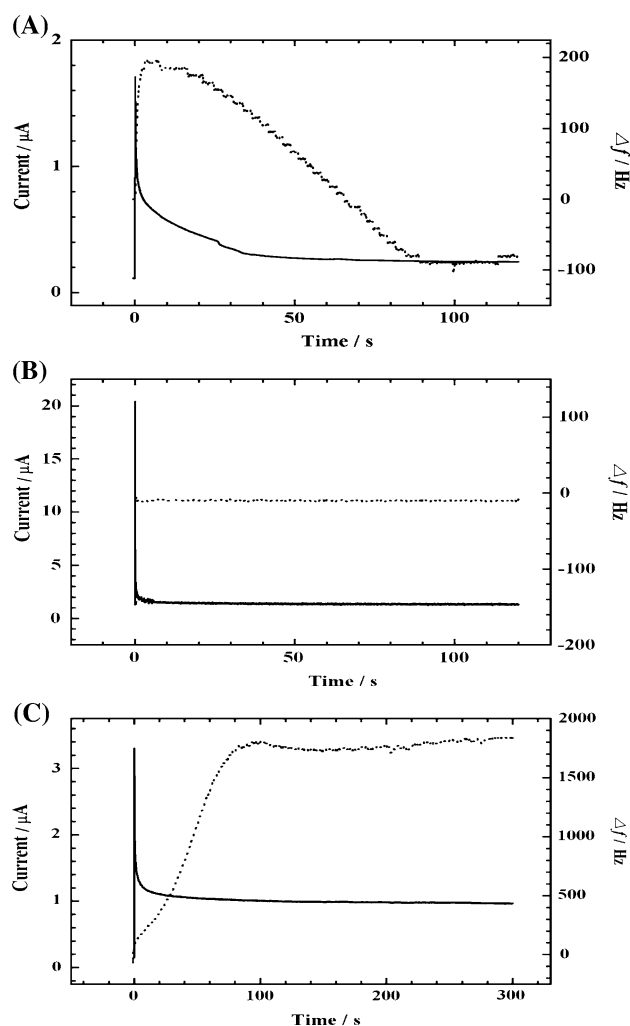


Fig. 2 (A) Current flow (—) and corresponding EQCM frequency change (---) for a Te modified Au electrode under light illumination in 0.1 M Na₂SO₄ containing 30 mM CdSO₄ at a fixed potential of -0.2 V. (B) As in (A) but with a stabilizer (5% PVP) and stirring in the “dark”. (C) As in (B) but with light illumination

obtained on a field emission scanning electron microscope (JEOL Model 6700F) equipped with an energy dispersive X-ray analysis (EDX) probe.

3 Results and discussion

Tellurium (Te) is a p-type semiconductor which exhibits photocathodic current flow under light illumination and generates Te²⁻ by photocorrosion [7, 10, 11]. Figure 1 shows the photoelectrochemical characteristics of a Te-modified Au electrode in 0.1 M Na₂SO₄ supporting electrolyte at a fixed potential of -0.2 V. A gold electrode was previously modified with Te by holding the potential at -0.3 V for 120 s in 0.1 M H₂SO₄ electrolyte containing 1 mM TeO₂. As shown in the figure, chopped illumination

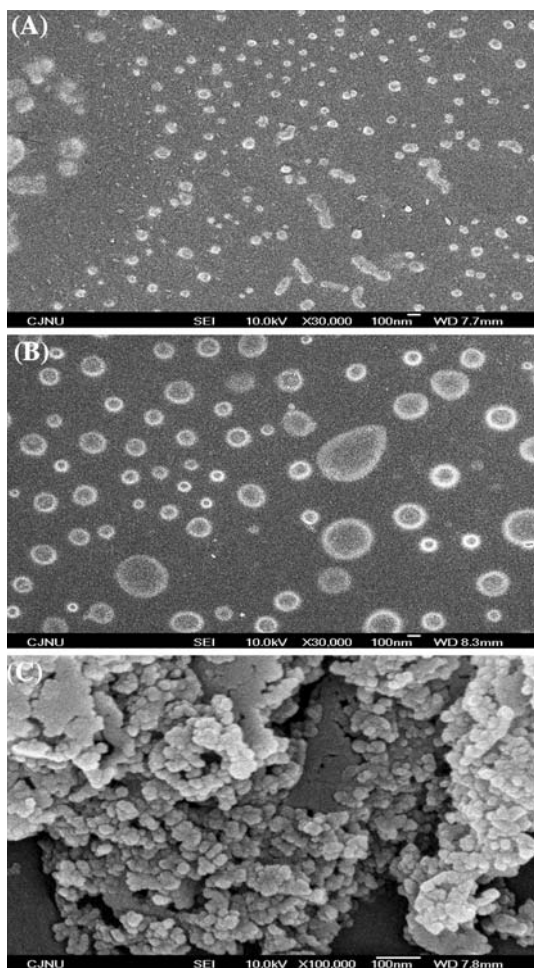


Fig. 3 (A) A typical SEM image (30,000 \times) of CdTe particles synthesized as in Fig. 2(C). (B) As in (A) but after 12 h at 70 $^{\circ}$ C. (C) As in (A) but without the PVP stabilizer, magnification: 100,000 \times

resulted in cathodic photocurrent flow, showing that the electrodeposited Te film acted as a p-type semiconductor. Also, the cathodic photocurrent resulted in a concomitant frequency increase (mass decrease) as a result of the photocorrosion of Te by the following reaction:



These photogenerated Te^{2-} species can react with Cd^{2+} ions in the electrolyte to produce CdTe nanoparticles in situ under the quiescent condition. Thus Fig. 2 contains combined chronoamperometry-EQCM data obtained for a Te-modified Au electrode at a fixed potential of -0.2 V. On irradiation of the electrode without stirring, a concomitant frequency decrease is observed indicating the precipitation of CdTe [7] on the electrode surface (Fig. 2A).

Figure 2B shows that light illumination is essential to corrode the Te film, which is manifest from the fact that frequency does not change in the dark in 0.1 M Na_2SO_4 supporting electrolyte containing Cd^{2+} ions. On the other

hand, a combination of light illumination on the Te/Au electrode and stirring the 0.1 M Na_2SO_4 electrolyte dosed with 30 mM of Cd^{2+} ions and 5% (w/w) PVP resulted in a frequency increase (mass decrease), because the photo-generated Te^{2-} species were removed from the electrode/electrolyte interphase by stirring. Mass loss and frequency increase due to the photocorrosion was completed within 100 s. Control experiments showed that PVP concentration did not affect the particles size of CdTe, but slightly changed the strip time of the Te films.

Poly(vinyl pyrrolidone) (PVP) has long been used as a stabilizer for the *chemical* synthesis of many types of nanoparticles including Ag [12–14], Au [15], Pd [15], Pt [16] and Se [17, 18]. In these cases, PVP plays a crucial role in the control of size and shape as a steric stabilizer or capping agent. Recently, we showed that PVP can reduce Se^{4+} species to Se nanoparticles [19]. In the present study, we have utilized PVP for the first time as a stabilizer for the photoelectrosynthesis of discrete CdTe nanoparticles.

As synthesized CdTe particles are polydisperse in size and irregular in shape (Fig. 3A). Interestingly, the particle size and shape became bigger (~ 100 nm) and spherical (presumably due to Ostwald ripening) when the as-synthesized CdTe particles in electrolyte were kept at 70 $^{\circ}$ C for 12 h. Figure 3B shows a typical scanning electron microscopy (SEM) image of such CdTe particles drop-coated on a polycrystalline gold electrode. It is well known that chemical synthesis of metal nanoparticles using PVP and a reductant results in particles with a spherical shape [15–18]. In our case, heat treatment was found to be effective to control particle size as well as shape; further studies will be directed at controlling the size and shape of CdTe particles. EDX scans on as-synthesized particles showed the expected Cd and Te signals with a stoichiometry of almost 1:1. Without PVP, CdTe synthesized by the same approach discussed above resulted in the formation of a morphologically ill-defined precipitate instead of discrete nanoparticles; the SEM image in Fig. 3C exemplifies this trend. Clearly, PVP plays a critical role in the formation of nanoparticles of CdTe.

Figure 4 contains data on the photocurrent transients and corresponding EQCM frequency changes for a CdTe modified Au electrode in 0.1 M Na_2SO_4 at a fixed bias potential of 0.2 V. For this experiment, CdTe particles were drop-coated on the polycrystalline gold (EQCM) electrode. Contrasting with the situation for p-Te (Fig. 1), the photocurrent now is anodic diagnosing that the formed CdTe semiconductor nanoparticles were n-type. The mechanistic origin of the mass changes (mass decreases when the light is “on” and increases in the “dark”) was described in the companion paper [7].

Finally, Raman spectroscopy of the CdTe nanoparticles revealed peaks at 98 cm^{-1} , 117 cm^{-1} , 136 cm^{-1} and

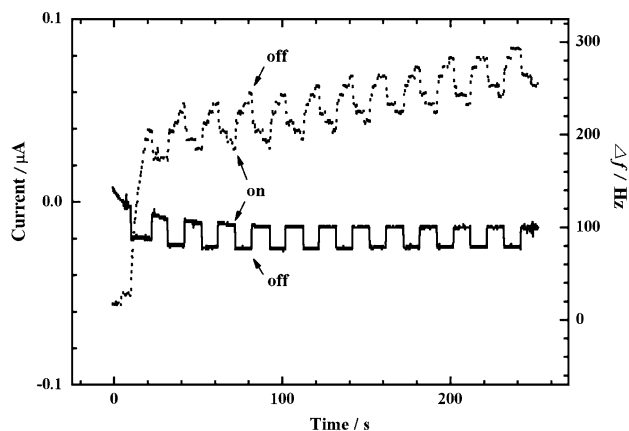


Fig. 4 Photocurrent transients (—) and corresponding EQCM frequency change (- - -) for a CdTe modified Au electrode in 0.1 M Na₂SO₄ at a fixed potential of 0.2 V. CdTe particles were drop-coated on the polycrystalline gold (EQCM) electrode

169 cm⁻¹ which are in agreement with values in the literature for this material [20, 21].

4 Concluding remarks

CdTe nanoparticles in the 20–40 nm size range were photoelectrochemically synthesized using a Te modified polycrystalline Au electrode in 0.1 M Na₂SO₄ electrolyte dosed with 30 mM of Cd²⁺ ions and 5% (w/w) PVP. Photogenerated Te²⁻ species at the interface were removed into the bulk electrolyte by convection to react with Cd²⁺ ions, which resulted in PVP-capped CdTe nanoparticles. It should be noted that PVP played a critical role in synthesis of discrete nanoparticles of CdTe, since larger aggregates formed when the polymer was absent. For *practical* application of this photoelectrosynthesis strategy (proof of concept for which was presented above), the Te²⁻ species generating surface has to be reasonably large (relative to the solution volume) and the two ionic fluxes (namely, Te²⁻ and Cd²⁺) have to be carefully matched.

Further work is needed to optimize the post-synthesis treatment for tuning the CdTe size and shape. Finally, and in a more general sense, semiconductor photocorrosion is a bane in the field of photoelectrochemistry. However, the results presented here and in our companion study [7] demonstrate that this subtractive process can be put to good use for materials synthesis applications.

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